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Research Article

Articular cartilage: Chemical, Physical, and Tribological Properties

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Abstract

The cartilage surface was characterized using wettability test fresh and depleted AC samples. In this work, we demonstrated experimentally that the cartilage smart biomaterial at varying pH is sensitive to friction and introduces a novel concept in joint lubrication on charged surfaces. The surface charge density of the articular cartilage surface is related to the amphoteric character of phospholipids, PLs functional groups ($-NH_3^+$) and ($-PO_4^-$). The maximum surface energy of AC was found to occur at pH for isoelectric point ~4.5 ($H_3N^+(CH_2)_n\ PO_4^-\ -R_1R_2$) and with a wide range minimum of pH 6.5 to 9.5 of the phospholipidic membrane covering biological pH ~7.4 lubrication condition. The hydrophilic and hydrophobic character of cartilage was determined.

Keywords:
articular cartilage; charge density; wettability

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Introduction

The chemical and physical nature of the biological surfaces is seen in an entirely different light than that of engineering surfaces immersed in water. Author [1] attempts to explain a new joint lubrication mechanism with surface-active phospholipids (PLs) as a lubricant. Joint lubrication is a complex problem and attributing macromolecules to the synovial fluid of the lubricant cannot fulfill all the functions. The self-organization process of a stable pore structure in phospholipid liposomes, bilayers, lamellar phases in the synovial fluid forces the lamellar-repulsive mechanism of lubrication. The lubricant is chemically attached to the surface, and is responsible for the biological lubrication mechanism [1], [2], [3].

The lamellar-repulsive joint lubrication mechanism is not so well-known in biotribology and therefore deserves to be published. The determination of the biophysical and biochemical parameters of articular cartilage and introduction of a new mechanism of lubrication in natural joints was an idea of "Articular cartilage: lamellar-repulsive lubrication of natural joints" publication [1].

The articular cartilage (AC) surface charge density is related to the amphoteric character of phospholipids (PLs) since they contain both ($-NH_3^+$) and ($-PO_4^-$) groups. Previous research mainly focused on examining the contribution of macromolecules to joint lubrication. While in this paper, the authors attempt to explain a joint lubrication mechanism in such a way that the AC surface phospholipids can act significantly as a lubricant. To prove the hypothesis, two experiments were used. In the first one, the authors attempt to determine that AC surface with phospholipids undergoes the conformational change in air-dry conditions. The second experiment attempts to determine the correlation between the AC surfaces' friction and the tissue charge density.

In this paper, we examine wettability of bovine cartilage (BC) surface in wet and dry conditions and the influence of pH on the surface charge density on friction on (cartilage/cartilage) surfaces.

Experimental

The articular cartilage specimens were collected from bovine knees aged ~1.5 years. Osteochondral plugs, of 5 and 10 mm in diameter, were harvested from lateral and medial femoral condyles. The cartilage discs were cut into 3-mm plugs with full attachment to the underlying bone. The specimens were stored at 253 K in 0.155M NaCl (pH = 6.9) and fully defrosted prior to testing. The discs were then glued to the disc and pin's stainless steel surfaces, and friction tests were conducted in the universal buffer solution.

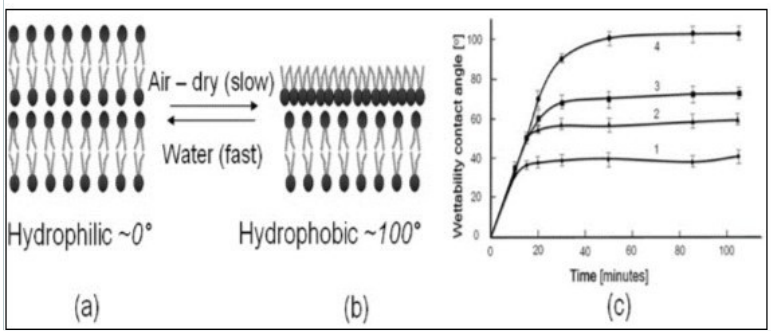
Wettability Measurements

A KSV CAM100 computerized tensiometer was used to measure the contact angle of cartilage samples. A drop of the 0.155M saline solution was deposited on the air-dry cartilage surface. The tests on the normal, partial and completely depleted cartilage samples were repeated five times.

