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Phosphonium-based ionic liquids mixed with stabilized oxide nanoparticles as highly promising lubricating oil additives

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Abstract. The lubricating performance of two oils (base oil PAO and synthetic motor oil denoted as 5w40) was clarified by doping them with phosphonium-based ionic liquids (P-ILs) and a mixture of P-ILs and metal oxide nanoparticles. The nanoparticles were synthesized by heating titanium tetrabutoxide and 1-methyl-3-(triethoxysilylpropyl)imidazolium chloride-based ionogel in trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (P-IL$_1$) or trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate (P-IL$_2$) media. Tribological experiments were performed using a standard four-ball tribometer. The nanoparticles were characterized by scanning electron microscopy and ^{1}H-NMR. The worn areas of the steel balls were visualized applying optical microscopy. The thermal stability of the solutions of ionic liquids–nanoparticles was determined by thermogravimetric analysis. The best anti-wear performance was achieved by using P-IL$_2$ with functionalized hybrid oxide nanoparticles as an additive in both selected lubricant oils. When the mixture of PAO and 1% P-IL$_2$ + nanoparticles was used as an additive, the wear scar area decreased by ~62% compared to pure PAO. In the case of synthetic motor oil with the addition of the mixture of 1% P-IL$_2$ + nanoparticles the wear trace decreased by ~48%. The wear scar area was found to be significantly reduced when smaller nanoparticles were used. It was shown that the synergistic effect of ionic liquids and hybrid oxide nanoparticles synthesized using the presented novel method can have a great potential for increasing the wear performance of conventional commercial oils. It is crucial from the commercial point of view that only a small amount of ionic liquids–nanoparticles additives (0.1<<1 ww%) in oils is required to induce an enormous effect on their tribological properties.

Key words: tribology, ionogel, ionic liquids, metal oxide nanoparticles.

1. INTRODUCTION

The topic of ionic liquids as potential lubricant media has been in the focus of many investigations with the main progress summarized in numerous reviews [1–5]. Such properties as thermal stability, non-flammability, low volatility, and inherent polarity make ionic liquids beneficial substitutes for traditional synthetic lubricants [6]. They are often considered in a 'green' context and some of them are even biodegradable [7]. The attractiveness of ionic liquids is due to the possibility of tuning their properties by using various anion–cation combinations [8]. It has been shown that alkylimidazolium tetrafluoroborates are promising versatile lubricants for steel on steel and steel on ceramics systems, resulting in excellent friction reduction, anti-wear performance,

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and high load-carrying capacity [9]. However, some $[BF_4]^-$ and $[PF_6]^-$ anion based ionic liquids are not stable enough and can already be hydrolyzed at room temperature [10,11]. Therefore, it is necessary to find alternatives for alkylimidazolium tetrafluoroborates and hexafluorophosphates.

Recently progress in using ionic liquids in the lubrication industry has been made in several directions: exploiting the possibility of tuning their properties by choosing beneficial anion–cation combinations [8,12], characterizing tribological interactions between them and contact surfaces, investigating synergistic effects [4,13], and using them for the synthesis of stabilized nanoparticles as lubricant additives [14,15].

In the current study, we show that considering the above-mentioned directions and using appropriate solutions, only a small amount of an ionic liquid with dispersed nanoparticles is required to significantly enhance tribological properties of a traditional lubricant.

The phosphonium-based ionic liquid (P-IL) is a great precursor to be used in a lubricant industrial process. Firstly, P-ILs are generally more thermally stable than imidazolium-based ionic liquids, and they are non-corrosive. Secondly, P-ILs are soluble in common non-polar hydrocarbon lubricating oils while most ionic liquids have low or no solubility ($\ll 1\%$) in them [14,15]. Thirdly, contrary to imidazolium-based ionic liquids, there is little potential for their interaction with solutes because phosphonium cations have neither acidic protons nor aromatic rings [16]. Also, the P-ILs do not contain so much water as the more polar imidazolium-based ionic liquids. Moreover, P-ILs are already manufactured on a multi-tonne scale, which makes them affordable. In multiple studies effective friction reduction and anti-wear functionality in tribological tests were achieved by using P-ILs as lubricant additives [17].

Numerous research works focus on the effect of nanoparticles as the extreme pressure and anti-wear additives to lubricating oils [18–22]. Reasons behind this include the remarkable tribological behaviour of nanoparticles even under severe frictional conditions (high temperature, high load, and high sliding speed), their self-repair function to the worn surface, and environmental friendliness (zero or low content of S, P, and Cl) [21–23]. Adding only a small amount of certain nanoparticles to a lubricant significantly improves its lubricating properties. For example, Li et al. [24] demonstrated that modified ZrO_2/SiO_2 composite nanoparticles as lubricant additives effectively improve the lubricating properties and reduce the friction coefficient by 16% at a concentration as low as 0.1 wt%.

