

# Covalently attached mesoporous silica–ionic liquid hybrid nanomaterial as water lubrication additives for polymer-metal tribopair



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## ABSTRACT

In order to further enhance the tribological performance of a polyimide composite subjected to water lubrication rubbing with stainless steel, functionalized mesoporous SiO<sub>2</sub> nanoparticles were blended into water as a new lubrication additive. Novel poly (1-(4-vinylbenzyl)-3-methylimidazolium chloride) IL was synthesized and grafted onto mesoporous SiO<sub>2</sub> (SiO<sub>2</sub>-IL) via an atom transfer radical polymerization route. It was demonstrated that SiO<sub>2</sub>-IL as water additives significantly reduced the friction coefficient and wear of the polyimide composite. Comprehensive analyses of the worn surfaces indicated that the grafted IL layer facilitated the formation of a protective tribofilm, separating the direct rubbing and alleviating tribo-oxidation of the steel surface. This work proposed a new route for enhancing water lubricated polymer-metal rubbing pairs.

## 1. Introduction

Polymers and their composites have been utilized in vast number of motion systems due to their excellent self-lubrication and high chemical stability. It has been demonstrated that even under harsh boundary lubrication conditions in water, formulated composites exhibited high tribological performance [1–4]. Owing to physical and chemical actions occurring on friction interface, polymers tend to transfer onto metallic counterface mitigating direct rubbing of the tribopair [5–7]. Usually, addition of reinforcing fibres and solid lubricants into a polymer matrix improves the load-carrying and self-lubrication capabilities [8–10].

In light of increasing demands for environmental protection, replacing oil lubricants by water in certain motion systems of hydropower plants and marine ships is of special interest [11–13]. Polymer composites are attracting intensive attentions in such applications for enhancing the lifespan and reliability of the motion systems. Nevertheless, the lubrication performance of water is often poor due to low viscosity-related bearing capability of water film. Moreover, unlike formulated oil lubricants, generation of protective tribofilm is usually difficult owing to the chemical inertness of water [14,15]. The presence of water on the interface hinders interfacial transfer of polymer composites [14,15]. As a result, polymer composites exhibit even lower tribological performance

in water than that obtained under dry sliding conditions [14,15]. Therefore, in order to develop high performance polymer-metal tribopairs subjected to harsh boundary lubrication, it is important to enhance the lubrication performance of water by using environment friendly additives.

Ionic liquids (ILs) comprising ion pairs of asymmetric cations and anions are regarded as effective “green” lubricant additives [16–18]. Liu et al. revealed that ILs with a bipolar structure can be adsorbed onto the friction surface and form a protective tribofilm, leading to excellent lubrication. Low energy electrons are emitted from contact convex points, yielding positive charge of the tiny sites and hence strengthening absorption of anions [19,20]. Counter cations successively assemble and thus help to form a double electrical layer yielding strong absorption film [21–23]. Moreover, especially for sliding under harsh conditions, active elements in ILs can react with freshly rubbed surfaces to form a robust tribofilm, probably due to coaction of high flash temperature, high stress on the interface and substrate-catalytic role [23,24]. It has been demonstrated that alkyimidazolium tetrafluoroborate and hexafluorophosphate ILs are suitable anti-wear additives used in water for the lubrication of metal-metal, metal-ceramic and ceramic-ceramic pairs [23,25–28].

Spherical ceramic nanoparticles (NPs) as water additives significantly

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reduce the friction and wear of glass lens and silicon wafer tribopair [29]. It was supposed that NPs entrapped on the sliding interface can take significant load behaving like “ball bearings” [29,30]. Moreover, a solid tribofilm consisting of high fraction of NPs was identified on rubbed surfaces and esteemed essential for enhancing boundary lubrication efficiency [30,31]. It was manifested in recent years that functionalization of inorganic nanomaterials, e.g. carbon nanotubes and graphene, by grafting ILs onto their surface led to excellent lubricating performance when the hybrid nanomaterials were used as additives in base oil [32–34]. Synergism of the inorganic NPs and the organic shell materials was identified in terms of physicochemical adsorption tendency and tribo-chemical actions [35,36]. In particular, NPs with pores and high specific surface area can increase the coverage of organic shell, improving its adsorption with counterpart. Nonetheless, functionalized porous ceramic NPs as lubricant additives for polymer-metal sliding pairs exposed to harsh conditions have been rarely reported. It is expected that functionalized porous nanomaterials can open novel opportunities for developing high performance lubricant additive.

