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Review Article

Nanostructures of Phospholipids on Articular Cartilage Surface and their Functions

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Abstract

Phospholipids bilayers fulfill an important role in natural joint lamellar-repulsive lubrication mechanism. Low friction between surfaces coated with negatively charged the phospholipid headgroup (–PO_4^-) as being due to a hydration layer. Wettability of the cartilage surface depends on the number of PLs that act as a lubricant. The cartilage can be classified as a group of intelligent material, which in the wet state has a contact angle of ~0º, and the air-dry state has a contact angle of ~104º.

Keywords: amphoteric cartilage; phospholipid bilayers; friction coefficient; wettability; hydrophilic and hydrophobic

Introduction

1. Phospholipid bilayers adsorbed on the cartilage surface

Phospholipids bilayers fulfill an important role in natural joint lamellar-repulsive lubrication mechanism [1, 2]. Low friction between surfaces coated with negatively charged the phospholipid headgroups (–PO_4^-) as being due to a hydration layer. Articular cartilage (AC) is a specific type of connective tissue without blood vessels and innervation. There is hyaline cartilage 3-5mm thick in the joints, which feeds in motion based on diffusion. About 65-80% of cartilage is water [1, 2]. During the movements, it allows the bones to move in relation to each other in the joint.

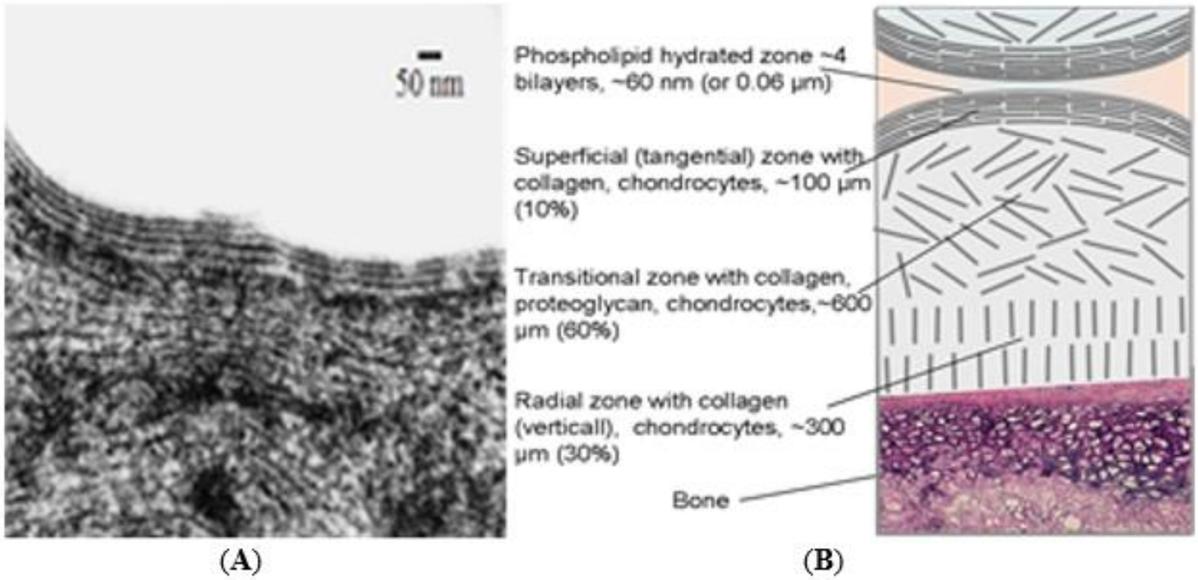

Figure 1A: *presents an image made by electron microscopy of human knee cartilage with phospholipid bilayers adsorbed on the surface [3].* **Fig. 1(B)** Scheme of articular cartilage with the presence of four zones with phospholipid bilayers adsorbed on the surface.

