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Repulsive lubrication on hydrophilic surfaces

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Abstract

The lamellar-repulsive mechanisms for aqueous boundary lubrication supported by phospholipid bilayers negatively charged and 80% hydrated surfaces. It is shown that cartilage being a smart material has a hydrophilic surface being intact and hydrophobic when the surface is the air-dry condition. We discuss a controversy associated with the hydrophobic mechanism of boundary lubrication introduced by Hills in 1984. By using a model bilayer membrane, we examined the influence of pH on phospholipid interfacial energy and friction coefficient. We also showed that cartilage surface wettability is a good indicator hydrophilic cartilage condition.

Introduction

Natural joints hydrophobic lubrication mechanism was adapted by Hills from classic Boundary Lubrication (BL), as first introduced by Hardy in 1925 [1]. Hills proposition is based on bilayers of phospholipids formed on cartilage surfaces and hydrophobic tail–tail sliding between the layers facilitated lubrication (Figure 1). Hills' model cited by many authors without acceptance is evaluated that it is not correct [2,3,4]. In our work based on experimental facts, we introduced the hydrophilic lamellar-repulsive mechanism of natural lubrication. Reviewing Hills cartilage hydrophobic surface model of joints lubrication (Figure 1) we are giving experimental facts, that Surface-Active Phospholipids (SAPL) on cartilage are hydrophilic, amphoteric and negatively charged [4]. Hills introduced his hydrophobic cartilage surface model of phospholipids molecules adsorbed to hydrophilic proteoglycan matrix without considering pH condition and properties of Phospholipids (PLs) in wet and dry conditions [5]. The strong adsorption of PLs molecules by their quaternary ammonium positive ion (Me_3N^+-) to the negative cartilage surface (a proteoglycan) to the hydrophilic bottom surface, Hills also indicated hydrogen bonding between (-PO_4H) groups to give good cohesion [5]. After year she introduced the new model of cohesion: Strong cohesion of phosphate ions by

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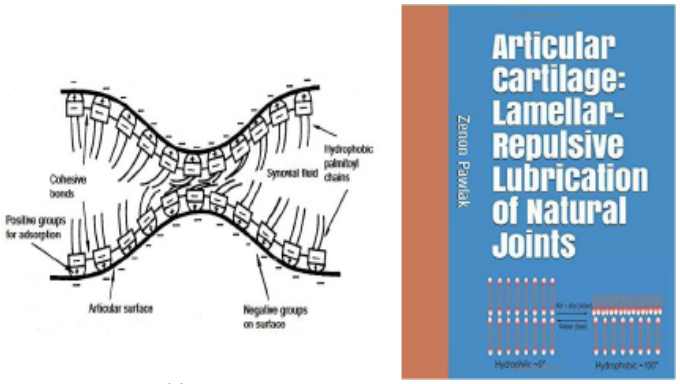
Ca (II) making the close-packed hydrophobic solid layer [6].

In this paper, Hills hydrophobic model is verified and the following studies have been undertaken (a) Determination of interfacial energy model bilayer, determination of friction (cartilage/cartilage) vs. pH (HL/HL, HB/HB) and determination of wettability cartilage surface (values measured for the air-dry surfaces). This study has been undertaken to reevaluate the cartilage lubrication system to demonstrate that pH influence the surface wettability and friction coefficient of charged and hydrophilic surfaces.



(a) (b)

Figure 1: (A) The hydrophobic Hills model for boundary lubrication of cartilage surfaces: (A) cartilage surfaces [5] (B) Book cover "Articular cartilage: Lamellar-repulsive lubrication of natural joints", with transformation scheme of hydrophilic bilayers to hydrophobic monolayer [4].

Methods and experimental materials

The articular cartilage specimens were collected from bovine knees aged 15-20 months. Osteochondral plugs, of 5 and 10 mm in diameter, were harvested from lateral and medial femoral condyles using a circular stainless steel cutter. The cartilage discs were cut into 3-mm plugs with underlying bone. Two types of samples were tested: Untreated bovine cartilage and bovine cartilage treated with a Folch reagent (a 2:1 v/v mixture of chloroform and methanol), and a lipid-rinsing solution to remove the lipids from the surface of the cartilage. After preparation, the specimens were stored at 253 K in a 0.155 M NaCl (pH = 6.9) solution and fully defrosted prior to testing. The cartilage discs were then glued to the disc and pinned to stainless steel surfaces, and friction tests were conducted in the universal buffer solution.

Tensiometer

The contact angle between the liquid and the tested cartilage was measured using a KSV CAM100 tensiometer and was between a droplet of a 0.15M saline solution and a given air-dry cartilage surface. The contact angle test was performed on the normal and completely depleted cartilage samples. Five tests were performed on each specimen and each set-up.

