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Influence of chain ordering on frictional properties of self-assembled monolayers (SAMs) in nano-lubrication

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ABSTRACT

Adhesion of organic films to substrates is important in applications that involve solid surfaces in sliding contact. Although the thickness of self-assembled monolayers (SAMs) is only a few nanometers, they can drastically modify the frictional properties of the underlying substrate, and thus have great potential for serving as boundary lubricants on micro- and nano-scales. This review focuses on the relationship between the structural and compositional properties of SAMs and their frictional response. Adhesion of SAMs to the substrate surface usually occurs through chemisorption of the head groups on the constituent molecules, with molecular interactions such as van der Waals interactions playing important roles in organizing the molecules into surface films, and in controlling their tribological behavior. The durability and wear resistance of SAMs depend on the nature and strength of the binding forces between the head groups and the substrate surfaces, while the adhesion and friction forces are strongly influenced by the interactions of the terminal groups with the counterfaces. Results from both experimental measurements and molecular dynamics simulations consistently indicate that structural ordering of alkyl chains in SAMs reduces their frictional response, and that SAMs formed by molecules with alkyl chains longer than 8 to 10 methylene units are well organized, exhibiting low levels of friction. Less densely packed or more disordered monolayers inherently possess greater numbers of conformational defects at room temperature and present lower barriers to defect creation under the action of a contacting surface, and thus exhibit higher friction. Cross-linking of the spacer chains can reduce the frictional response of disordered films by increasing the chain ordering, but has little impact on SAMs that are already well ordered. On the other hand, introduction of sterically demanding terminal groups and dissimilar molecules reduces molecular ordering in SAMs and increases their frictional response. Significant growth in the application of SAMs to control the adhesion, friction, and wear of materials is expected with better understanding of the frictional properties of SAMs controlled by their structures and compositions and with technological progresses.

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1. Introduction

Friction between solid surfaces sliding against each other brings many undesired effects and minimal level of friction is sought after in many mechanical systems. Since surface properties are generally considered to be controlled by the outmost 5–10 Å layer [1], a logical solution to modify the adhesion, friction, and wear properties of solid surfaces is through adsorption of lubricant layers. Boundary lubrication usually occurs under high-load and high-speed conditions, where the solid surfaces are so close together that surface interactions between mono- or multi-molecular films of lubricants and the solid asperities dominate the contact. Strong adhesion may arise from capillary, electrostatic, and van der Waals forces, and in certain cases from "chemical" forces such as hydrogen bonding and solid bridging [2–4]. Films of boundary lubricants can form on the bearing surfaces through physical adsorption, chemical adsorption, and/or chemical reaction, which significantly reduce the adhesion and friction forces of the contacting solid surfaces. Recent developments in high-density storage technologies (hard drives) and micro-/nanoelectromechanical systems (MEMS/NEMS) have significantly increased the demand for ultrathin lubricant films that can modify the frictional properties between contacting surfaces on micro- and nano-scales [1–8]. These applications require molecular lubricants with ultimate thickness of less than 10 nm, which should provide reduced surface energy, low shear modulus and friction coefficient, tailored dynamic behavior, along with the self-repairing ability, tolerance to temperature and humidity variations, and long shelf-lives [9].

Because of their ability to modify the interfacial properties on the nano-scale, ultrathin polymer films, Langmuir–Blodgett (LB) monolayers and multilayers, nanocomposite molecular layers, and self-assembled monolayers (SAMs) all have been explored as boundary lubricants [10–12]. Adhesion of organic molecules to the substrate is important for molecular lubricants, thus monolayers that are covalently bonded to the substrate, such as those formed from self-assembly, are better candidates for boundary lubricants than LB films [13–15]. Compared to the poor wear resistance of the physisorbed organic monolayers, molecules in SAMs adhere to the substrate surface through strong chemical bonds and can provide robust molecular lubrication. SAMs with well organized, densely packed spacer chains can serve as excellent boundary lubricants and hold the potential to solve many practical adhesion- and friction-related problems [6,16].