Friction Test in Universal Buffer Solutions (pH 2.0 - 9.5)

The measurements were performed using a sliding pin-on-disc tribotester T-11 manufactured by the NISTR, Poland. The tests were conducted at room temperature, at a speed of 1 mm/s during 5 minutes, and under a load of 15 N (1.2 MPa) which corresponded to the physiological lubrication condition.

Prior to the friction tests, the lubricants were prepared using the Britton-Robinson universal buffer solution and its pH values were measured. The samples were equilibrated with each buffer solution under a load for 5 minutes and the results of *(f)* as a function of pH are given in Figure 2. A total number of five tests were conducted using fresh samples for each experimental set-up with at least four repetitions per specimen pair, from which the mean and standard deviation were calculated.



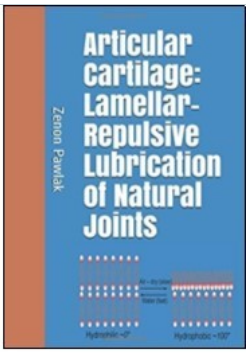


Figure 1. The wettability contact angle (°) as a function of air-drying time (a) in aqueous electrolyte and (b) air-dry conditions; (c) AC surface depleted in chloroform/methanol (2:1,v/v). Curve (1) after 17 min, Curve (2) 7 min, Curve (3) 3 min; Curve (4) normal (untreated) AC surface; (n = 7, error bars = 95% confidence limit). (d) Book cover "Articular cartilage: Lamellar-repulsive lubrication of natural joints" [1].

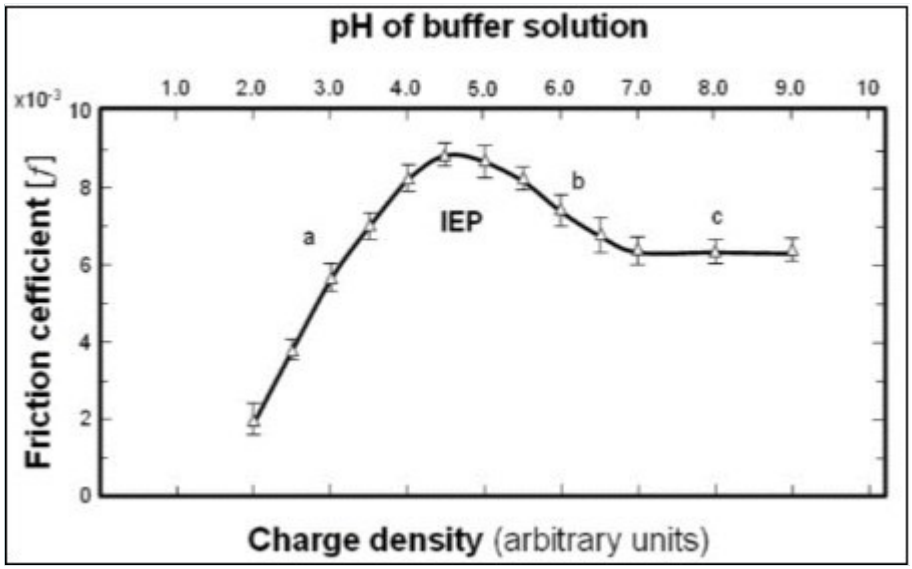


Figure 2. Friction coefficient *f* vs. charge density for bovine cartilage (AC) obtained in the buffer solution.
For isoelectric point IEP, molecule has equal charge distribution (H_3N^+ $(CH_2)_n$ PO_4^- -R_1R_2).
Standard deviation SD of (*f*) 11 to 15 (%).

Results and Discussion

Hydrophilic and Hydrophobic Character of the Articular Cartilage

The wetted surfaces (pH~7.3) of the phospholipid membranes are negatively charged ($–PO_4^-$). Biosurface wettability can be measured relative to differences in the charge density of the functional phosphate ($–PO_4^-$) groups. In this regard, the wettability of a hydrated surface is characterized by the concentration of charged anionic phosphate ($–PO_4^-$) groups that become deactivated when the surface is dehydrated. The dehydration of the phospholipid bilayer surface activates hydrophobic groups, R $(CH_2)_n$ - due to the formation of a hydrophobic monolayer [3]. The hydrophilic surface in the course of dehydration, say via air-drying, undergoes a slow increase in the wettability contact angle indicating conformational changes in the surface (*flip-flop*) of phospholipidic molecules (Figure 1). Poor lubrication in animal joints, particularly on the articular surface of cartilage, can be attributed to deterioration of the bilayer surface, where the wettability or contact angle (θ) changes from 100° (healthy) to less than 70° (unhealthy) [4], [5]. The smart-surface of articular cartilage constitution of the superficial phospholipid bilayer in (a) aqueous electrolyte solution and (b) air-dry conditions. A change in surface energy leads to

conformational changes in the surface of the bovine patella from bilayer (super hydrophilic ~0° contact angle) to monolayer (hydrophobic ~100°).

