

Tribological evaluation of environmentally friendly ionic liquids derived from renewable biomaterials

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Abstract: Unlike most of the conventional ionic liquids (ILs) derived from non-renewable resources, five environmentally friendly ILs ([Ch][AA] ILs) derived from amino acids (AAs) and choline (Ch) were synthesized using biomaterials by a simple, green route: acid–base reaction of Ch and AAs. The thermal and corrosion properties, as well as viscosity, of the prepared ILs were examined. The results revealed that the anion structure of ILs plays a dominant role in their thermal and viscosity behavior. These ILs exhibited less corrosion toward copper, related to their halogen-, sulfur-, and phosphorus-free characteristics. The tribological behavior of the synthesized ILs was examined using a Schwingungs Reibung und Verschleiss tester, and the results indicated that these ILs exhibit good friction-reducing and anti-wear properties as lubricants for steel/steel contact. Results from energy-dispersive spectroscopy and X-ray photoelectron spectroscopy indicated that the good tribological properties of [Ch][AA] ILs are related to the formation of a physically adsorbed film on the metal surface during friction.

Keywords: choline; amino acids; ionic liquids; lubricant; tribological behavior; environmentally friendly

1 Introduction

Currently, toxicity, safety, and environmental compatibility of lubricants are attracting increasing attention as almost half of the lubricants are estimated to eventually enter the environment by evaporation, leakages, or spills, leading to adverse negative effects on the environment and ecosystem [1, 2]. Therefore, environmentally friendly lubricants have attracted extensive attention, and a considerable number of studies have been conducted in this field [3–8]. Generally, environmentally friendly lubricants are divided into two categories according to their raw material sources. The primary environmentally friendly lubricants are derived from nature resources and are utilized in the modern industry, e.g., natural vegetable oils [9], chemically modified vegetable oils [7, 8], genetically modified vegetable oils, and synthetic

lubricants derived from biomaterials [10–12]. On the other hand, petrochemical-derived lubricants with good biodegradability are considered as the second type of environmentally friendly lubricants, e.g., synthetic esters, polyether, and low-viscosity polyalphaolefins [1]. Among these environmentally friendly lubricants, synthetic lubricants derived from natural resources have attracted extensive scientific attention because of their flexible molecular structures, controllable performance, and renewable features, and recently, various biomaterials have been used as raw materials to develop environmentally benign lubricants [10–12].

Ionic liquids (ILs), which are solely composed of ions, are salts that are liquids with a melting point of around or less than 100 °C [13]. In the past two decades, ILs have attracted extensive attention in sustainable chemistry and industrial applications because of their low flammability, low vapor pressure, excellent thermal

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stability, and high ionic conductivity [14–16]. Moreover, ILs exhibit excellent tribological performance because of the tribochemical reaction between the frictional pairs. In 2001, Liu and coworkers were the first to report alkylimidazolium ILs as lubricants with excellent friction-reducing and anti-wear properties [17]. Since their report, ILs have been extensively investigated as lubricants and lubricant additives [18, 19]. However, most of the conventional ILs reported typically contain tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and bis(trifluoromethylsulfonyl)imide (TFSI^-) anions. Halogen-containing ILs are more prone to reaction with water, generating haloid acid; haloid acid can cause severe metal corrosion and environmental pollution [20, 21]; the same issues are also observed for sulfur- and phosphorus-containing ILs [22]. Therefore, in view of environmental protection, it is crucial to develop halogen-, sulfur-, and phosphorus-free ILs. Recently, some exploratory studies have been reported. Aspartic-acid- and glutamic-acid-derived ammonium-cation-based ILs have been reported as efficient anti-wear and friction-reducing additives for mineral base oil [23]. Song et al. have prepared tetrabutylammonium-based amino acid ILs and reported excellent tribological performance for steel/steel, steel/copper, and steel/aluminum contacts [24].

Choline (Ch), a water-soluble nutrient, is an important component of lecithin and sphingomyelin, and it is typically categorized as a B-complex vitamin. Ch is a promising candidate as the cation for ILs, and some choline-based ILs have been reported to exhibit low toxicity and facile biodegradability [25]. On the other hand, amino acids (AAs) are common cost-effective biomaterials, which are abundant in nature and readily available in bulk. [Ch][AA] ILs were prepared with Ch and AAs by a simple method. Different from conventional ILs containing halogen-, sulfur-, and phosphorus in their molecules, [Ch][AA] ILs have been reported to be environmentally friendly, sustainable, non-toxic, and biodegradable materials [26, 27]. Several studies have reported the preparation of novel [Ch][AA] ILs, and their potential applications in various fields have been investigated [28, 29]. Recently, Mu and coworkers have reported lignin-[Ch][AA] ILs as non-corrosive green lubricants [30]. Nevertheless, to the best of our knowledge, few systematic studies on the

structure and properties of Ch-based ionic liquids as environmentally friendly lubricants have been reported.