In the present work, hydrophilic IL 1-vinyl-3-butylimidazolium chloride (VBIM-Cl) and spherical mesoporous SiO<sub>2</sub> NPs were synthesized. In particular, the VBIM-Cl was grafted onto the wall of SiO<sub>2</sub> via an Atom Transfer Radical Polymerization (ATRP) route [37]. The lubrication performance of synthesized mesoporous SiO<sub>2</sub>-ILs as water lubrication additives was evaluated by measuring the friction and wear when a polyimide (PI) composite sliding against stainless steel (SUS316) in deionized water. Tribological mechanisms were investigated via comprehensive characterizations of worn surfaces. It was the objective of the present work to explore the potential of mesoporous SiO<sub>2</sub>-ILs hybrid nanomaterials as water additives for polymer-metal tribopairs. We expect that this work can be helpful for developing high performance tribopairs for applications exposed to water lubrication.

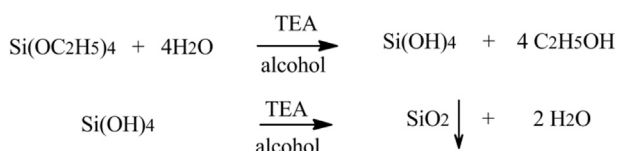
## 2. Materials and experimental

### 2.1. Materials

Cetyltrimethylammonium bromide (CTAB) and cuprous chloride (CuCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Tetraethylorthosilicate (TEOS), triethanolamine (TEA) and N-methylimidazole were of analytical agents purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). 4-(chloromethyl)styrene (CMS), 3-chloropropyl (trimethoxy)silane (CPTMO) and 2,2'-bipyridyl (BiPy) were purchased from Aladdin (China). All the chemicals were of analytical grade and used as received without further purification. Polyimide composites filled with 10 vol% fibres and 8 vol% graphite (PI/SCF/Gr) were prepared by compression moulding technique and detailed information is available in a previous work [38].

#### 2.1.1. Synthesis of SiO<sub>2</sub> NPs

SiO<sub>2</sub> NPs were synthesized following a procedure similar to Stöber process in an alkali ethanol/water solution by hydrolysis and polycondensation of TEOS, for which the synthesis principle is in Scheme 1. Firstly, 0.90 g alcohol was diluted with 6.4 mL deionized water and a mixture of 2.86 g CTAB and 8.6 mL deionized water (25 wt%) was added into the diluted solution upon stirring. Then, 0.28 g TEA and 10.0 mL Na(OH) (0.2 M) were added into the solution. Subsequently, 7.3 mL TEOS was a dropwise added into the solution. As the reaction occurred at



Scheme 1. The preparation mechanism of SiO<sub>2</sub> NPs.

70 °C, a homogeneous milky colloidal solution was gradually formed with continuous stirring. After stirring for 2 h, the product was collected by centrifugation and washed with deionized water and ethanol alternatively. After that, CTAB templates were removed by circumfluence extraction of the collected solid sample in a mixture of 12 M HCl (30.0 mL) and ethanol (120.0 mL) at 50 °C for 8 h, leading to the formation of holes in SiO<sub>2</sub>. Silica NPs were collected by centrifugation, followed by thoroughly alternative washing using ethanol and deionized water for 3 times, and finally vacuum-dried overnight.

