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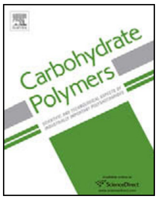

Lubrication of starch in ionic liquid–water mixtures: Soluble carbohydrate polymers form a boundary film on hydrophobic surfaces

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ABSTRACT

Soluble starch polymers are shown to enhance the lubrication of ionic liquid–water solvent mixtures in low-pressure tribological contacts between hydrophobic substrates. A fraction of starch polymers become highly soluble in 1-ethyl-3-methylimidazolium acetate (EMIMAc)–water solvents with ionic liquid fraction ≥60 wt%. In 65 wt% EMIMAc, a small amount of soluble starch (0.33 wt%) reduces the boundary friction coefficient by up to a third in comparison to that of the solvent. This low-friction is associated with a nanometre thick film (ca. 2 nm) formed from the amylose fraction of the starch. In addition, under conditions where there is a mixture of insoluble starch particles and solubilised starch polymers, it is found that the presence of dissolved amylose enhances the lubrication of starch suspensions between roughened substrates. These findings open up the possibility of utilising starch biopolymers, as well as other hydrocolloids, for enhancing the performance of ionic liquid lubricants.

1. Introduction

Ionic liquids (ILs), a class of low-melting-point organic salts, are promising candidates as high performance "green" lubricants due to their negligibly low vapour pressure, excellent thermal stability, electrical conductivity and controllable physical and chemical properties. ILs are thus proposed to solve some of the most difficult lubrication problems occurring in a number of engineering applications (Palacio & Bhushan, 2010). For example, micro electrical mechanical systems (MEMS) require low-viscosity lubricants to overcome high static friction, while a number of medical- and bio-engineering applications require use of low vapour pressure lubricants with high electrical conductivity and heat capacity (Nainaparampil, Eapen, Sanders, & Voevodin, 2007; Palacio & Bhushan, 2008; Pu, Jiang, Mo, Wang, & Xue, 2011).

It was hypothesised that ILs may be effective lubricants due to formation of molecularly ordered layers at a static IL/solid interface that in turn would facilitate formation of a low-friction boundary when surfaces are set in relative motion (Horn, Evans, & Ninham, 1988). However, experimental results demonstrated that these ordered layers can be disrupted in a rubbing contact, which results in the disappearance of an effective slip plane (Atkin & Warr, 2007) (Gebbie et al., 2013; Min et al., 2009; Perkin et al., 2010; Perkin, 2012; Smith et al., 2012). This complication can potentially be overcome through the use of additives. In particular, polymer additives are commonly used to enhance lubrication of aqueous and oil

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based lubricants to yield superior thin film and boundary lubrication properties. For ILs it was shown that the presence of adsorbed polymer layers that are also highly solvated can protect molecularly layered ionic structures from immediate destruction by shear forces, thereby preserving the low friction slip plane (Perkin, Albrecht, & Klein, 2010). In addition, in comparison to solvents alone, the presence of adsorbed polymers with high viscoelasticity have significantly better load bearing capacity, i.e., they cannot be easily squeezed out under compression (Harvey, Yakubov, Stokes, & Klein, 2011).

Polysaccharide polymers, such as pectins, starches, chitosan, and cellulose are promising additives due to their low cost and abundance, and because they are highly soluble in ILs, which is a key pre-requisite for the formation of a solvated polymer film (Liu & Budtova, 2012). As it was recently shown, IL salts solvate polysaccharides by forming hydrogen bonds with their hydroxyl groups (Mateyawa et al., 2013; Remsing et al., 2006; Zhang et al., 2014). These interactions disrupt the complex intermolecular hydrogen bonding network present in many polysaccharides and promote their dissolution. For examples, an IL, 1-ethyl-3-methylimidazolium acetate (EMIMAc) is used to solubilise waxy starches (Liu & Budtova, 2013), with the suggested conformation of amylopectin in EMIMAc being similar to the one observed in water, i.e., as a compact ellipsoid. It was also found that the mixed solvents of EMIMAc and water contribute to the complex phase transition in starches that involves gelatinisation and dissolution, whereby two processes can occur either competitively or synergistically depending on the EMIMAc/water ratio (Mateyawa et al., 2013; Xie et al., 2014; Zhang et al., 2015).

Despite a promising set of properties, such as solvation, the mechanism of polysaccharide lubrication in ionic liquids remains totally unexplored. Furthermore, there is a degree of uncertainty whether addition of polymers will result in significant modification of boundary lubrication properties. In the boundary regime, the lubrication is dominated by the presence of an adsorbed film, the formation of which may be energetically unfavourable due to strong hydrogen bonding between IL and polymer molecules.