In this study, five [Ch][AA] ILs were designed and synthesized with an identical cation (choline), but different anions (i.e., AAs), by a green route with only water as the by-product. The effects of anion symmetry and alkyl chain length on the viscosity, thermal stability, corrosion, and tribological properties of [Ch][AA] ILs were examined. In addition, the tribological mechanism of the green ILs was discussed on the basis of energy-dispersive spectroscopy (EDS) and XPS results.

2 Experimental method

2.1 Materials

Choline hydroxide (48–50 wt% in water, Tokyo Chemical Industry Co., Ltd.) was used as received. L-glycine (>99 wt%), L-alanine (>98 wt%), L-isoleucine (>98 wt%), L-phenylalanine (>98 wt%), and L-serine (98 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further treatment. A conventional halogen-containing IL, e.g., 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_6\text{mim}][\text{NTf}_2]$), was prepared according to a previously reported method and used for the comparison of the tribological properties [31].

2.2 Synthesis of [Ch][AA] ILs

Figure 1 shows the synthetic route of [Ch][AA] ILs according to a previously reported method [32]. First, 0.1 mol AAs (e.g., 7.58 g L-glycine, 9.09 g L-alanine, 13.38 g L-isoleucine, 16.86 g L-phenylalanine, and 10.72 g L-serine) were dissolved in 30 mL of water, and then choline hydroxide (24.7 g, 0.1 mol) was added dropwise into the AA solution with stirring. Second, the AA was neutralized using an equimolar choline hydroxide aqueous solution by stirring at room temperature for 18 h. Water was then evaporated under

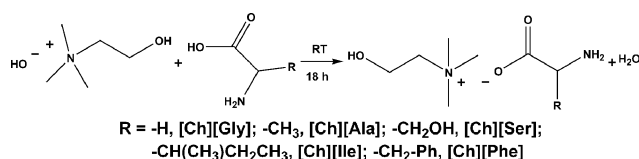


Fig. 1 General synthetic route for [Ch][AA] ILs.

vacuum at 65 °C, and excess AAs were precipitated using methanol. Next, the prepared choline glycine ([Ch][Gly]), choline alanine ([Ch][Ala]), choline isoleucine ([Ch][Ile]), choline phenylalanine ([Ch][Phe]), and choline serine ([Ch][Ser]) ILs were dried at 65 °C under vacuum for 24 h. The data for the [Ch][AA] IL structures confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy are reported below:

[Ch][Gly]: δ : 3.15 (2H, s, CH₂NH₂), 3.17 (9H, s, N(CH₃)₃), 3.48–3.50 (2H, m, CH₂CH₂OH), 4.01–4.05 (2H, m, CH₂CH₂N).

[Ch][Ala]: δ : 1.19–1.21 (3H, d, CH₃CH), 3.17 (9H, s, N(CH₃)₃), 3.27–3.32 (1H, q, CHNH₂), 3.47–3.50 (2H, m, CH₂CH₂OH), and 4.01–4.05 (2H, m, CH₂CH₂N).

[Ch][Ser]: δ : 3.18 (9H, s, N(CH₃)₃), 3.31–3.34 (1H, m, CHNH₂), 3.49–3.51 (2H, t, CH₂CH₂OH), 3.65–3.74 (2H, m, CHCH₂OH), 4.02–4.06 (2H, m, CH₂CH₂N).

[Ch][Ile]: δ : 0.83–0.88 (3H, t, CH₃CH₂, 3H, d, CHCH₃, overlap), 1.10–1.15 (1H, m, CH₂CH₃), 1.35–1.37 (1H, m, CH₂CH₃), 1.61–1.64 (1H, m, CHCH₃), 3.06 (1H, d, CHNH₂), 3.17 (9H, s, N(CH₃)₃), 3.47–3.49 (2H, t, CH₂CH₂OH), 4.00–4.04 (2H, m, CH₂OH).

[Ch][Phe]: δ : 2.81–2.86 (1H, m, C₆H₅CH₂), 2.96–3.00 (1H, m, C₆H₅CH₂), 3.14 (9H, s, N(CH₃)₃), 3.47 (2H, m, CHCH₂OH), 3.88–4.04 (2H, m, CH₂CH₂N), 7.25–7.36 (5H, m, C₆H₅CH₂).