According to Chiñas and Spikes' mechanical entrapment theory [25], nanoparticles penetrate in the contact area and then deposit on it because they are smaller or similar in size to the lubricant film thickness. The presence of nanoparticles in the friction zone results in the switch from sliding friction to rolling friction, leading to a reduction of the friction coefficient. The tribological effect that nanoparticles exert on a lubricant strongly depends on the concentration, size, size distribution, shape, hardness, and deposition of nanoparticles on wear surfaces. Nanoparticles can also possess deleterious effects under non-optimized conditions, increasing either friction or wear [26]. Due to the well-established Hall–Petch relationship, the hardness of common nanoparticles used in lubricants is often higher than the hardness of the lubricated materials, even taking into account the inverse Hall–Petch relation [27,28]. This leads to an abrasive behaviour if particle parameters are not chosen properly [29]. For example, at a given concentration bigger particles of hard materials cause wear of the surfaces, whereas finer particles more easily form a complete and continuous film than coarser particles because more particles are available [30].

The interactions between nanoparticles and ionic liquids are different from the interactions with the base oils, being heavily patterned by the self-assembling properties of the ionic liquids. It was shown that ionic liquids based on 1-alkyl-3-methylimidazolium salts tend to aggregate and self-assemble in a 3D network [31]. The same phenomenon also plays a role in film formation on the wear surface.

A novel approach for the preparation of nanoparticles is synthesis carried out in ionic liquids media, which ensures homogeneous dispersion and stability of the nanoparticles. Application of the sol–gel method in an ionic liquid medium enables to synthesize oxide nanoparticles with greater specific surface areas than the analogues whose synthesis was carried out without ionic liquids. In the creation of such materials, ionic liquids are used as nanopore templates inside a host matrix. This is particularly promising from a technological point of view because ionic liquids can disperse particles very efficiently and simultaneously act as a medium for synthesis. In our previous work [32] we showed that sol–gel synthesized ionogels combine the properties of two systems (oxide and ionic liquids) intermingled on the nanometre scale. In other words, by combining an ionic liquid with metal alkoxides, it is possible to create new nano-fine metal oxide porous cross-linked systems that have practical applications in various fields, e.g. solid electrolyte membranes, selective absorbing materials, optical component synthesis of nanoparticles and catalyst carriers [33,34].

The goal of this work was an elaboration of a novel oil additive based on P-IL and metal oxide nanoparticles. The novelty of the demonstrated technology is of general importance in tribology and other fields of

nanotechnology, e.g. for covering internal surfaces of porous materials with metal oxides. In Section 2 we demonstrate a technologically highly promising method of synthesis of well dispersed and stable nanoparticles in ionic liquids. In Section 3 we show that addition of solutions of synthesized ionic liquids–nanoparticles to the base oil (PAO) and to the commercial synthetic motor oil significantly enhances their tribological performance as evaluated by the wear scar volume and friction coefficient in a standard four-ball test.

2. MATERIALS AND METHODS

2.1. Materials used in research

1-Methylimidazole (≥99%), 3-chloropropyl(triethoxy)silane (≥95%), titanium tetrabutoxide (≥97%), bis(2-ethylhexyl) phosphate (≥97%), trihexyltetradecylphosphonium chloride (≥95%), trihexyltetradecylphosphonium bis(2,4,4-tri-methylpentyl)phosphinate (P-IL$_1$; ≥95%) (Fig. 1), and hexane were purchased from Sigma-Aldrich and used as received without additional purification. Diethyl ether was obtained from Lachner. *n*-Butanol (≥99%, Sigma-Aldrich) was dried and distilled over CaH$_2$. Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate (P-IL$_2$; Fig. 1) was synthesized according to the method described in Subsection 2.3. Commercially available base oil PAO (hydrogenated petroleum distillates, flash point >180°, kinematic viscosity 12 mm^2/s at 40 °C) and synthetic motor oil (hydrogenated heavy paraffinic base oil, heavy paraffinic distillate, zinc dialkyl dithiophosphate, flash point >199°, d = 0.8520 g/cm^3, 5w40) were used as received and with developed additives.

2.2. Methods used for sample characterization

The scanning electron microscopy (SEM) was performed on a Vega microscope at 10 kV (Tescan). Carbon tape was used for sample preparation. Optical characterizations of worn areas of steel balls were carried out on a BX 51 optical microscope (Olympus). The ^{1}H-NMR and spectra were recorded at ambient temperature on an Avance II 200 spectrometer (Bruker), using DMSO-d6 and CDCl$_3$ as solvents. The ^{1}H-NMR spectra were measured at 200 MHz. The chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. Infrared spectra were recorded on a Spectrum BXII FTIR spectrophotometer (Perkin Elmer). Differential scanning calorimetry was carried out on a DSC analyser DSC 7 (Perkin-Elmer) with heating and cooling rates 10 °C/min. Nitrogen was used as the furnace purge gas. Temperature and heat flow calibrations were done with indium and tin standards.