In Figure 1(B), four zones in the articular cartilage (~ 0.06)µm 3-5 phospholipid bilayers, 100 µm horizontally arranged collagen fibers with chondrocytes, ~ 600 µm middle zone with indirectly arranged collagen, proteoglycan and chondrocytes, ~ 300 µm collagen (vertical arrangement) with chondrocytes) were distinguished. The surface of the cartilage in the joint is hydrophilic, and the cartilage on the air loses its moisture and becomes hydrophobic.

2. The surface of AC and synovial fluid

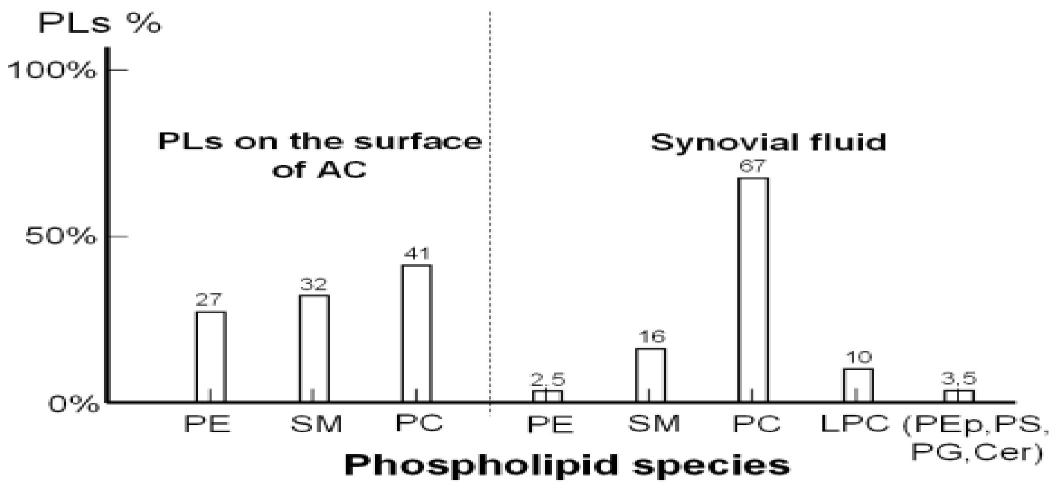

Figure 2: *Surface-active phospholipids on the surface of the cartilage and in the synovial fluid*

Figure 2 shows the range of concentrations of phospholipids present on the surface of AC [4] and the concentration of particular types of phospholipids in a healthy synovial fluid [5]. Concentrations (%) of phospholipids adsorbed on the AC surface are as follows: phosphatidylcholine (PC) 41%, sphingomyelin (SM) 32% and phosphatidylethanolamine (PE) 27% whereas the synovial fluid is dominated by PC (67%), sphingomyelin, lysophosphatidylcholine (16% and 10% respectively), PE 2.5% and 3.5% (PEp = phosphatidylethanolamine-based plasmalogens; PS = phosphatidylserine; PG = phosphatidylglycerol; Cer = ceramide).

Chondrocytes naturally produce phospholipids in the joints. Phospholipids support the majority of organ functions such as the cardiovascular system, nervous system, liver functions digestive system and, most importantly, selectively settle on the cartilage surface [4, 6] and create bilayers that are involved in border friction.

3. Hydrophilic and hydrophobic character cartilage surface

The uniqueness of natural cartilage tissue can be determined by its amphoteric, hydrophilic and hydrophobic character, wettability, and resistance to load. The cartilage can be classified as a group of intelligent material, which in the wet state has a contact angle of ~0º, and the air-dry state has a contact angle of ~104º.

One of the tribochemical parameters of the cartilage surface is its wettability. Wettability characterizes the surface of various materials, which are generally referred to as wettable (highly hydrophilic, ~ 0 to 45º) or non-wettable (highly hydrophobic, ~ 90º to 180º). Evaporation of surface water in the air leads to changes in surface energy and conformational changes of phospholipids on the surface, (a) the wet surface of the cartilage is hydrophilic (~ 0º contact angle), (b) after water evaporation, the bilayers self-reorganize into a monolayer (hydrophobic) 104º of the contact angle. Change in the contact angle depending on the time of drying of the cartilage surface in the air (see Figure 3).