2.3 Characterization of [Ch][AA] ILs

Before characterization, all of the [Ch][AA] ILs were dried under vacuum at 65 °C for 48 h. The structures of [Ch][AA] ILs were confirmed by ¹H NMR (400 MHz) spectroscopy. Differential scanning calorimetry (DSC 200F3, Netzsch) was employed to record the glass transition temperatures (*T_g*). First, samples were heated to 120 °C to evaporate the solvent from the ILs, cooled to –100 °C with liquid nitrogen, and finally heated to 100 °C at a rate of 10 °C·min⁻¹. The decomposition temperatures (*T_d*) of the samples were recorded on an STA449F3 instrument (TGA, Netzsch) at a heating rate of 10 °C·min⁻¹ under nitrogen. An SYP1003-III kinematic viscosity tester was used to measure the kinematic viscosity of the prepared ILs at 40 and 100 °C.

2.4 Copper strip corrosion test

The copper strips used in this experiment were 10 mm

in length, 10 mm in width, and 3 mm in thickness. Before corrosion tests, all of the copper strips were polished using an abrasive paper, followed by cleaning by ultrasonication in acetone for 10 min. The samples were immersed in the IL solutions and heated at 100 °C for 72 h. After the test, the copper strips were washed with acetone, and the corrosion level was confirmed according to the corrosion standard tint board.

2.5 Tribological tests

The friction and wear tests were carried out using an Optimol SRV-IV oscillating reciprocating friction and wear tester. The upper ball with a diameter of 10 mm was composed of AISI 52100 steel (hardness of approximately 59–61 HRC). The upper ball reciprocally slides against the lower stationary discs (Φ 24 mm × 7.9 mm) at an amplitude of 1 mm. The lower stationary discs were composed of AISI 52100 steel, with a hardness of approximately 61–64 HRC. All tests were conducted at 20 °C for 30 min at a frequency of 25 Hz, a load of 100 N, and a relative humidity of 30%–40%. The volume loss of the lower disc was measured using a MicroXAM-3D non-contact surface mapping microscope profilometer. Scanning electron microscopy (SEM) and EDS analysis images were recorded on an SEM instrument (JSM-5600LV, JEOL). The chemical composition of the wear scars was confirmed by X-ray photoelectron spectroscopy (XPS), and XPS profiles were recorded on a PHI-5702 electron spectrometer (Perkin-Elmer, USA). Before SEM and XPS analysis, the lower discs were cleaned by ultrasonication in acetone for 20 min to remove the residual lubricants on the surface.

3 Result and discussion

3.1 Thermal analysis

Figure 2(a) shows the DSC curves of the prepared ILs, and Table 1 summarizes the *T_g* of the ILs. As can be observed in Fig. 2(a), all five ILs do not exhibit melting temperatures in the range of the measured temperature, and their *T_g* values ranged between –62.2 and –48.2 °C. [Ch][Gly] exhibited the lowest *T_g* of –62.2 °C. With the increase in the anion size (from glycine, alanine,

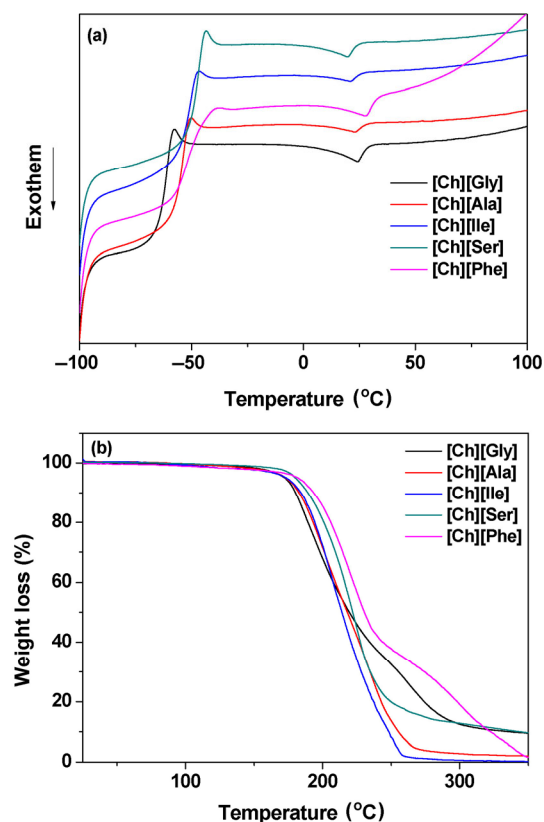


Fig. 2 DSC (a) and TG (b) curves of [Ch][AA] ILs.

Table 1 Physical properties of [Ch][AA] ILs.

