Hydrophilic and charged cartilage surface for reducing the friction coefficient

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Abstract

It is a physical phenomenon for biological systems that the cartilage surface is hydrophilic and negatively charged. However, there is a lack of knowledge about some parameters possess by cartilage surface, e.g., interfacial surface energy, amphoteric, wettability, negatively charged bilayers, and lamellar slippage. Some of these parameters will be taken from literature to support and correct Hills hydrophobic lubrication model which is hydrophilic and negatively charged.

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Friction test

A sliding pin-on-disc tribotester T-11, manufactured by the NIST Research from Radom, Poland, was used to perform the friction measurements. Before the friction measurements, the lubricants were prepared on the base of the universal Britton-Robinson buffer solution [5], where pH ranged from 2.0 to 9.5. Because of the assumption of preserving conditions of the physiological state of the lubricant [6], the measurements of AC/AC tribopairs friction coefficients were completed at room temperature, in the time of 5 and 10 minutes, when the velocity was 1 mm/s and load 15N.

The friction coefficient measurements of cartilage/cartilage tribopair were carried out over the pH range between 2.5 and 9.5. The samples were equilibrated with each buffer solution under a load 15N for 5 minutes with previously measured pH. During the experiment, AC specimens were immersed in the lubricant to ensure its presence at their contact interface. A total number of 5 tests, where fresh sample were used, were performed. During each test, at least four repetitions per the specimen pair were carried out. Finally, the mean and standard deviation were calculated, and the graph of the friction coefficient of the pH solution was prepared.

The interfacial energy measurements method

In the literature, the effect of pH on the interfacial energy ($\gamma$) of spherical lipid bilayers formed from phospholipid (PLs) has already been described in details [3,7-9], phosphatidylserine, and sphingomyelin) is around pH 4, and the model phospholipidic membrane the interfacial energy “bell-shaped curve” vs. pH based on literature data was made.

Results and discussion

Hydrophilic cartilage model with negatively charged phosphate ions of surface

The strong adsorption of PLs molecules by their quaternary ammonium positive ion (Me3N$^+$) to hydrophilic cartilage surface (a proteoglycan) is [10] hydrophobic model of the cartilage surface. Strong cohesion between phosphate ions and calcium (II): $\text{(-PO}_4^-\text{-Ca}^{++}\text{-PO}_4^-\text{)}$ making making the close-packed hydrophobic solid layer (Figure 2a). However, considering pH 7.4 condition and properties of phospholipids (PLs) of being highly self-organized, bilayer is formed and the surface is negatively charged (Figure 2b). The multilamellar structure of phospholipids, namely the surface amorphous layer (SAL), covers the natural surface of articular cartilage. We conclude that a very high porosity (75%) is a critical factor in providing excellent hydration lubrication properties of articular cartilage.

Changes in interfacial energy of spherical lipid bilayers and cartilage friction coefficient

The effect of pH on the interfacial energy ($\gamma$) of spherical lipid bilayers formed from phospholipids (PLs) all four (phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, and sphingomyelin) has been described previously in details [3,7-9]. The isoelectric point of all four phospholipids is around pH 4, and the model phospholipidic membrane the interfacial energy vs. pH based on literature “bell-shaped curve” was created (Figure 3).
In Figure 3 (A) the isoelectric point, IEP, with the pH at which a phospholipid molecule carries no net electrical charge, IEP; $\text{H}_3\text{N}^+(\text{CH}_2)_n\text{PO}_4\text{H}\cdot\text{R}_1\text{R}_2 \Leftrightarrow \text{H}_2\text{N}^+(\text{CH}_2)_n\text{PO}_4^-\cdot\text{R}_1\text{R}_2$

\[ \text{pH} \text{ 0.2 to 4.0 (-NH}_3^+ \rightarrow -\text{NH}_2^-) \quad (\text{pH 4.0 to 6.5 (-PO}_4\text{H} \rightarrow -\text{PO}_4^-) \]

(a) (Left-hand side of the curve) (b) (Right-hand side of the curve)

The isoelectric point, IEP, of all four phospholipids is around pH 4.0 ± 0.2 an interfacial energy (mJ/m²) is summarized as follows: phosphatidylcholine (3.53), phosphatidylethanolamine (4.06), phosphatidylserine (2.93) and sphingomyelin (4.42) (values taken from Table 1 in [10] and [3]). Changes in interfacial energy correspond well to the amino (-NH$_3^+$→ -NH$_2^-$) transition at a low pH; after IEP pH 4.0, and the phosphate (-PO$_4$H→ -PO$_4^-$) transition at a higher pH range of 4.0 – 6.5

Friction tests were conducted to investigate the role of the phospholipid bilayers charged positively (+/±), negatively (−/−) and at an isoelectric point, IEP, (±/±). Cartilage/cartilage friction tests were conducted on fresh, healthy cartilage.

Figure 3 summarizes the interfacial energy, the wettability and coefficient of friction (f) obtained for PLs terminated with a spherical bilayer (Figure 3A) and (cartilage/cartilage) friction (Figure 3B) of either PLs of functional groups (-NH$_3^+$→ -NH$_2^-$) and (-PO$_4$H→ -PO$_4^-$) over the buffer solution pH range of 0.2-9.0. The interpretation of the results requires consideration of the charge density of the functional groups.

At low pH buffer solution, PLs bilayer the amino groups almost all in the (-NH$_3^+$) form, but as the pH of the buffer is increased, the amino groups begin to lose their charge (-NH$_3^+$→ -NH$_2^-$) leaving the bilayer with a more hydrophobic character, which causes an increase in the contact angle. After IEP, in the case of (-PO$_4$H) groups of PLs bilayer, the contact angle decreases with increasing buffer pH because the (-PO$_4$H) groups begin to gain their charge (-PO$_4$H→ -PO$_4^-$) (Figures 3A and 3B). In contrast, at pH values above pH 6.5 – 9.0, the cartilage surfaces are both negatively charged, with the charge density (repulsive interactions) and low friction with increasing pH. Dependence of the surface friction on the solution pH was previously observed for (poly (L-lysine)/ hyaluronic acid and SiO$_2$ surface) [11,12].

**Conclusion**

1. The bilayers on the surface of articular cartilage at pH 7.4 of synovial fluid are hydrophilic and negatively charged.
2. Model of boundary lubrication of natural surfaces supported by lamellar slippage of the bilayers lubrication mechanism.
3. Hills hydrophobic surface model of AC has no support in all experimental facts presented in this paper and current literature which actually supports the concept that AC is amphoteric, hydrophilic with the negatively charged surface (-PO$_4^-$), Figure 4 [3].

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