7th World Tribology Congress, WTC 2022
July 10-15, 2022, Lyon, France

Adsorption mechanism of Tributylmethylphosphonium dimethylphosphate ionic liquid on diamond-like carbon coatings: Neutron reflectometry study

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The study of the adsorption mechanism of ionic liquids (ILs) on diamond-like carbon coatings is particularly important to understand their lubrication properties. We invesigated an adsorption mechanism between tributylmethylphosphonium dimethylphosphate ($[P_{4441}]^+[DMP]^-$) IL and tungsten-doped diamond-like-carbon (WDLC) and hydrogenated diamond-like-carbon (hDLC) coatings using neutron reflectometry (NR). We employed $[P_{4441}]^+[DMP]^-$ IL because of a large difference in scattering length density (SLD) between cations ($[P_{4441}]^+$) and anions ($[DMP]^-$) which is desirable to detect the ionic accumulation. NR investigation revealed a 0.75 nm thick adsorbed layer based on anions $[DMP]^-$ formed on the WDLC surface. On the contrary, no IL-based adsorbed layer was found on the hDLC surface. In conclusion, doping of DLC coatings with tungsten (i.e. WDLC) significantly improves its reactivity with $[P_{4441}]^+[DMP]^-$ ILs, thus can improve their lubrication properties.

Keywords: WDLC coatings, hDLC coatings, adsorbed mechanism, ionic liquid, neutron reflectometry measurement

1. Introduction

Diamond-like-carbon (DLC) coatings are employed in different machine-driven applications, because of their excellent tribological properties, for example, low friction, high protection to wear and long endurance. DLC coatings have low adsorption and poor reactivity with conventional lubricants, which results in their poor lubrication control. To overcome their inertness and thus to enhance and optimize their interactions, the DLC coatings are doped with different metal ions such as tungsten (W). Ionic liquids (ILs) have several characteristics in bulk and at the interface with metals that other molecular liquids do not possess. Because to their reactive nature, they possess great potential to interact with inert materials, such as DLC coatings, however, their potential has not yet been explored to any relevant extent. Aim of this study is to explore the adsorption mechanism of the IL with undoped and doped DLC coatings. Neutron reflectometry (NR) is a powerful tool to investigate the interaction between different molecules and surfaces. NR provides direct quantitative information about the adsorption on free surfaces and buried interfaces. This technique provides unambiguous results because there is no need for sample preparation and no high vacuum is involved.

2. Methods

Direct-current magnetron sputtering was used to deposit WDLC and hDLC coatings on atomically-flat (R_q<0.2 nm) Si-substrate. We maintained a low deposition rate to achieve the ultra-smooth coatings (R_a<1 nm) with thickness 50 nm. We calculated the theoretical SLD of the WDLC and hDLC coatings to be 6.52×10^{-6} Å^{-2} and 4.32×10^{-6} Å^{-2}, respectively.
Polar deuterated glycerol (DG) was used as a base oil and $[P_{4441}]^+[DMP]^-$ (PP) IL as additive because of their excellent adsorption properties. The scattering length density at 100 °C is provided in Table 1.

Table 1: data

Species	SLD (10^{-6}, Å^{-2})
DG	5.49
$[P_{4441}]^+[DMP]^-$	-0.0312
$[DMP]^-$	0.93
$[P_{4441}]^+$	-0.694

3. Results and Discussions

The Figure 1a and Figure 1b is showing the interface between coatings (hDLC and WDLC) and IL. The WDLC coatings indeed interact with $[P4441]^+[DMP]^-$ IL. SLD profiles concluded that the adsorbed layer consists of anions $[DMP]^-$ with a thickness of 0.75 nm. On the contrary $[P4441]^+[DMP]^-$ IL doesn't interact with the hDLC coatings. However, there is a DG-based 2.7 nm thick adsorbed layer form on the surface due to the presence of OH-terminated surface bonds.

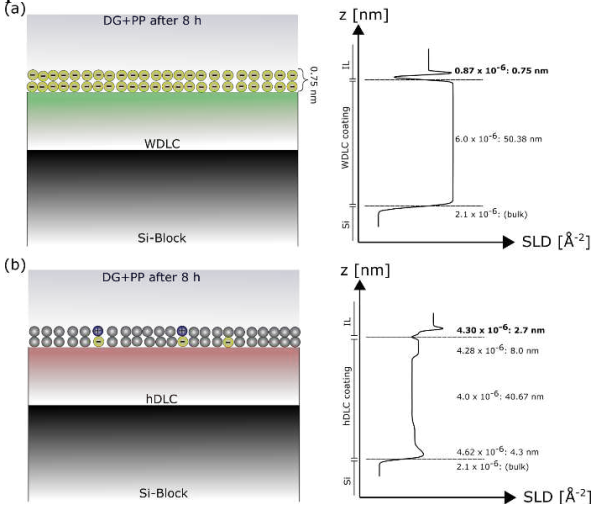

Figure 1: Adsorption mechanism with $[P_{4441}]^+[DMP]^-$ IL additives on the (a) WDLC and (b) hDLC coatings.