ILs	Kinematic viscosity (mm ² /s)		Viscosity Index	T_g (°C)	T_d (°C)
	40 °C	100 °C			
[Ch][Gly]	330.10	28.70	118	-62.2	173.8
[Ch][Ala]	385.18	26.45	92	-54.9	179.6
[Ch][Ser]	475.76	30.05	91	-48.2	186.6
[Ch][Ile]	1742.78	68.17	92	-52.0	183.6
[Ch][Phe]	2641.96	65.10	57	-50.5	195.0

and isoleucine to phenylalanine anions) of the ILs, the T_g increased. For [Ch][Ser], the introduction of a hydroxyl group led to the highest T_g (-48.2 °C), which can be explained by the strong hydrogen-bond interactions between its molecules [29, 32]. The thermal decomposition properties of the ILs were examined by measuring the weight loss as a function of temperature. Figure 2(b) shows the results, and Table 1 summarizes the T_d of ILs. From Fig. 2(b), the five ILs were stable up to 170 °C, indicative of good thermal stability. The thermal stability of the five ILs were closely related to their molecular structures: With the

increase in the alkyl chain length of the anion group, T_d increased. The thermal stability of the five ILs increased in the order of [Ch][Gly] < [Ch][Ala] < [Ch][Ile] < [Ch][Ser] < [Ch][Phe]. The highest T_d was observed for [Ch][Phe] (195 °C), which was explained by the presence of the phenyl substituent in its anion group.

3.2 Viscosity

Viscosity is defined as the resistance of a fluid to flow, reflecting the manner in which molecules interact to resist motion. Viscosity affects the ability of a lubricant to form a lubricating film, which is considered as one of the most important properties of lubricants. Viscosity is closely related to the chemical structures of the lubricant, as well as their molecular size and shape. To investigate the structure–viscosity relationship of the AA–Ch-based ILs, the kinematic viscosity of the synthesized ILs were measured at 40 and 100 °C. Table 1 summarizes the results. The anion group of the prepared ILs significantly affected their kinematic viscosity: The increase in the size of the anion group possibly led to the increased viscosity of the ILs, related to the strong van der Waals interactions [31, 33]. [Ch][Gly] and [Ch][Ala] with a short chain length exhibited a lower viscosity compared to [Ch][Ile] and [Ch][Phe]. [Ch][Ser] exhibited a higher kinematic viscosity compared to [Ch][Gly] and [Ch][Ala], which can be explained by the strong hydrogen-bond interactions between hydroxyl groups. A hydroxyl group is present in the anion of [Ch][Ser], and two hydroxyl groups are present in its molecular structure; as a result, hydrogen bonds among hydroxyl groups can be easily formed, thereby increasing its viscosity [34]. The different viscosities for the developed ILs suggested that a large number of [Ch][AA] ILs with different viscosities and properties can be obtained by simply changing the anion groups.

3.3 Corrosion

The widely employed copper strip corrosion test is a straightforward method to measure the corrosion of lubricants. In this study, the copper strip corrosion test was carried out to investigate the corrosion properties of the synthesized [Ch][AA] ILs. Figure 3 shows the photographs of the copper strips after the

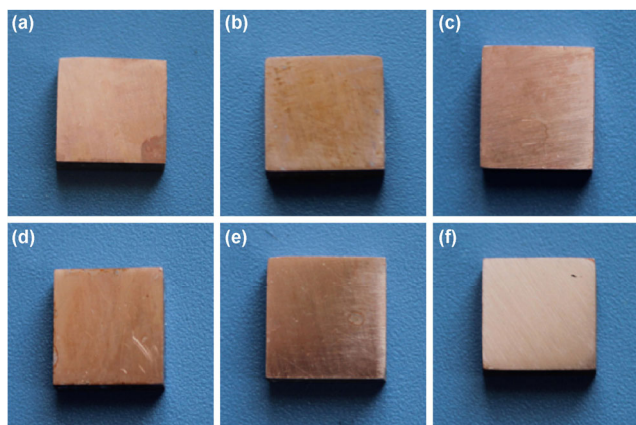


Fig. 3 Photographs of the copper strips after immersion in (a) [Ch][Gly]; (b) [Ch][Ala]; (c) [Ch][Ser]; (d) [Ch][Ile]; (e) [Ch][Phe]. (f) is the photograph of the copper strip before the corrosion test.

test, and the test strips are compared with the standards to determine the corrosion level. From the copper strips tested with the green ILs, almost no corrosion was detected, with a corrosion grade of 1a or 1b in Fig. 3. The non-corrosive property of these ILs is possibly related to the absence of halogen, phosphorus, and sulfur in their molecules.