2.3. Method for the synthesis of ionic liquids

1-Methyl-3-(triethoxysilylpropyl)imidazolium chloride (MTICl) was synthesized according to the method reported previously [32,35]. In the experiment, 3-chloropropyl triethoxysilane (36.23 g; 0.15 mol) was added dropwise to 1-methylimidazole (12.29 g; 0.15 mol) dissolved in toluene (150 mL). Then the mixture was refluxed at 111 °C for three days in Ar atmosphere. As a result, two layers were formed: brown MTICl at the bottom and toluene at the top. Layers were separated, and the MTICl layer was purified by washing three times with diethyl ether (50 mL). After drying overnight at room tempe-
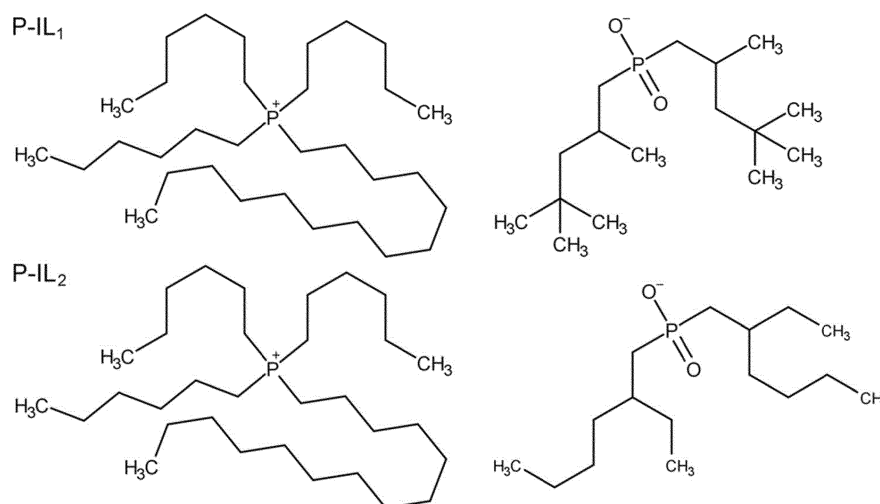

Fig. 1. Molecular structures of phosphonium-based ionic liquids used in this work as additives to the lubricating oils. Here P-IL$_1$ denotes trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [THTP][TMPP] and P-IL$_2$ denotes trihexyltetra-decylphosphonium bis(2-ethylhexyl) phosphate [THTP][DEHP].

rature under vacuum (1.3 mbar), 17.23 g of MTICl as a yellowish viscous liquid was obtained in 36% yield.

^{1}H NMR (200 MHz, DMSO-d6): δ 9.31 (s, 1H, –N–CH–N–), 7.83 (s, 1H, –N CH=CH–N–), 7.77 (s, 1H, –N–CH=CH–N–), 4.17 (t, 2H, *J* = 7.0 Hz, –N–CH2–), 3.88 (s, 3H, –N–CH3), 3.77 (q, 6H, *J* = 7.0 Hz, –O–CH2–), 1.84 (quint., 2H, *J* = 7.6 Hz, –CH2–CH2–CH2), 1.16 (t, 9H, *J* = 7.0 Hz, –CH2–CH3), 0.53 (t, 2H, *J* = 7.6 Hz, Si–CH2–).

Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([THTP][DEHP]) was synthesized following similar procedures previously reported in the literature [16]. To synthesize [THTP][DEHP] 1 : 1 mole ratio of bis(2-ethylhexyl) phosphate and tetradecyl trihexyl phosphonium chloride was used. In the synthesis, 5.13 g (15.9 mmol) of bis(2-ethylhexyl) phosphate was mixed with 8.96 g (15.9 mmol) tetradecyl trihexyl phosphonium chloride. The mixture was dissolved in 14 g hexane and stirred for 1 hour. Then 5% aqueous solution of KOH (1.0196 g KOH and 19.37 g distilled water) was added dropwise into the reaction system, and the mixture was stirred at room temperature for 24 h. As a result, two transparent layers were formed with the ionic liquid layer at the top. The layers were separated, and the [THTP][DEHP] layer was purified by washing four times with distilled water (20 mL) to ensure the removal of KCl. After that, the solvent was removed in vacuum at 335 mbar using a rotary evaporator and 70 °C oil bath. After drying the product for 5 h under vacuum (1.3 mbar) at 70 °C, 13.8 g of [THTP][DEHP] as a transparent viscous liquid was obtained in 98% yield.

^{1}H NMR (200 MHz, chloroform-d): δ 3.78–3.62 (m, 4H), 2.40 (dq, *J* = 14.6, 6.2, 4.5 Hz, 8H), 1.59–1.19 (m, 49H), 0.96–0.76 (m, 24H).

