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主 論 文 の 要 旨

論文題目　**Effects of Shear Viscoelasticity and Free Polymers on Tribological Properties of Phospholipid Polymer Brushes (リン脂質ポリマーブラシの摩擦特性に及ぼすずり粘弾性とフリーポリマーの影響)**

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論 文 内 容 の 要 旨

This thesis undertakes a detailed exploration of hydration lubrication by phospholipid polymer brushes, vital for diminishing friction in mechanical constructs such as artificial joints. It comprises two key research targets: dissecting the dynamics of 2-Methacryloyloxyethyl phosphorylcholine (MPC) polymer brush films and their synergy with free MPC polymers in a lubricative milieu. The first target aims to decode the lubrication processes by analyzing the shear viscoelasticity of these hydrated films and its linkage to friction characteristics, focusing specifically on the impact of shear gap width on lubrication efficacy. This is integral for connecting theoretical insights with practical applications, especially in scenarios where irregular surfaces result in a spectrum of gap sizes. The second target investigates the contribution of free polymers within the lubricating medium and their potential to augment the lubricative quality of polymer brush films. The outcomes of this research are expected to enhance the longevity and performance of polymer brush coatings in artificial joints.

Chapter 1 presents an overview of ultralow friction through hydration lubrication, emphasizing its importance in energy saving and achieving carbon neutrality. The chapter explores the details of using polymers for hydration lubrication, featuring a comprehensive review of past research on polymer brushes and the role of free polymers in enhancing lubricative properties. Previous studies have suggested that the lubrication properties of these films depend on their load and shear rate, implying that their lubricity could be attributed to shear viscoelasticity. On the other hand, there are reports interpreting high lubricity because of the formation of a low-viscosity hydration layer due to the high hydrophilicity of the phospholipid polymer. Thus, a unified understanding of the mechanism has not been achieved. For the second target, prior studies reported that the deterioration in lubricity of polymer brushes decelerates with increasing friction cycles. This phenomenon is thought to occur when parts of the polymer brush are sheared off the surface to become free polymers, which then adsorb to the surface and reduce friction. Therefore, it was hypothesized that adding a small amount of free polymer to the water swelling the brush film could improve its lubricity. Subsequently, the chapter defines the research aims, delineating the study's scope and trajectory. First, this study focuses on the gap dependence of shear viscoelasticity. As the shear gap changes with the load, the density and hence the shear viscoelasticity of the film change. Therefore, the gap dependence of shear viscoelasticity was hypothesized to play a role in the mechanism, though no reports have confirmed this. Next, the second target is to elucidate the mechanism by which free polymers (polymers present in solution, not adsorbed on the substrate) enhance the frictional properties of polymer brush films.

Chapter 2 details the deployment of the fiber wobbling method (FWM). This innovative technique, crucial for assessing the behavior of thin films across different shear gaps, was specifically developed for measuring shear viscoelasticity. To elucidate the gap dependence of the shear viscoelasticity of polymer brush films, the FWM combined with an inverted microscope was developed, allowing simultaneous measurement of shear viscoelasticity and shear gap. A unique measurement method using optical interference was proposed for gap measurement, achieving an accuracy of 5 nm.

In Chapter 3, the preparation of MPC polymer brush films is detailed, focusing on photo-induced polymerization, patterning process by photolithography, and analysis of films' characterization. Films with thicknesses of 50 nm and 70 nm were produced, and photolithography was used to create film patterns approximately 10 μm in diameter. Graft density, confirmed by NR measurements, was around 5%, and the films' swelling due to hydration was verified. This chapter also covered the measurement of the gap dependence of shear viscoelasticity. The results revealed a characteristic gap dependence of the loss tangent, suggesting that changes in water content within the polymer brush film due to load and osmotic pressure balances predominately influenced the results. Furthermore, by estimating the load from the axial deformation of the FWM probe, the gap dependence of the coefficient of friction (COF) was obtained. The MPC polymer brush films demonstrated exceptional lubrication with a COF lower than 0.0001. By comparing the gap dependence of the loss tangent and COF, it was discovered that the polymer brush film achieves high lubricity in two different shear gaps. In one state, the film is flexible and supports the load through osmotic pressure; in the other, the film is compressed and fully elastic, with the hydration layer formed by the hydrophilicity of the polymer brush contributing to lubrication. These results indicate that different lubrication mechanisms proposed in previous studies manifest in different gap regions, thus providing a unified understanding of the lubrication mechanism by clarifying the gap dependence of shear viscoelasticity of the polymer brush.

Chapter 4 examines the synergistic effects of free MPC polymers and MPC polymer brushes. Pin-on-disk (POD) type friction testing demonstrated that the addition of free polymers halved the COF. To elucidate this mechanism, neutron reflection (NR) measurement was used to analyze the hydration interfacial structure. Results showed that the adsorption of free polymers to the brush film forms a mixed film with the highest volume fraction, and the exclusion volume effect of the polymer brush film prevents the adsorbed free polymers from approaching the substrate, creating a layer rich in water on the outermost surface of the substrate. The increased volume fraction (polymer concentration) at the interface enhances the osmotic pressure, improving load-bearing capacity. Additionally, the water-rich layer formed on the substrate surface allows the adsorbed layer of free polymers to easily detach from the polymer brush film, reducing shear resistance. This reduction in shear resistance was also confirmed by shear viscoelasticity measurements using FWM.

In summary, this thesis represents a substantial advancement in the field of tribology, particularly in the study of hydration lubrication. It primarily addresses two areas: a detailed examination of the hydrated MPC polymer brush films' shear gap dependence of shear viscoelastic properties, and an exploration of how free polymers contribute to improved lubrication. Key findings elucidate the mechanisms through which phospholipid polymer brush films exhibit high lubricity and how the addition of free polymers enhances lubrication. This work is especially relevant to the design of artificial joints, where reducing friction is critical. The study demonstrates that the hydrated MPC polymer brush can withstand pressures higher than those typically found in human hip joints, suggesting its suitability in artificial joint applications. However, challenges remain in understanding how gap changes due to surface roughness affect lubrication properties and exploring the normal viscoelastic properties of the polymer layer. The research underscores the importance of material hardness and surface roughness in artificial joint design. It suggests that advancements in surface uniformity and the use of softer materials could achieve ultra-low friction levels, with implications for improving the design of artificial joints. The study also points to the potential of free MPC polymers in enhancing lubrication and extending the lifespan of artificial joints with MPC polymer brush coatings. Overall, this thesis not only enriches the theoretical understanding of lubrication mechanisms but also lays a solid foundation for developing more efficient and effective lubrication systems, bridging the gap between scientific inquiry and practical application.