3.4 Tribological properties

The tribological properties of the synthesized ILs were tested using a Schwingungs Reibung und Verschleiss (SRV) tester. A conventional halogen-containing IL, e.g., [C₆mim][NTf₂], was used for comparison. Figure 4 shows the evolution of the friction coefficient of these lubricants at room temperature. All lubricants exhibited a relatively short running-in time. The coefficient of friction (COF) of all the tested lubricants increased in the order of [Ch][Gly] < [Ch][Ala] < [Ch][Ile], [C₆mim][NTf₂], [Ch][Ser] < [Ch][Phe]. The lowest COF was observed for [Ch][Gly] (0.085), which showed a 20% reduction compared to the traditional IL [C₆mim][NTf₂]. No friction modifiers or other lubrication additives were present in ILs, and the friction properties of [Ch][AA] ILs were not dominated by the performance of the boundary additives. As shown in Table 1, an increase in the anion size of [Ch][AA] ILs resulted in the increase in viscosity. [Ch][Phe] exhibited significantly higher viscosity compared to [Ch][Gly] and [Ch][Ala], and the inferior anti-friction performance of [Ch][Phe] compared to

[Ch][Gly] and [Ch][Ala] indicated a greater dependence on lubricant viscosity for [Ch][AA] ILs [35]. The above results suggested that the friction-reducing behavior of the developed halogen-, phosphorus-, and sulfur-free ILs is comparable or even better than the traditional halogen-containing ILs, with the exception of [Ch][Phe]. Figure 5 shows the wear volume of the steel discs with different lubricants. The wear volume losses of [Ch][Gly] and [Ch][Ala] were greater than that of [C₆mim][NTf₂], while those of [Ch][Ile], [Ch][Ser], and [Ch][Phe] were considerably less than that of [C₆mim][NTf₂]. The lowest wear volume was observed for ILs with the longest alkyl chain [Ch][Phe], with a 46% wear reduction compared to [C₆mim][NTf₂]. Similar trends were observed between the wear scar diameter (WSD) of the ball lubricated with ILs and the wear volume of the discs (Table 2). The anti-wear

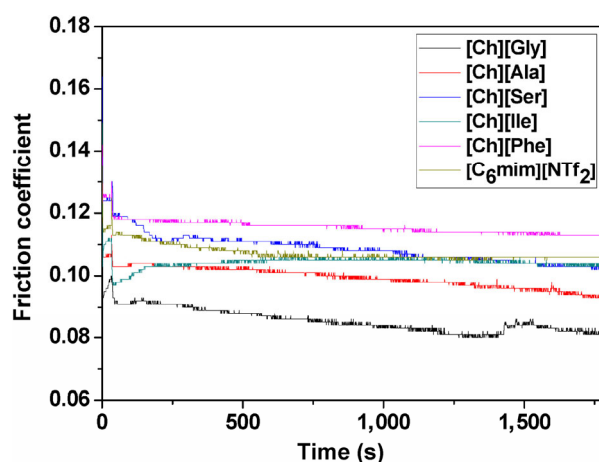


Fig. 4 Evolution of the friction coefficients of the system lubricated with [Ch][AA] ILs and [C₆mim][NTf₂].

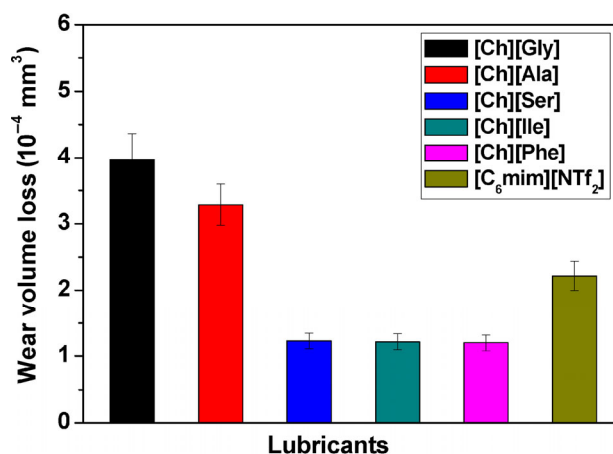


Fig. 5 Evolution of the wear volume loss of steel discs lubricated with [Ch][AA] ILs and [C₆mim][NTf₂].

Table 2 Ball wear diameter after the SRV test for different ILs.