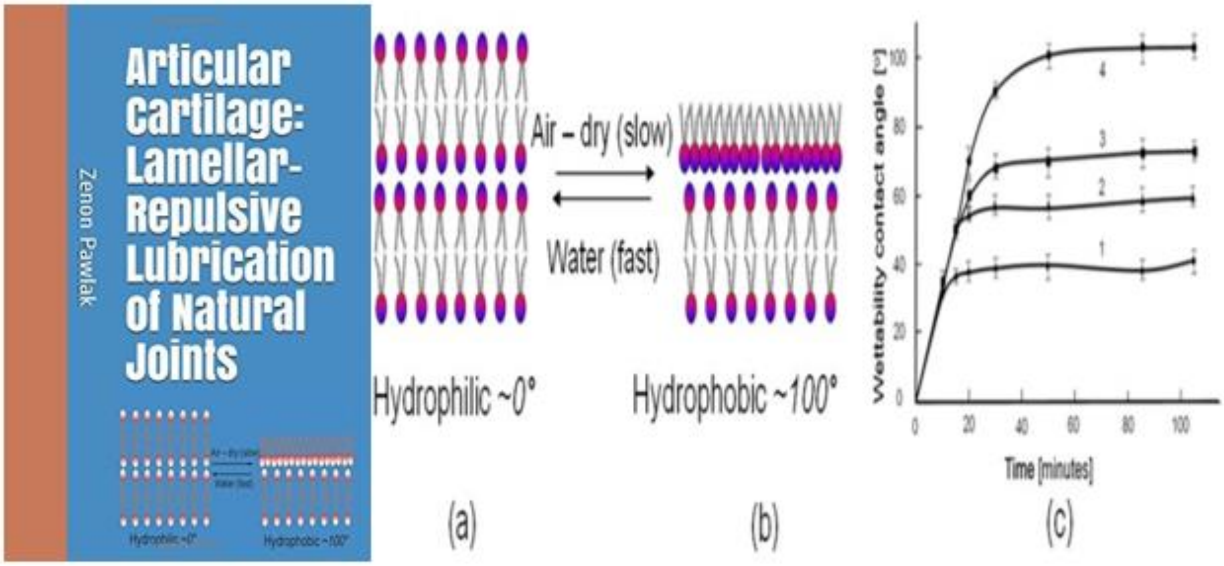

Figure 3: *Structure of the double phospholipid bilayer of articular cartilage, (a) in the wet state, (b) after air-drying, (c) change in the contact angle depending on the drying time in the open air. Curve: (1) after 19-minute cartilage delipidation (chloroform/methanol (2: 1, v/v), contact angle is 40º; (2) after 9 minutes of delipidation, contact angle 63º, (3) after 3 minutes of delipidation, contact angle is 73º, (4) the contact angle of the healthy cartilage surface is 104º. Air-dried cartilage samples (n = 5, mean value, 95% confidence level) [2, 7].*

The contact angle of the cartilage surface will depend on the charge density of the amine ($-NH_2$) and phosphate ($-PO_4^-$) functional groups, which is expressed in the number of PLs bilayers on the cartilage surface [2, 10]. During the evaporation of water molecules from the surface of the cartilage (dehydration), the process of transformation from the hydrophilic state to the hydrophobic state (HL → HB) takes place. The polar part of the phospholipid molecule (amino ($-NH_2$) and phosphate ($-PO_4^-$)), the outer bilayer is flipped (*flip-flop*) to have a contact with the moisture of the cartilage interior and the surface bilayer is reorganized into a monolayer [2, 8, 9]. The high value of the contact angle (dry surface measurement) corresponds to high hydrophilicity when the surface is wet (process reversibility) (see Fig. 4 a, b). A low contact angle (for dry cartilage) corresponds to low hydrophilicity when the surface is wet.