Friction test

The measurements were performed using a sliding pin-on-disc tribotester T-11 manufactured by the NIST Research, Radom, 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 correspond to the physiological lubrication condition [6]. Prior to the friction tests, the lubricants were prepared using the Britton-Robinson (1931) buffer solution, and their pH values were measured. The friction coefficient measurements of (cartilage/cartilage) pair were carried out over the pH range between 2.0 and 9.0.

The interfacial energy measurements method

The effect of pH on the interfacial energy (γ) of spherical lipid bilayers formed from Phospholipid (PLs) has been described previously [7,8,9]. The interfacial energy measurements method used was based on the Young and Laplace's (Y-L) standard formula (1), the interfacial energy (γ) was determined by measuring the radius of curvature (R) of the convex surface formed when a static pressure difference, , was applied to both its sides [10]:

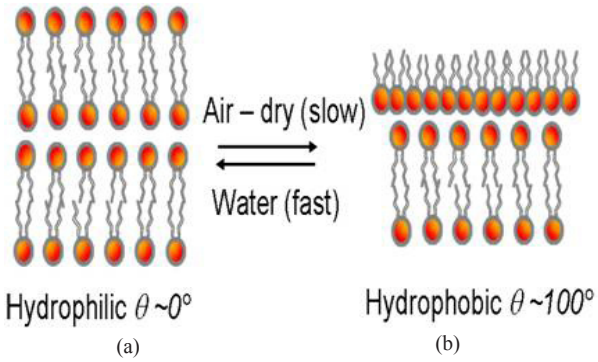
$$2\gamma = R\Delta p \qquad (1)$$

The gamma value obtained from (Y-L) equation was applied to the equation in an expanded form involving interfacial energy on the pH using a Britton-Robinson universal buffer solution as developed by Petelska and Figaszewski [7,8,9]. The apparatus and the interfacial energy measurements method used are described in [7,8,9,10,11]. The (γ) values were measured in 7-10 replicates with up to 5 readings of the lipid's spherical cap. The results of interfacial energy (γ) as a function of pH are shown in Figures 3.

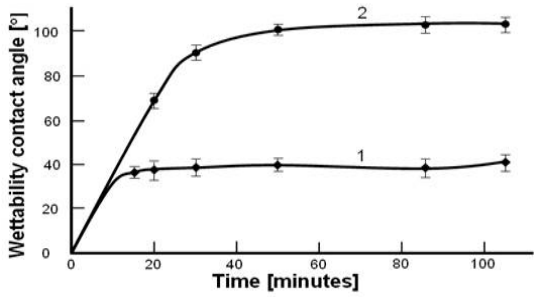
Results and discussion

Most tissue surfaces possess the ability to adsorb Surface-Active Phospholipid (SAPL), as a barrier against adhesion, corrosion, microorganisms, improve lubrication and reduce wear [2]. There exists strong adsorption of the Phosphatidylcholine (PC) quaternary ammonium positive ion (Me_3N^+-) to negative cartilage surface (a proteoglycan), there is also hydrogen bonding between (-PO_4H) groups to give good cohesion [6]. After years [6] Hills introduced the new model of strong cohesion with the participation of phosphate ions by Ca (II) making close-packed hydrophobic solid layer (Figure 4a). Moreover, when more experiments were done, Hills corrected his model with the involvement of calcium ions: Strong cohesion between (-PO_4^--Ca-PO_4^--) is the essential property needed for a surfactant to maintain the lamellate structure of cartilage, which is hydrophilic (not hydrophobic when cartilage is intact).

The air-drying time of cartilage surface is a process of transformation from the hydrophilic to the hydrophobic (HL→ HB) condition. Over turning phospholipid molecules (flip-flop) is described by the surface reorganization of PL of the bilayer into monolayer [12,13,14]. High contact angle (in dry surface condition) corresponds to high hydrophilicity (when the surface is wet), while low contact angle (for dry cartilage) corresponds to low hydrophilicity (when the surface is wet) (Figure 2).



(a) (b)



(c)

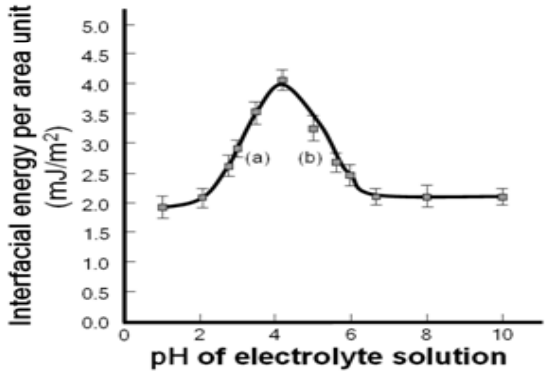
Figure 2: The smart-surface of superficial phospholipid bilayer of articular cartilage in (A) in aqueous solution and (B) air-dry atmosphere condition. (C) The wettability contact angle as a function of air-drying time. Curve: (1) depleted of phospholipid (chloroform/methanol (2:1, v/v), contact angle of 39°; curve (2) normal articular surface; contact angle of 104°, (n = 5, error bars = 95% confidence limit).