In this work, we show for the first time the enhanced lubrication of an IL-based solvent, which is achieved by using starch polysaccharides as an additive (0.1–0.5 wt%). Starch, as a biopolymer from agro-sources, has already attracted intense interest in materials science, especially for developing biodegradable plastics (Shogren, Fanta, & Doane, 1993). Naturally in plants, it exists in the form of granules 1 mm –100 μm in size; each granule is composed of alternating amorphous and semi-crystalline layers (growth rings) (100–400 nm in thickness); with the semi-crystalline layer in turn being formed by stacking crystalline and amorphous lamellae with periodicity of 9–10 nm. Starch consists of two major carbohydrates: amylose (mainly linear) and amylopectin (hyper-branched) (Fu, Wang, Li, Wei, & Adhikari, 2011; Jane, 2009; Pérez, Baldwin, & Gallant, 2009 Pérez & Bertoft, 2010). The structure of the granules varies significantly depending on the amylose/amylopectin content. For example, the granules of high-amylose starches are more compact with fewer voids, which makes them less accessible for solvents compared to low-amylose starches (Chen et al., 2009; Chen et al., 2011).

In the current work, we discover that the starch polymers leach into EMIMAc–water mixtures from starch granules at room temperature. The leached polymer is capable of reducing boundary friction between rough polydimethylsiloxane (PDMS) elastomer substrates by up to 2.5 times compared to the pure solvent and up to 3 times compared to water. We also show that the presence of such soluble polymers results in the facilitation of suspension lubrication thereby enabling the use of starch suspension as lubricants without the need of separating insoluble materials.

2. Materials and methods

2.1. Materials, solution and suspension preparations

Two varieties of commercially available maize starches are used in this work, including waxy maize starch (Mazaca 3401X) (WMS), and Gelose 50 (G50); WMS is supplied by New Zealand Starch Ltd. (Onehunga, Auckland, New Zealand), and G50 by Ingredion ANZ Pty Ltd. (LaneCove, NSW, Australia). Both starches are chemically unmodified and the amylose contents for these two types of starches are 3.4 wt% and 56.3 wt% respectively, as measured by Tan, Flanagan, Halley, Whittaker, and Gidley (2007) using the iodine colorimetric method. The original moisture contents are 12.4% and 13.6% respectively.

1-Ethyl-3-methylimidazolium acetate (EMIMAc) of purity ≥90%, produced by BASF, is supplied by Sigma–Aldrich, and is used as received without further purification. Deionised water is used in all instances.

EMIMAc–water mixtures are prepared by adding water to obtain desired EMIMAc/water mass ratios of 50/50, 55/45, 60/40, 65/35, and 70/30. Solutions are then placed on ice to minimise heating upon mixing. After 10–15 min, the solutions are placed in the fume hood at room temperature (24 °C) to equilibrate for ∼1 h.

2.2. Starch suspension and solution preparations

Suspensions are prepared by mass by mixing an aliquot of starch into a measured amount of the EMIMAc-water mixture at room temperature (24 °C). The suspensions are shaken for 1 min and then stored for 24 h prior to use.

Solutions of soluble starch are prepared by centrifugation of the suspension (4000 g, 30 min) and separating the supernatant. Thereafter, an aliquot of the supernatant is precipitated with ethanol (v:v = 1:5). The precipitate is separated, dried (110 °C, 12 h), and weighed. The solute content in the supernatant is then back calculated based on the mass of the precipitate. EMIMAc–water solvent is then used to adjust the concentration to the desired value. The precipitated material is also used for size exclusion chromatography (SEC).

The precipitate can be easily re-dissolved in the EMIMAc–water solvent, and the properties of the obtained solutions are identical to that of a supernatant. For simplicity, the supernatant solutions are used in a majority of the experiments.

2.3. Tribological measurements

The friction measurements are performed using a Mini Traction Machine (MTM, PCS Instruments Ltd., UK). The rubbing contact consists of a polydimethylsiloxane (PDMS) (SYLGARD® 184 Silicon Elastomer Kit, Dow Corning, MI) ball of radius 0.95 cm and PDMS disc of radius 23 mm and thickness 4 mm. The discs used are with two surface roughness values: 'smooth' with a root-mean-square (RMS) roughness of 9 nm, and 'rough' with an RMS roughness of 380 nm. The PDMS ball has only one surface RMS roughness at 26 nm. The Young's modulus of the PDMS is 2.4 MPa (Bongaerts, Fourtouni, & Stokes, 2007). Untreated hydrophobic PDMS surfaces, water contact angle ca. 95°, were used unless stated otherwise.

In a typical MTM experiment, the ball and disc are driven independently at velocities v_b and v_d respectively, yielding the entrainment speed $U = (v_b + v_d)/2$. The relative motion of the moving ball and disc determine the slide-to-roll ratio, $\mathrm{SRR} = (v_b - v_d)/U$. The lateral friction force F_i experienced by the ball is measured using a force transducer. To prevent offset errors, lateral force measurements are taken at each entrainment speed when $v_b > v_d$ and $v_b < v_d$, both rotating in the same direction, and the average was taken. Further details of the soft contact friction experiments are