2.4. Method for the preparation of MTICl–Ti(OBu)4 ionogels

Ionogels were prepared after the optimization of several critical parameters such as water/Ti(OBu)4 molar ratio, appropriate MTICl mass percent, and hydrolysis temperature using the following procedure. MTICl (0.05–0.30 g) was added directly to Ti(OBu)4 (1.80 g). After that, the mixture was left to stir for 10 min. To generate the sol–gel process, H2O/BuOH solution with an appropriate water concentration was added to the mixture portion-wise, 1 mL after every 5 min. As a result, water/alkoxide molar ratio (also called *R* parameter) *R* = 0.8 was achieved. The mixture was stirred overnight at room temperature. After that, the solvents and other low molecular mass organic compounds were removed portion-wise to get the requisite concentration using a rotary evaporator and a 70 °C water bath. Before

detaching the bulb from the evaporator, it was filled with argon until the ambient pressure was achieved.

2.5. Method for the preparation of oxide nanoparticles

Ionogels with different MTICl concentrations, preparation of which was described in the previous section, were mixed with phosphonium-based ionic liquids (P-IL$_1$ or P-IL$_2$) (2–20% of w/w %). After that, the mixtures were heated at temperatures in the range 300–350 °C under the inert atmosphere. The heating temperature was carefully selected to induce the decomposition of MTICl ionic liquid and to avoid the decomposition of P-IL. After heating the mixture of two ionic liquids and metal alkoxide for 12 h under Ar atmosphere, selected P-IL gels with dispersed functionalized metal oxide nanoparticles were obtained.

2.6. Methodology of tribological tests

The wear scar experiments were performed with a four-ball tribometer, according to ASTM standard D 4172 – 94 [36]. Test balls (AISI E52100) with a diameter of 12.7 mm were used. The rotational speed of the top ball was 1200 rpm. The temperature was regulated with a tolerance of ±4 °C at 75 °C. The balls were cleaned with *n*-hexane. The chosen duration was 60 min and the load was 15 kg.

3. RESULTS AND DISCUSSION

3.1. Synthesis of oxide nanoparticles in P-ILs

Metal alkoxide Ti(OBu)4 and ionic liquid MTICl were used to obtain stable homogeneous ionogels via the aqueous sol–gel approach. For homogeneous ionogel formation, miscibility of those two components is essential. In our case, MTICl mixes readily with Ti(OBu)4, thus overcoming the problem of poor miscibility between polar and non-polar compounds. A triethoxysilyl functionalized ionic liquid has similar to the Ti(OBu)4 structure of the functional group, which possibly induces better miscibility between the ionic liquid and the used metal alkoxide.

As a result of the condensation reaction, the precursor of oxide nanoparticles is stabilized in the form of a covalently bonded ionogel. The presence of a covalent bond between the functionalized ionic liquid and metal alkoxide matrix was shown directly using ^{29}Si NMR spectroscopy [32]. The structure of the ionogel could be changed depending on the mass concentration of MTICl (0.1–20%). The best wear results were obtained using

an 8% ionogel (nanoparticles ~10–15 nm). By using lower concentrations, larger nanoparticles (~70 nm) were formed. The PAO with smaller nanoparticles showed a reduction of the wear trace by approximately 80% compared with the PAO with larger nanoparticles.

The density and distribution of the channels with nanoscale webs formed by the ionic liquid can be altered using hydrolysis and condensation processes of the sol–gel method. The size of the product's nanoscale particles is determined by the concentration of the precursors. The obtained ionogels were admixed with [THTP][DEHP], which is a heat-resistant (over 360 °C), incorrodible, and low hygroscopic compound with a good tribological behaviour. In selecting the ionic liquid, the main application of the product was taken into account, namely its ability to improve the lubricating quality.

The overall possible process of the formation of functionalized nanoparticles in P-IL is described in Fig. 2. The first step is the synthesis of MTICl, which participates further in the sol–gel reaction forming covalent bonds with Ti(OBu)$_4$. In the final step, the formed ionogel is mixed with [THTP][DEHP] and heated in the oven under an inert atmosphere to ensure the decomposition of MTICl. In the decomposition process, MTICl loses its ring. As a result, hybrid oxide nanoparticles with covalently bound Si-alkyl chains are stabilized in the polar environment of [THTP][DEHP], without being chemically attached to it. The structure of the product was verified by ^{1}H-NMR (Fig. 3).