Lubricant	[Ch][Gly]	[Ch][Ala]	[Ch][Ser]	[Ch][Ile]	[Ch][Phe]	[C ₆ mim][NTf ₂]
WSD (mm)	0.337	0.333	0.293	0.302	0.297	0.343

property of [Ch][AA] ILs is thought to be related to the effective boundary films between friction pairs. To characterize the boundary films, *in situ* average contact resistance measurement was carried out using the SRV tester [36, 37]. Figure 6 shows the contact resistance change using [Ch][AA] ILs and [C₆mim][NTf₂] as the lubricants. [Ch][Ala] and [Ch][Gly] ILs exhibited an extremely low contact resistance for the sliding contact, while [Ch][Ile], [Ch][Ser], and [Ch][Phe] exhibited considerably higher contact resistance, indicating that the significantly thicker films lubricated with [Ch][Ile], [Ch][Ser], and [Ch][Phe] ILs exhibit considerably effective anti-wear properties.

3.5 Surface characterization

Figure 7 shows the SEM micrographs and 3D optical microscopic images of steel discs lubricated with different ILs: All wear scars were obtained under the same conditions. As can be observed in the SEM micrographs, the worn surfaces lubricated by [Ch][Gly] and [Ch][Ala] exhibited severe scuffing and significantly wider and deeper wear scars, which were further confirmed by the 3D optical microscopic images. From the SEM micrograph of the worn area lubricated with [C₆mim][NTf₂], an extremely rough surface was

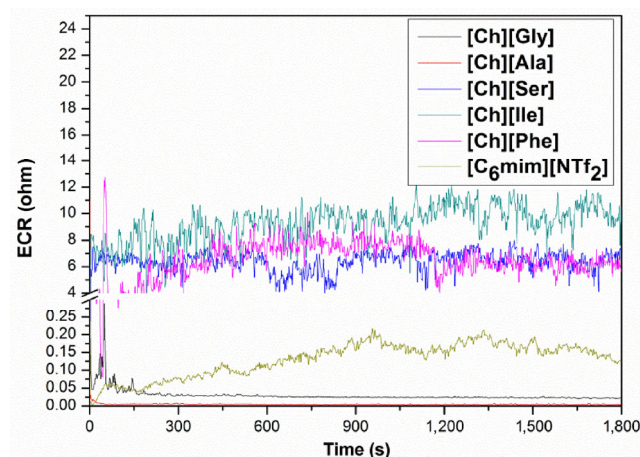


Fig. 6 Contact resistance of [Ch][AA] ILs and [C₆mim][NTf₂] recorded using the SRV tester.

observed, with several small furrows and scratches, while the wear depth was considerably reduced compared to [Ch][Gly] and [Ch][Ala] ILs. The worn surfaces lubricated with [Ch][Ile], [Ch][Ser], and [Ch][Phe] were comparatively smoother, and severe scuffing was considerably reduced. The widths and depths of the wear scars lubricated with [Ch][Ile], [Ch][Ser], and [Ch][Phe] were smaller and shallower, as shown in the 3D optical microscopic images. This result is consistent with those obtained for the measured wear volume and wear diameter in Fig. 5 and Table 2, respectively.

The chemical composition of the wear scars was confirmed by EDS and XPS after tribological tests. From the EDS images of the worn steel surface in Fig. 8, C, O, Cr, and Fe were abundant on the discs lubricated with [Ch][Gly] and [Ch][Ser]. However, nitrogen was not detected by EDS possibly because of its low content. XPS was also carried out to accurately analyze the composition of the surface after lubrication by [Ch][AA] ILs. No obvious difference was observed in the XPS spectra of C1s, O1s, N1s, and Fe2p after lubrication with [Ch][Gly] and [Ch][Ser] (Fig. 9). The peaks of Fe2p were observed at approximately 725.1 and 711.2 eV (Fig. 9), corresponding to Fe₂O₃, Fe₃O₄, Fe(OH)O, and FeOOH. A wide O1s peak was observed at 531.2–530.0 eV, corresponding to Fe₂O₃, Fe₃O₄, Fe(OH)O, and FeOOH [38]. The iron surface may easily undergo oxidation during sliding, with the formation of an oxide layer. A N1s absorption peak was not observed in the XPS spectrum, indicating that the excellent tribological properties of [Ch][AA] ILs may lead to the formation of a physically adsorbed film rather than the tribochemical reaction films on the friction pairs. During the tribological process, the carboxyl groups from AA anions are easily adsorbed on the positively charged metallic surface via electrostatic attractions, which effectively prevent the frictional pairs from direct contact [24, 39]. This physically adsorbed film may have been thoroughly cleaned by ultrasonication, leading to the absence of N in the EDS and XPS