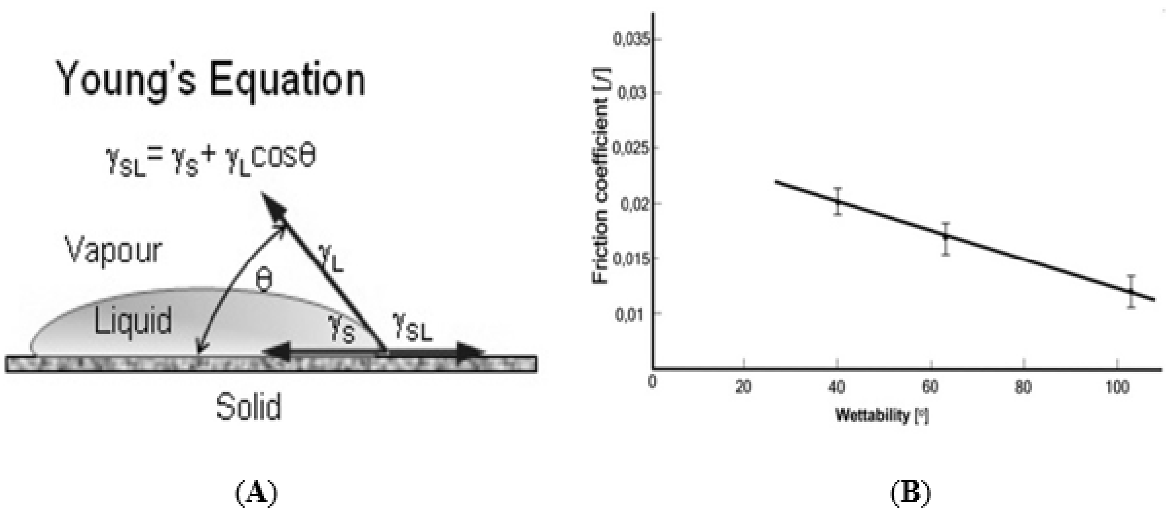

Figure 4A: *Contact effects in surface wetting, where: θ is the contact angle [º], γ_L denote free energy at the liquid/cartilage interface, γ_S - free energy at the border cartilage / liquid, γ_{LS} - free energy at the border cartilage / air; (B) coefficient of friction (f) vs. wettability: healthy bovine cartilage (~ 103º), sick cartilage (~ 65º) and degenerative cartilage (39.1º).*

4. Friction vs wettability of the cartilage surface

Wettability of the cartilage surface depends on the number of PLs that act as a lubricant [2, 10]. The study aimed to confirm the hypothesis that healthy and degenerate cartilage samples can be easily identified by measuring wettability. Observations led to the conclusion that the coefficient of friction is significantly dependent on the wettability of the tissue surface. This part of the study analyzed the surfaces of healthy and degenerated samples of articular cartilage through atomic force microscopy (AFM) methods, by measurements of wettability of cartilage surfaces and friction of pairs (cartilage/cartilage) [2, 11].

The most common characteristic of the degree of wettability of the joint cartilage surface is the wetting angle θ, which can be determined from the Young-Dupree relationship (Figure 5).

$$\cos\theta = (\gamma_S - \gamma_{LS}) / \gamma_L$$

Figure 5A presents the energy distribution of the droplets on the surface of the cartilage and Figure 5B shows the dependence of the coefficient of friction (f) vs. wettability for healthy and degenerate surfaces of bovine cartilage (result after 5 minutes of the test). It has been also shown that phospholipids organized in bilayers on the AC surface are a lubricant and reduce the friction of the surface.