The choice of heating temperature depends on the decomposition temperature of 1-methyl-3-(triethoxylyl-propyl) imidazolium chloride and the temperature of
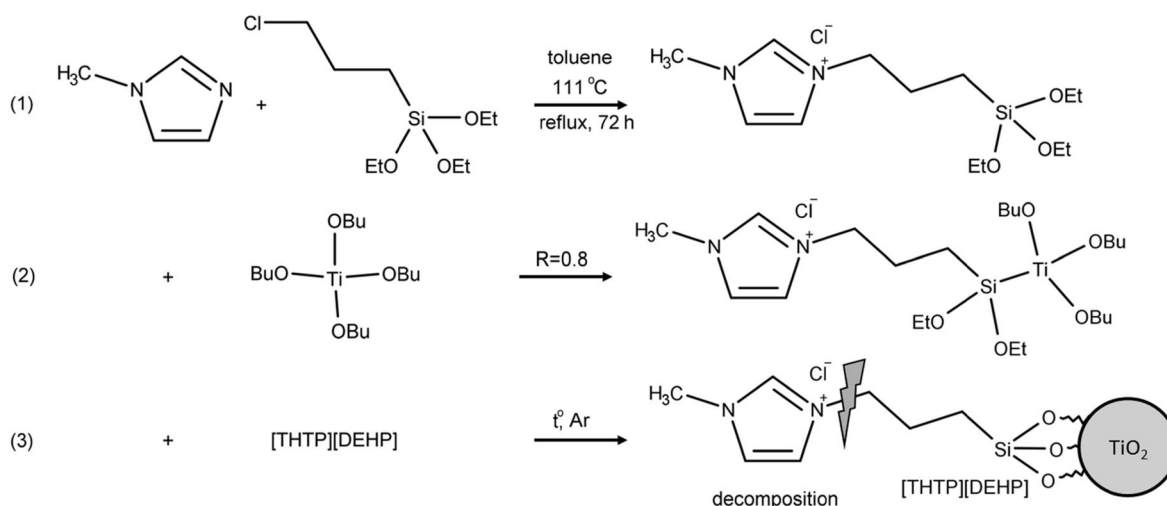

Fig. 2. (1) Synthesis of MTICl; (2) synthesis of ionogel (a possible initial product of the condensation reaction between MTICl and metal alkoxide is shown); (3) formation of hybrid oxide nanoparticles in the P-IL$_2$ medium. Bu – butyl group, Et – ethyl group, R – water/alkoxide molar ratio.
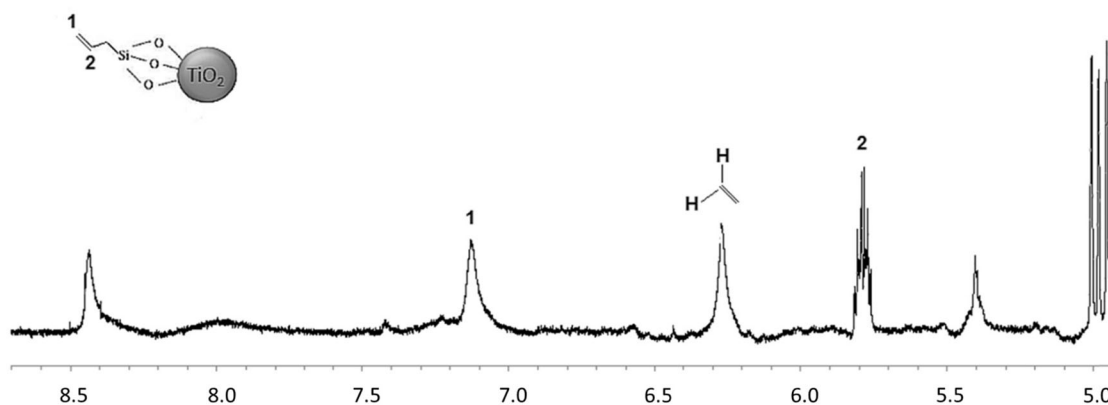

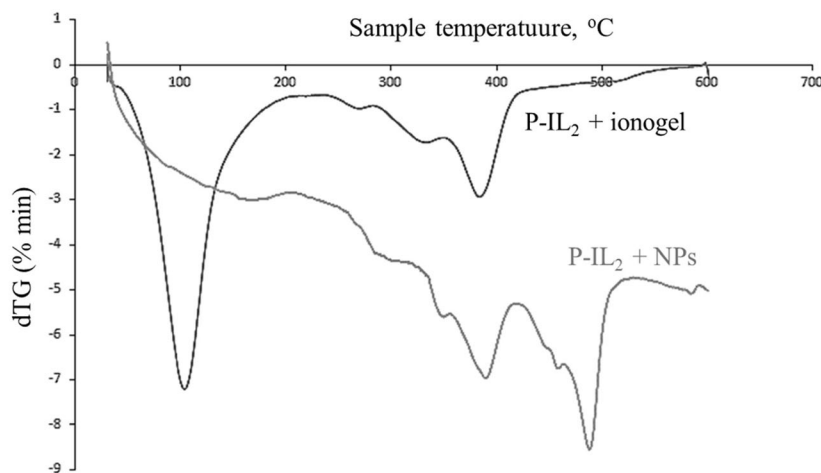**Fig. 3.** ^{1}H-NMR spectrum of TiO$_2$-MTICl in [THTP][DEHP] (P-IL$_2$).