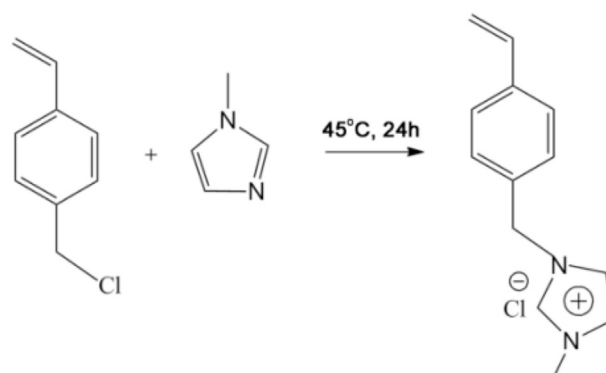
#### 2.1.2. Synthesis of IL

Hydrophilic IL monomer of 1-(*p*-vinylbenzyl)-3-methylimidazolium chloride (VBMI-Cl) was synthesized following a nucleophilic substitution reaction route. A mixture of 4-(chloromethyl)styrene (3.05 g, 20.0 mmol) and N-methylimidazole (1.64 g, 20.0 mmol) was stirred at 45 °C for 24 h under nitrogen atmosphere and the synthesis route was shown in Scheme 2. The reaction mixture was cooled down to room temperature, and the target product was extracted from the mixture of ethyl acetate and deionized water, and finally dried at 60 °C overnight. <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectra and <sup>13</sup>C NMR were measured on a Bruker Avance 400 Spectrometer operating at 400 MHz using D<sub>2</sub>O as the solvents. D<sub>2</sub>O, 400 MHz. <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz): δ<sub>H</sub> = 8.72 (1H, s, -N-CH-N-), 7.31–7.40 (6H, m, -N-CH-CH-N- and Ph), 6.63 (1H, dd, CH<sub>2</sub>=CH-), 5.77 (1H, d, CH<sub>2</sub>=CH-), 5.26 (2H, s, Ph-CH<sub>2</sub>-N-), 5.25 (1H, d, CH<sub>2</sub>=CH-), 3.82 (3H, s, -N-CH<sub>3</sub>); <sup>13</sup>C NMR: δ<sub>C</sub> = 35.8, 52.5, 138.0, 115.0, 122.0, 123.0, 127.0, 135.0, 137.0 and 115.0. Detailed NMR data was given in Fig. S1, Table S1 and Table S2. As seen from Fig. S2, white precipitate was obtained when silver nitrate was added into the IL, corroborating the presence of Cl<sup>-</sup> ions.

#### 2.1.3. Synthesis of SiO<sub>2</sub>-IL

First, CPTMO was immobilized on mesoporous SiO<sub>2</sub> surface. That is, a solution of 20.0 mL toluene containing 0.50 g BiPy and 0.50 g CPTMO was mixed with 1.00 g mesoporous SiO<sub>2</sub> under nitrogen atmosphere and the mixture was refluxed for 24 h and the preparation procedure was shown in Scheme 3. The SiO<sub>2</sub> immobilized with CPTMO was then washed with acetone and water to remove any unreacted solvent. Finally, the solid product was dried under vacuum at 100 °C overnight.

We followed ATRP route to graft ILs onto the SiO<sub>2</sub> surface. 3.5 mg CuCl and 7.8 mg BiPy were added to a 100 mL three-necked, round-bottom flask with a magnetic stirrer bar under nitrogen atmosphere, and then a solution of 40.0 mL DMF with 1.00 g VBMI-Cl was transferred to the above round-bottom flask. After that, 1.00 g CPTMO-grafted mesoporous SiO<sub>2</sub> was added into the flask and the mixture was well-stirred and heated with an oil bath to 50 °C. After 12 h reaction time, SiO<sub>2</sub>-IL nanomaterials were obtained. The solid product was removed from the flask, washed with DMF and copious amount of water, and then dried under vacuum at 100 °C overnight. Finally, 0.5 and 2.0 wt% SiO<sub>2</sub>-IL was dispersed in pure water, respectively. The mesoporous SiO<sub>2</sub> and SiO<sub>2</sub>-IL



Scheme 2. Synthetic route of VBMI-Cl.

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