A change in surface energy leads to conformational changes in the surface phospholipids from bilayer (hydrophilic) to monolayer (hydrophobic). The contact angle parameter is reflected in the charge density of the functional group on the surface, especially in the number of PLs bilayers on the cartilage surface. Bio surface wettability can be measured relative to differences in the charge density of the functional amino ($-NH_3^+$) and phosphate ($-PO_4^-$) groups. In this context, we note that Hills [15] reported by the wettability of a surface that is characterized by charged anionic phosphate ($-PO_4^-$) groups are lower than surface activating hydrophobic groups. The contact angle parameter is reflected in the charge density of the functional group on the surface, especially in the number of PLs bilayers on the cartilage surface (Figure 2c) [16,17,18].

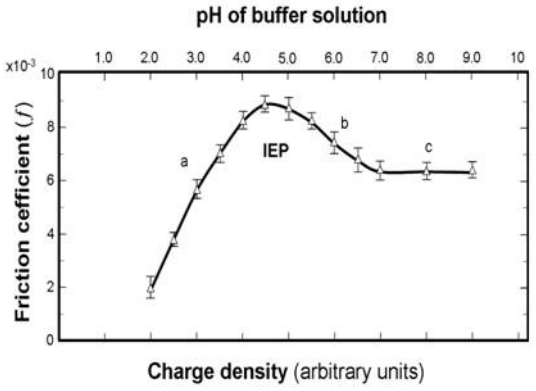
The interfacial energy of spherical lipid bilayers and cartilage friction coefficient

The interfacial energy of phospholipidic liposomal membrane vs. pH, determined by microelectrophoresis supports the hypothesis of the amphoteric character of phospholipidic cartilage surface (Figure 3a). Experimental values are compared with [19]. The isoelectric point, IEP, is at a pH of 4.12; (a) The left-hand branch of the curve) pH 1.0 to 4.12 $(CH_3)_3N^+) \rightarrow (CH_3)_3N^+OH^-)$. The maximal point of the curve was (pH 4.12, IEP, $(CH_3)_3N^+ (CH_2)_2 PO_4^- R_1R_2$). (b) Right-hand branch of the curve pH 4.12 to 6.5 (-PO4H → -PO4-).

The friction coefficient of the (cartilage/cartilage) tribological par surfaces (a) with positively charged surface (+/+) at pH 3.5, with negatively charged surface (-/-) at pH 6.0, 7.4, and 9.0 and at isoelectric point, IEP, (±/±) at a pH 4.12 and (b) the friction coefficient the bovine (cartilage/cartilage) surfaces against pH 2.0 to 9.0 of buffer solutions under a 15N load and 1 mm/s sliding velocity during 600 seconds. The isoelectric point determined for cartilage by friction coefficient vs. pH is comparable to isoelectric point obtained from the study of interfacial energy for the model phospholipidic spherical lipid bilayer formed by phosphatidylcholine.



(a)



(b)

Figure 3a: The interfacial energy of the model phospholipidic spherical lipid bilayer formed byphosphatidylcholine vs. buffer solution pH range 1.0 to 10.0. (b) The friction coefficient of the (cartilage/cartilage) tribological par vs. pH of buffer solution.

The liquid/liquid interface at pH 7.4

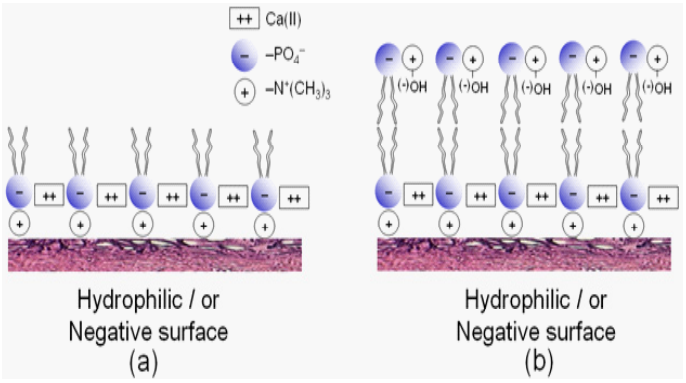


Figure 4: Model for natural surfaces boundary lubrication imparted by phospholipids bilayers: (a) Hills hydrophobic cartilage model at pH 7.4 (Hills, 2000), (b) Hydrophilic cartilage model negatively charged at pH 7.4 [4].

The hydrophobic Hills model cartilage surface is in contradiction to the fact that PL forms multi lamellar structures as manifested in all natural membranes hydrophilic in aqueous solution.

Conclusions

Hills hydrophobic surface model of AC has no support in all experimental facts which are given in this paper and current literature in support that AC is amphoteric, hydrophilic with the negatively charged surface (-PO4-) (Figure 3b, 4b).Values of the isoelectric point determined for cartilage by friction coefficient and obtained from the study of interfacial energy for the model phospholipidic spherical lipid bilayer formed by phosphatidylcholine are much closed.

Acknowledgment

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