Fig. 4. Thermograms of P-IL$_2$ + ionogel precursor mixture and P-IL$_2$ + nanoparticles heated product by using MTICl 8% w/w. A peak starting from 282 °C corresponds to the decomposition of MTICl (darker line), the peaks from 350 °C and 400 °C correspond to the decomposition of P-IL$_2$ (lighter line).

oxide-matrix formation. MTICl begins to decompose at 282 °C in TiO$_2$ oxide matrix [32] (Fig. 4).

It is known that thermal decomposition of imidazolium salts proceeds through the E2 elimination on the N-substituent, which is the reversible reaction of S$_N$2 substitution carried out for the preparation of imidazolium cations [37]. The thermal stability of ionic liquids is influenced by anion nucleophilicity. For imidazolium salts with a Cl$^-$ anion, the first step of decomposition is reported to occur between 250 and 300 °C (Fig. 4, IL + ionogel). The peaks in a temperature range 350–400 °C can be attributed to the degradation of phosphonium ionic liquids and pyrolysis of all organic matter. The decomposition of the ionic liquid (MTICl) can be regulated by the speed of heating.

3.2. Oil miscibility and anti-wear functionality

Both ionic liquids, [THTP][TMPP] and [THTP][DEHP], were found to be fully miscible, irrespective of their concentration, with PAO base oil and synthetic oil ready to use as a commercial motor oil. By visual inspection, all oil–ionic liquid mixtures appeared to be clear without any aggregation or phase separation. Also, no colour changes were detected in oils after blending them with ionic liquids. The selected P-ILs showed very good miscibility in oils in comparison with ionic liquids based on imidazolium or small hydrocarbon chain. It is explainable because P-ILs have three-dimensional quaternary structures with high steric hindrance caused by long hydrocarbon tails that dilute the charge of the ions and therefore improve the compatibility with neutral oil molecules [18].

The lubricating performance of the mixtures oil + ionic liquid and oil + ionic liquid + nanoparticles in different concentrations was compared with the pure base PAO and synthetic motor oils. The wear scar areas are presented as graphs in Fig. 5 and as optical microscope images in Fig. 6. The measured wear scar areas of the steel balls after rubbing to surfaces according to the standards, described in Subsection 2.5, using different oils and additives are shown. Tribological experiments were carried out several times for each lubricant in order to vertify the repeatability of the experiments. The concentrations of ILs were varied, but the concentration of added nanoparticles remained constant (0.1%) in all cases. By using base oil PAO and 1% P-IL$_2$ + nanoparticles as an additive, the wear scar decreased by 61.7% compared to pure PAO. In the case of synthetic motor oil (5w40) with the addition of only 1% of the P-IL$_2$ + nanoparticles mixture, the wear trace decreased by 47.7% compared to the basic synthetic oil.

Nanoparticles reduce friction and improve anti-wear properties of a lubricant by depositing on the contacted surfaces and creating a protective layer between them. However, the best results were obtained using ionic liquid–nanoparticle mixtures. Friction coefficients of pure PAO (0.135), pure synthetic motor oil (0.172), and nanoparticle-doped PAO (0.11) and motor oil (0.135) are presented in Fig. 7. The lowest coefficient of friction – 0.1 on steel on steel surface – was shown by nanoparticles-doped base oil PAO. As expected, doped oils had significantly lower friction coefficients than pure oils.

