

TRIINU VIHMANN

Ionic liquids: synthesis and  
application in lubrication and  
lithography





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## LIST OF ORIGINAL PUBLICATIONS

- I. Põhako-Esko, K.; **Taaber, T.**; Saal, K.; Lõhmus, R.; Kink, I.; Mäeorg, U. New Method for Synthesis of Methacrylate type Polymerizable Ionic Liquids. *Synth. Commun.* **2013**, 43, 1–7.
- II. **Taaber, T.**; Põhako-Esko, K.; Joost, U.; Külasalu, K.; Antsov, M.; Antonov, M.; Veinthal, R.; Saal, K.; Lõhmus, R.; Mäeorg, U. Covalent coupling of ionic liquid to carbon nanotubes: preparation and tribological properties. *MRS proceedings.* **2014**, 1707, 1–6.
- III. **Taaber, T.**; Enok, A. E.; Joost, U.; Oras, S.; Järvekülg, M.; Lõhmus, R.; Mäeorg, U.; Saal, K. Tribological properties of protic ionic liquid and functionalized copper oxide nanoparticles as additives to base oil. *Mechanika.* **2015**, 21 (2), 148–153.
- IV. **Taaber, T.**; Antsov, M.; Vlassov, S.; Mäeorg, U.; Dorogin, L.; Järvekülg, M.; Saal, K.; Lõhmus, R. Formation and Characterization of Micro-cantilevers Produced from Ionic Liquid by Electron Beam Radiation. *J. Mol. Liq.* **2017**, 229, 45–50.
- V. Välbe, R.; Tarkanovskaja, M.; Mäeorg, U.; Reedo, V.; Lõhmus, A.; **Taaber, T.**; Vlassov, S.; Lõhmus, R. Phosphonium-based ionic liquids mixed with stabilized oxide nanoparticles as highly promising lubricating oil additives. *Proc. Est. Acad. Sci.* **2017**, 66, (2), 174–183.

### Author's contribution

- I. Synthesis and characterization of first step ionic liquids.
- II. The author planned and performed all experiments and analysed the results. The author was responsible for manuscript preparation.
- III. The author planned and performed all experiments and analysed the results. The author was responsible for manuscript preparation.
- IV. Synthesis and characterization of ionic liquids. Responsible for preparation of the manuscript.
- V. Responsible for measurements and characterization of the composite lubricating performance.

## ABBREVIATION AND SYMBOLS

AFM	atomic force microscopy
ASTM	American Society for Testing and Materials
$\text{BF}_4^-$	tetrafluoroborate
COF	coefficient of friction
CNT	carbon nanotube
DEHP	bis(2-ethylhexyl) phthalate
EDX	energy-dispersive X-ray spectroscopy
FAP	tris(perfluoroalkyl)trifluorophosphate
HF	hydrogen fluoride
IL	ionic liquid
ILMC	ionic liquid microcantilever
IR	infrared spectroscopy
MEMS	microelectromechanical systems
MWCNT	multiwalled carbon nanotube
NMR	nuclear magnetic resonance
$\text{PF}_6^-$	hexafluorophosphate
SEM	scanning electron microscopy
TFSI	bis(trifluoromethane)sulfonimide
THTP	trihexyltetradecylphosphonium
TMPP	bis(2,4,4-trimethylpentyl)phosphinate
VOS	volatile organic solvents
XPS	x-ray photoelectron spectroscopy
ZDDP	zinc dialkyldithiophosphates

## INTRODUCTION

Ionic liquids (ILs) are liquids comprised entirely of ions [1]. They have attracted excessive attention due to their extraordinary physico-chemical properties like negligible volatility, wide liquid state temperature window, good ionic conductivity and excellent chemical and thermal stability. The most impressive feature of ILs is tunability, where the properties of ILs are influenced by selection of cations and anions. Recently, ionic liquids have been used in lubrication industry. This is because of the possibility to tune their properties by varying anion-cation combinations that determine the tribological interactions between ILs and sliding contact surfaces. By choosing appropriate anion-cation combinations, sufficiently low viscosity and friction coefficient can be achieved. Furthermore, ILs have been used to synthesize stabilized nanoparticles as lubricant additives. Imidazolium-based ILs have been studied as lubricants and lubricant additives, but their complicated synthesis process, high cost and limited solubility in oils are obstacles in application as lubricant. Therefore, the synthesis process of different ILs (protic, phosphonium, ammonium, imidazolium) needs to be further simplified and studied. ILs as lubricants can be expensive, however as a lubricant additive a small amount is needed to markedly improve the lubricant performance.