Surface Charge Density in Tribological Contact (AC/AC).

Figure 2 presents a typical plot of a friction test between two normal surfaces (AC/AC), and these results indicate that the friction on cartilage surfaces is largely dependent upon the charge density of the tissue. It is evident that friction coefficient increases (curve part a), to reach a maximum at the isoelectric point, IEP, and then decreases gradually while sliding (curve part b) takes place over the pH range of the test. The cartilage surface carrying the positive charge, that changes to negative, can be attributed to the proton transfer reaction. Equation 1 depicts a cartilage surface carrying positive charges; after IEP, negative charges can be attributed to the proton transfer reaction [9].

$$-NH_3^+ + OH^- \rightarrow -NH_2 + H_2O;\ -PO_4H + OH^- \rightarrow -PO_4^- + H_2O \quad \textbf{(1)}$$

Curve part (a) friction increase, pH 2 → 4.5: $-NH_3^+ \rightarrow -NH_2$ (surface losing charge)

The maximum point, IEP, pH 4.5, no net electrical charge,

$$H_2N(CH_2)_nPO_4H\text{-}R_1R_2 \Leftrightarrow H_3N^+(CH_2)_n\ PO_4^-\text{-}R_1R_2 \quad \textbf{(2)}$$

Curve part (b), friction decrease, pH 4.5 → 6.8: $-PO_4H \rightarrow -PO_4^-$ (gaining negative charge)

Curve part (c), constant friction, pH ~ 7 to 9.0 ($-PO_4^-$, surface is negatively charged)

By varying the charge density, the friction coefficient can be varied by about one order of magnitude over the experimental range studied. Cartilage's extremely low friction is significantly dependent on the electrostatic interaction between two cartilage surfaces [6], [7]. In an animal's body, where the tissues slide over each other, the lubrication mechanism has been referred to as a "lamellar-repulsive", because the surfaces coated with PL bilayers and lamellar phases negatively charged on articular surface with synovial fluid support this mechanism [8].

The amphoteric PLs are the main solid-phase components on the surface of articular cartilage (AC). The cartilage phospholipidic membrane has been shown to undergo conformational reorientation when wettability changed from the wet (~ 0°) super hydrophilic to dry-air (103°) hydrophobic state (named smart material), Figure 1.

It has been well established that low friction is supported by the PLs bilayers mechanism which essentially consists of a surface amorphous layer (SAL) surrounded by a 0.155 M electrolyte synovial fluid (SF) of pH ~7.4 with high-molecular-weight charged biomacromolecules. The cartilage implication from osteoarthritis disease by a gradual erosion of the surface amorphous layer has shown an increased friction coefficient [10], [11].

The surfaces, coated with PL bilayers and a lamellar structure negatively charged on the articular surface with synovial fluid, have been referred to as a "lamellar-repulsive" mechanism. The role, played by hydration or structural force, is believed to arise from a strongly bound and oriented first layer of the water molecules on charged surfaces. The water molecule allows participating in strong polar (electrostatic charge - dipole or hydrogen - bonding) interactions. The short-range repulsion often observed between biological surfaces is not due to the layered structure of water but to entropic repulsion. The cartilage surfaces experience weak van der Waals attractive forces and much stronger short-range repulsive forces due to hydration repulsion. Hydration repulsion dominates the interaction between charged cartilage surfaces at nanometer separations and ultimately prevents the sticking together of cartilage surfaces, even at high load. A hydration water layer strongly binds to the negatively charged cartilage surface and, when in contact with synovial fluid components (charged biomacromolecules, PL lamellar aggregates, and liposomes), acts to reduce the friction between cartilage surfaces [1], [12].

In this work, we demonstrated experimentally that the smart cartilage biomaterial at varying pH is sensitive to friction and introduces a novel concept in joint lubrication on charged surfaces. The cartilage surface was characterized using wettability test fresh and depleted AC samples.

Competing Interests

The authors have declared that no competing interests exist.

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