It is suggested that the viscous ionic liquid additive (the viscosity of P-ILs is four times higher than that of PAO) may potentially allow the use of lower viscosity
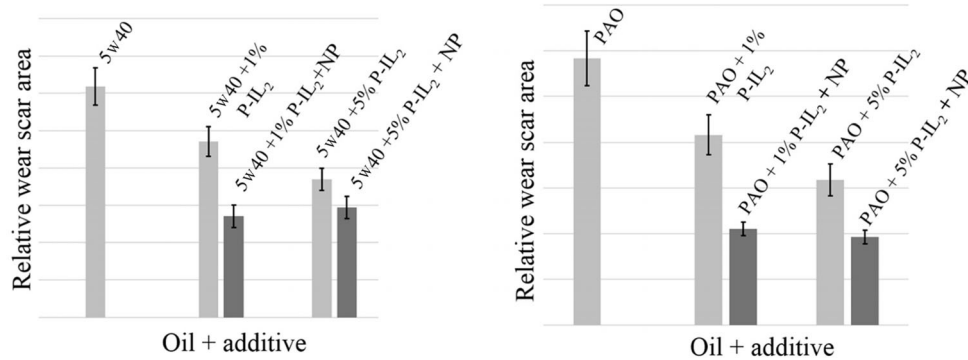
Fig. 5. Steel ball wear scar area dependence on the various oils in the tribological test. Wear scar areas of pure PAO and additives (1% P-IL$_2$, 5% P-IL$_2$, 1% P-IL$_2$ + NPs, 5% P-IL$_2$ + NPs) are shown on the right, wear scar areas of pure synthetic motor oil (denoted as 5w40) with the same additives are presented on the left. NPs – nanoparticles.
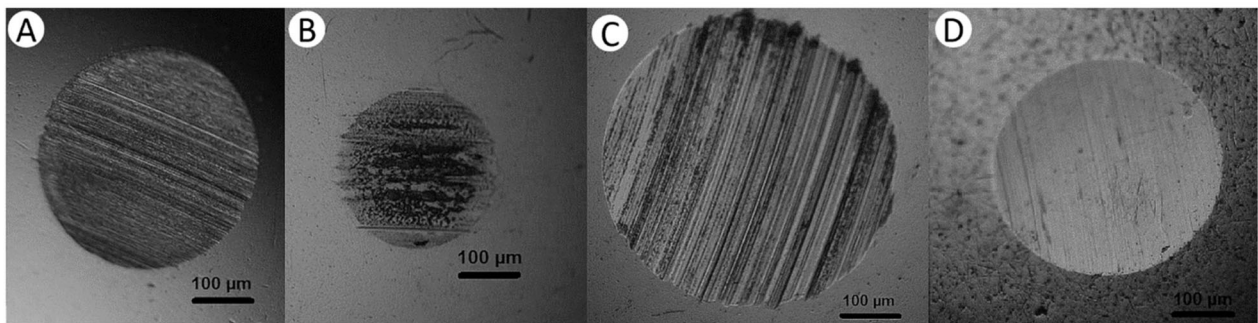

Fig. 6. Optical microscope images of the worn area of the steel ball. (A) Friction by synthetic motor oil; (B) friction by synthetic motor oil + 1% P-IL$_2$ + nanoparticles additive; (C) friction by base oil PAO; (D) friction by base oil PAO + 1% P-IL$_2$ + nanoparticles additive. Only the best results compared to the standard oils are shown.
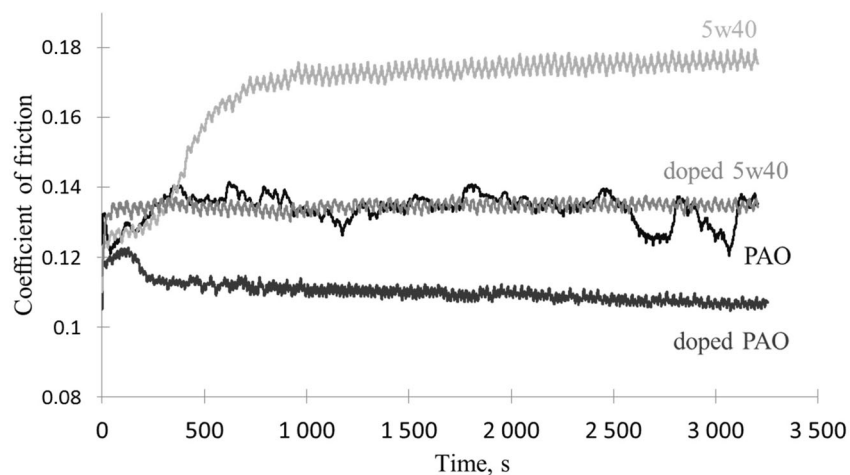

Fig. 7. Friction coefficients of pure base oil PAO, pure synthetic motor oil 5w40, 1% nanoparticles + P-IL$_2$ doped PAO, and 1% nanoparticles + P-IL$_2$ doped synthetic motor oil 5w40.

engine oil, which in turn improves the engine efficiency by reducing churning losses [38]. Synthetic motor oil 5w40 already contains an additive, zinc dialkyl dithiophosphate, provided by the manufacturer. Physical and chemical properties of this additive depend on the specific alkyl groups: they have good thermal stability but are less efficient in terms of anti-wear protection and hydrolytic stability. The secondary alkyl type provides the best anti-wear protection and hydrolytic stability but does not provide good thermal stability [39].

The enormous improvement of lubricating performance by adding ionic liquids into a synthetic motor oil could be described as a possible synergistic effect between the mixture of ionic liquids and nanoparticles and the existing anti-wear additive, zinc dialkyl dithiophosphate [40]. It is reported that zinc dialkyl dithiophosphate decomposes into Zn^{2+} and dialkyl-dithiophosphate. Therefore a high contact pressure and higher temperatures are necessary to form a boundary film between the rubbing metallic areas [39]. On the other hand, the ionic form of the ionic liquids may give rise to a better film formation process, leading to a thicker boundary film than in the case of only zinc dialkyl dithiophosphate. Thus, the thickness of the film formed due to the synergetic effect of zinc dialkyl dithiophosphate and an ionic liquid increases, which leads to an enhanced lubricating performance of the oil mixtures.