Molecular self-assembly is a natural phenomenon that has been observed in many biological, chemical, and physical processes [17]. SAMs are highly ordered, quasi-two-dimensional structures formed by adsorption of active precursors from solution onto a solid substrate, and ordering in the SAM system is produced by a spontaneous chemical synthesis at the interface as it approaches equilibrium [2,10,18,19]. As illustrated in Fig. 1a, there are three basic building blocks for SAM molecules: a head group that binds strongly to the substrate, a surface terminal (tail) group that constitutes the outer surface of the film, and a spacer chain (backbone chain) that connects the head and terminal groups [6,19,20]. The kinetics and equilibrium of SAM formation involve a delicate interplay between molecule-solvent interactions, substrate-adsorbate interactions, nonbonded interactions between adsorbates, and intra-molecular interactions such as bond stretches, angle bends, and torsion [1,19]. Both chemisorption and intra- and inter-chain nonbonded interactions (e.g., van der Waals, steric, repulsive, and electrostatic forces) contribute to the packing and ordering of molecules in SAMs [19–21]. The conformation of the individual chains within the assembly, and their packing and ordering with respect to each other depend on the balance between inter-chain forces, the interactions with the surface, and the entropic effects as well [19,21]. Overall, molecules in SAMs rely on weaker and less directional bonds, such as ionic bonds, hydrogen bonds, and van der Waals interactions, to organize atoms, ions, or molecules into structures, with the molecules or ions adjusting their own positions to minimize the thermodynamic energy [6,22].

A wide range of groups both in the spacer chain and the chain terminal can be incorporated into SAM molecules to produce stable two-dimensional assemblies with certain ordering, wetting, adhesion, and lubrication properties [1,19]. Fundamental understandings of the relationship between the frictional properties of SAMs and the structure and chemical functionality of the molecules from which they form are critical for the successful design and application of SAMs as molecular lubricants. The molecular structure, mechanical properties, and tribological properties of SAMs have been studied in great detail experimentally using scanning probe microscopy techniques, including atomic force microscope (AFM), friction force microscope (FFM), chemical force microscope (CFM), interfacial force microscope (IFM), and surface force apparatus (SFA). Meanwhile, molecular dynamics simulation provides a valuable theoretical tool for studying the frictional response of SAMs with varying structural and compositional properties. In this review, we provide an overview of the relationship between the frictional properties of SAMs and their structures, particularly chain ordering of the constituent molecules, observed from both macro- and micro-scale experimental investigations, as well as from molecular dynamics simulations. This review is not intended to be comprehensive, as our focus is on exploiting SAMs toward the development of boundary

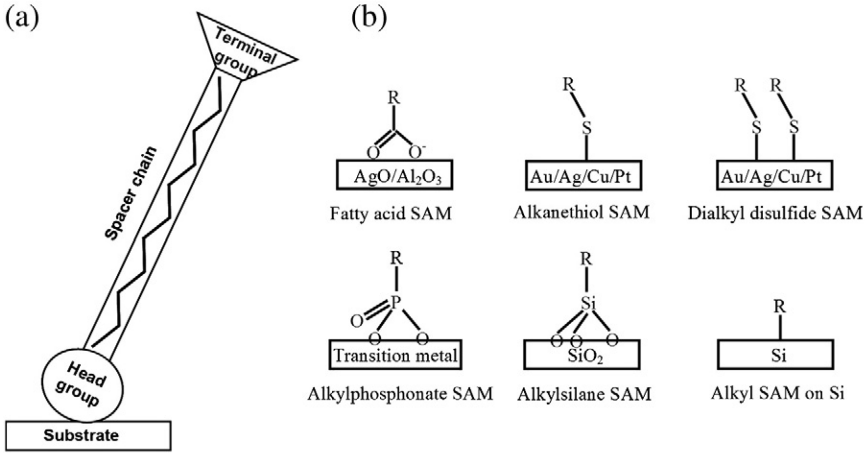

Fig. 1. Schematic illustrations of SAM structure: (a) representation of the molecule that can form a SAM; (b) structures of some typical SAMs, where R represents the alkyl spacer chain.