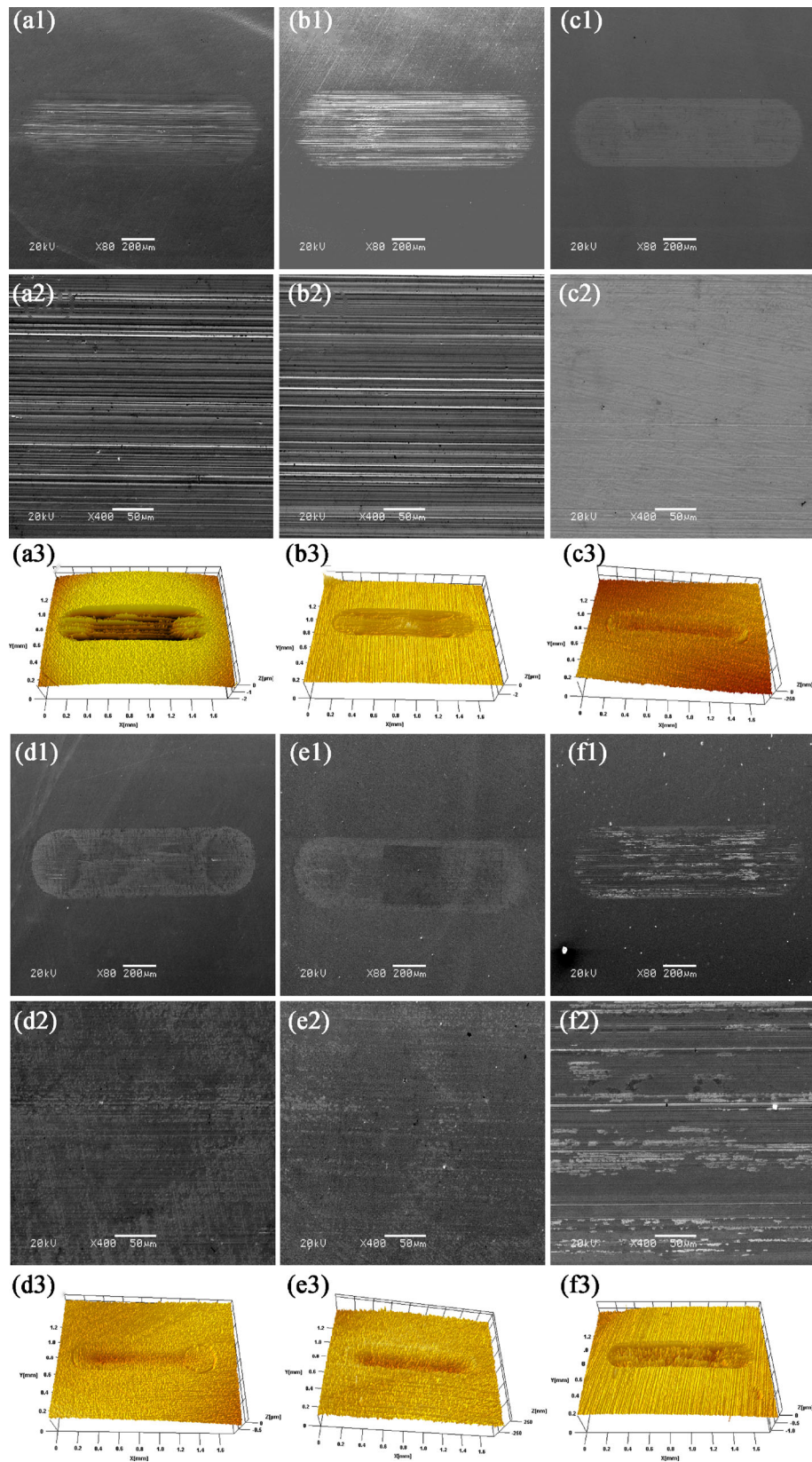


Fig. 7 SEM micrographs and 3D optical microscopic images of the worn steel discs with different lubricants: [Ch][Gly] (a1, a2, and a3); [Ch][Ala] (b1, b2, and b3); [Ch][Ile] (c1, c2, and c3); [Ch][Ser] (d1, d2, and d3); [Ch][Phe] (e1, e2, and e3); and [C₆mim][NTf₂] (f1, f2, and f3).