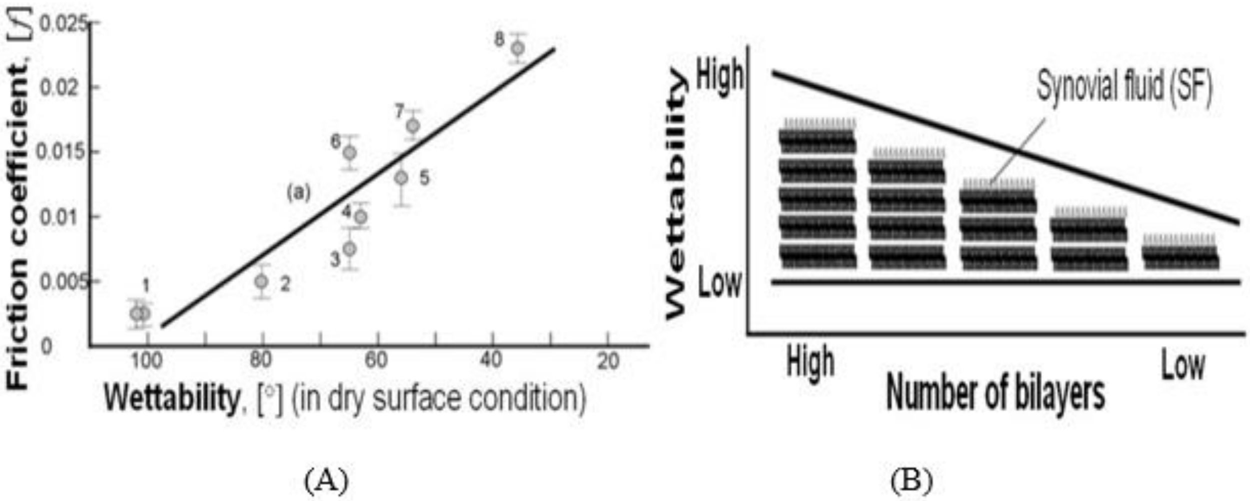

Figure 5A: *Coefficient of friction (AC)/(AC) vs. surface wettability of articular cartilage: (1) human and bovine cartilage 101º and 103º; (2) knee 79º; (3) sick cartilage 65º; (4) knee 63º; (5) hip disease 56.3º; (6) bovine cartilage partially degenerate 63º; (7) bovine cartilage partially degenerate 53º; (8) degenerate bovine cartilage 35.1º [6, 15]. Wettability of the cartilage surface was measured in a dry state at room temperature. (B) Dependence relationship between AC vs. the number of phospholipid bilayers [2, 10].*

Figure 5A shows the dependence of the coefficient of friction vs. contact angle for pairs of healthy (cartilage/cartilage) and degenerate surfaces. The friction coefficient test confirms the hypothesis about the relationship between the number of phospholipid bilayers (wettability) and friction [12-14]. In the case of healthy cartilage, the coefficient of friction is f=0.004-0.012 and for unhealthy 0.015-0.024 cartilage. The coefficient of friction for sick cartilage increased 2 to 3 times. In Figure 6A, literature values of the coefficient of friction of pairs (cartilage/cartilage) of healthy samples and samples in various degeneration states were collected [6]. Own research supported by the observation of other authors has shown that wettability is an essential parameter in the evaluation of biological surfaces.

Coefficient of friction vs. wettability for natural joints with healthy and degenerated cartilage surfaces of bovine cartilage samples for partially and wholly degenerate samples is presented in Figure (5A and 5B) shows changes in wettability of the AC surface depending on the number of bilayers. Increased values of the coefficient of friction are interpreted by a decrease in the number of bilayers [2, 6]. The implication of this condition was observed in osteoarthritis, where the increase in the coefficient of friction was associated with the gradual loss of surface amorphous layer, SAL [16, 17]. Phospholipid lamellar phases and biomacromolecules in SF participate in the electrostatic repulsion of the surface during friction. Strongly hydrated lamellar PLs are expected to cover cartilage surfaces and participate in hydrophilic-lamellar lubrication [2, 16, 17].

Conclusion

The cartilage surface was characterized using a combination of the pH, wettability and friction coefficient testing methods to support lamellar-repulsive mechanism of hydration lubrication. Wettability of the cartilage surface depends on the number of PLs that act as a lubricant. Phospholipids bilayers fulfill an important role in natural joint lamellar-repulsive lubrication mechanism. The cartilage can be classified as a group of intelligent material, which in the wet state has a contact angle of ~0º, and the air-dry state has a contact angle of ~104º.

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