The role of nanoparticles in the reduction of wear was summarized in [41] in the form of four general mechanisms: rolling effect, protective film, mending effect, and polishing effect. For these mechanisms to be realized, the nanoparticles are presumed to be stable and resistive to agglomeration under the harsh conditions of local heating in the rubbing contact and to tribochemical reactions. The hybrid oxide nanoparticles dispersed in ionic liquids might possess this property and serve as a 'dust' suspension preventing steel-to-steel direct contact, which is the main reason of wear. The friction coefficient in boundary lubrication with an ionic liquid prominently depends on the lubrication film thickness [42]. In our case, the nanoparticles linked to ionic liquids chains stronger than to the steel surface might prevent wiping off the lubrication film and decrease the friction coefficient.

4. CONCLUSIONS

The lubricating performance of two oils (base oil PAO and a synthetic motor oil) was significantly enhanced by the elaborated additive described in the current paper. Phosphonium-based ionic liquids (P-ILs) and a mixture of P-ILs and oxide nanoparticles were used as the additives. Oxide nanoparticles were prepared via the sol–gel process from titanium butoxide and 1-methyl-3-

(triethoxysilylpropyl)imidazolium chloride by heating the mixture in trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [THTP][DEHP] or trihexyltetradecyl-phosphonium bis(2,4,4-trimethylpentyl)phosphinate [THTP][TMPP] ionic liquids. The method reported for the synthesis of nanoparticles solves the problem of general importance for simple preparation of highly stable metal oxide nanoparticles with a number of applications, e.g. covering internal surfaces of porous materials with metal oxide nanoparticles. Laboratory tribological testing showed a significant anti-wear functionality of the selected P-ILs as additives in the synthetic base oil and in the fully formulated motor oil. The best wear performance was achieved using [THTP][DEHP] ionic liquid with functionalized hybrid oxide nanoparticles as an additive in both selected standard oils. This ionic liquid binds synergistically to the tested oils and forms a tribo-boundary film between the rubbing areas. It was demonstrated that the synergistic effect of ionic liquids and hybrid oxide nanoparticles synthesized using the presented novel method can have a great potential for improving the wear performance of standard commercial oils. It is extremely important from the commercial point of view that only a small amount of such additives (0.1<<1ww%) in oils is required to induce an enormous effect on their tribological properties.

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Stabiliseeritud metalloksiidi nanoosakeste ja fosfooniumioonse vedeliku segu kui paljulubav lisand määrdeõli omaduste parendamiseks

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Töö käigus selgitati metalloksiidi nanoosakeste ja fosforil baseeruva ioonse vedeliku segu lisamise mõju kahe erineva õli (baasõli PAO ja sünteetiline mootoriõli 5w40) määrimisomadustele. Nanoosakesed sünteesiti titaan-tetrabutoksiidi ja 1-metüül-3-(trietoksüsilüül)propüülimidasooliumkloriidi segu kuumutamisel kahes erinevas ioonses vedelikus: triheksüültetradetsüülfosfoonium-bis(2,4,4-trimetüülpentüül)fosfinaat (P-IL$_1$) ja triheksüültetradetsüül-fosfoonium-bis(2-etüülheksüülfosfaat) (P-IL$_2$). Triboloogilised mõõtmised viidi läbi, kasutades standardset nelja kuuli tribomeetrit. Nanoosakeste karakteriseerimiseks kasutati skaneerivat elektronmikroskoopi ja prooton-tuumamagnet-resonantsspektroskoopiat, teraskuulidest testobjektide kulumisjälgi visualiseeriti optilise mikroskoobiga ning ioonsete vedelike temperatuuristabiilsust hinnati termogravimeetriliste mõõtmistega. Parim kulumiskindlus saavutati mõlemas testitavas õlis, kasutades P-IL$_2$ koos funktsionaliseeritud metalloksiidi nanoosakestega. Kasutades baasõlina PAO-d ja lisandina 1% P-IL$_2$ ning metalloksiidi nanoosakeste segu, kahanes kulumisjälje pindala puhta PAO kulumisjälje pindalaga võrreldes ~62%. Lisades sünteetilisele õlile 5w40 1% P-IL$_2$ ja metalloksiidi nanoosakeste segu, kahanes kulumisjälje pindala puhta 5w40-ga võrreldes ~48%. Lisaks täheldati, et kulumise pindala väheneb märgatavalt, kui kasutatakse väiksemaid metalloksiidi nanoosakesi. Töös näidati, et uudsel ioonses vedelikus läbiviidud metalloksiidi nanoosakeste sünteesi meetodil on standardsete õlide määrimisomaduste parendamiseks suur potentsiaal. Tööstuse vaatepunktist on erakordselt tähtis, et väikest kogust metalloksiidi nanoosakeste ja ioonse vedeliku lisandit (0,1<<1ww%) on vaja, et tekitada triboloogiliste omaduste muutmiseks suurt efekti.