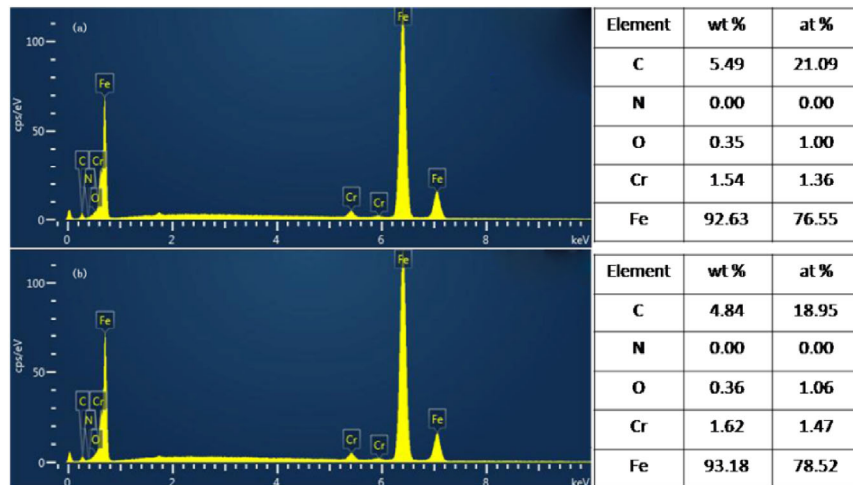


Fig. 8 EDS imaging profiles for the worn steel surface lubricated with (a) [Ch][Gly] and (b) [Ch][Ser].

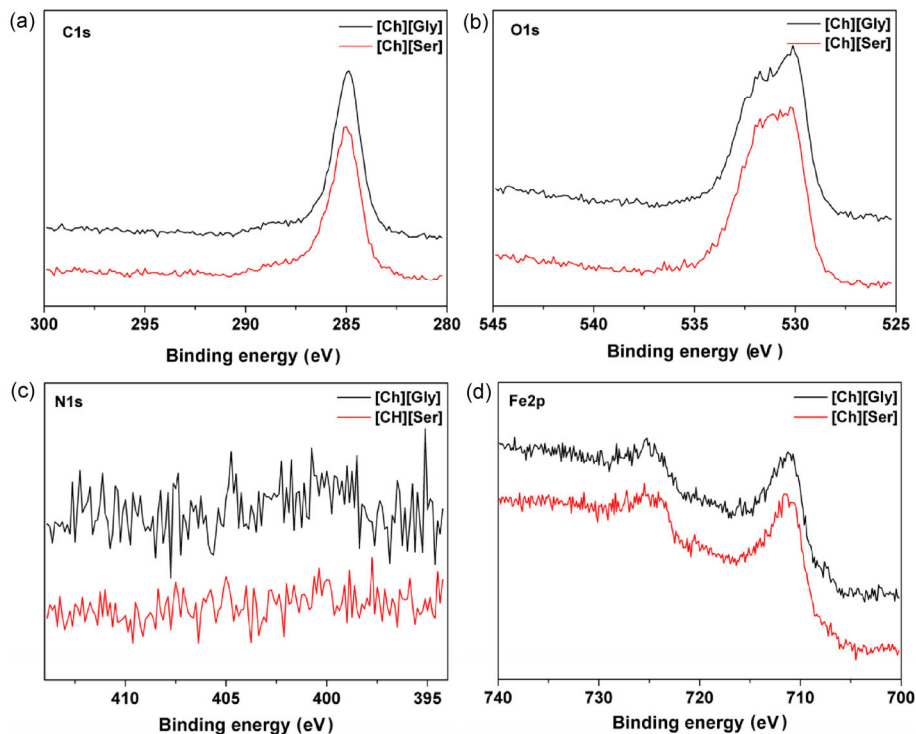


Fig. 9 C1s, O1s, N1s, and Fe2p XPS region scans for wear scars with [Ch][Gly] and [Ch][Ser] lubricants.

images. The halogen-, sulfur-, and phosphorus-free ILs were more prone to form a physically adsorbed film on friction pairs. This result is in good agreement with those reported previously [23, 24, 30].

4 Conclusion

In this study, five environmentally friendly halogen-, sulfur-, and phosphorus-free [Ch][AA] ILs were

synthesized by a simple, green method with only water as the by-product. The results indicated that the physical and thermal properties of ILs are closely related to their molecular structures. The copper strip test suggested that ILs exhibit slight corrosion toward copper at 100 °C for 72 h. In addition, [Ch][AA] ILs also exhibited good tribological properties for steel/steel contact, which are comparable to conventional [C₆mim][NTf₂]. The excellent tribological properties

of [Ch][AA] ILs were related to the formation of a physically adsorbed film on the metallic surface, which can effectively prevent the friction pairs from direct contact during rubbing. Notably, because of the abundance of AAs in nature, different [Ch][AA] ILs can be obtained by simply changing amino acids. The design, synthesis, lubricating properties, and tribological mechanism of other [Ch][AA] ILs still need to be further examined. Overall, the excellent tribological properties, low toxicity, high biodegradability, cost-effectiveness, as well as halogen-, sulfur-, and phosphorus-free characteristics of these [Ch][AA] ILs make them promising candidates for use as green lubricants in the modern industry.

Acknowledgments

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