There is a vast demand for new lubricants due to increased service intervals and reduced volumes and emissions. Frictional loss transmutes to energy loss. This can be decreased by addition of nanoparticles in between sliding surfaces. Nanoparticles have good lubricating behaviour under severe frictional conditions: high load, temperature and sliding speed. Furthermore, they have self-repair function to the worn surface and therefore decrease wear. Nanoparticles have different working mechanisms, but they are believed to roll and slide between sliding surfaces or form a protective film by adsorbing to the surface. The main concern in using nanoparticles as lubricant additives is their stability and homogeneous distribution in media. Nanoparticles tend to form aggregates and then they act as abrasives in lubricant. One possibility to prevent aggregation is the functionalization of nanoparticles with ionic liquids or detergents.

Ionic liquids have low vapor pressure, which opens up new and exciting possibilities in vacuum technologies. They can act as functional reaction medium or they can polymerize by exposure to radiation. Polymerized ILs have various applications, including electrolytes, conductors and microstructures. Positioned pattern on substrates have been achieved by polymerization of IL precursors in scanning electron microscopy (SEM).

In the current thesis a literature overview of ionic liquid synthesis and applications as lubricant and in lithography is given. Experimental work focuses on synthesis of suitable ILs for lubrication. In order to achieve better anti-wear properties, functionalized nanoparticles are synthesized, characterized and investigated as lubricant additives. Furthermore, of the synthesized IL microcantilevers are fabricated and their mechanical properties are measured *in situ* SEM.



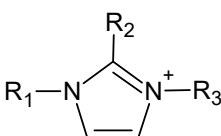
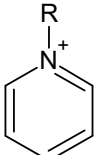
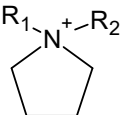
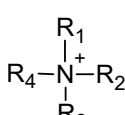
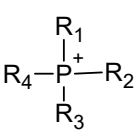
# 1. LITERATURE OVERVIEW

## 1.1 Ionic Liquids

### 1.1.1 Definition

Ionic liquids (ILs) are organic salts that usually consist of asymmetric organic cation and mainly inorganic anion, which can be combined and the number of combinations could be up to  $10^{18}$  [2, 3]. Due to the large size of their molecules, the charges on the ions are typically diffuse and electrostatic forces between the anion and cation are reduced. As a result, it is hard to form a regular crystalline structure, and therefore ILs have low melting points [4]. Conventionally, ILs typically contain large nitrogen or phosphorus containing cations with linear alkyl chains, such as imidazolium, pyridinium, quaternary ammonium or tetraalkylphosphonium. Anions are usually poorly coordinated inorganic or organic compounds. A selection of typical cations and anions is shown in Table 1.

**Table 1.** Schematic representation of selected structures of ionic liquid cations and anions.

Cations	Anions
	$\text{Cl}^-$ $\text{Br}^-$
	$\text{BF}_4^-$ $\text{PF}_6^-$
	$(\text{CF}_3\text{SO}_2)_2\text{N}^-$ $(\text{C}_2\text{F}_5)_3\text{PF}_3^-$
	$\text{CFSO}_3^-$ $\text{EtSO}_4^-$
	$(\text{CN})_2\text{N}^-$

The origins of ionic liquids can be traced back to 1888, when Gabriel synthesized protic ionic liquid ethanolammonium nitrate [5]. In 1914, Walden published the synthesis of ethylammonium nitrate, which was the first room-temperature IL described in the scientific literature [6]. Progress was subsequently slow, the next significant development was reported in 1951, when Hurley and Wier discovered that mixtures of aluminum chloride and ethylpyridinium halides are molten at room temperature [7]. The real innovation with the

preparation of air and water stable 1-ethyl-3-methylimidazolium ionic liquids was in 1992 [8].

Today, the sheer number of potential ILs is estimated to be as high as  $10^{18}$  [9]. In the last decade more than 60000 papers have been published in the field of ILs.

### 1.1.2 Properties

In early days, ILs were used as electrolytes in batteries and in electrodeposition, due to their good ionic conductivity and wide electrochemical window. The main advantage of ILs stands in the possibility to control their properties via their composition. Physical and chemical properties can be tuned by: switching anions or cations; designing specific functionalities into the cations/anions; mixing different ILs. ILs have negligible vapor pressure and high thermal stability compared to volatile organic solvents (VOS), and therefore they are sometimes called “green solvents” [10]. They are non-flammable and compatible with various organic solvents (hydrophilic, hydrophobic) and other materials.

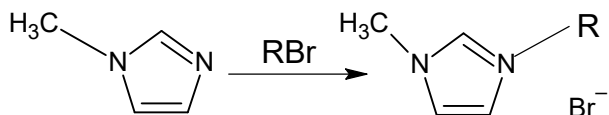
ILs have significantly wider liquid ranges than molecular compounds, i.e. they have a large gap between melting point or glass transition temperature and that of thermal decomposition temperature. For example, glass transition temperatures of 1-alkyl-3-methylimidazolium salts are typically in the range of -70 to -90°C, while the respective thermal decomposition temperatures are in the range of 250–450°C. The main factors that influence melting point are size of the ions, symmetry and charge distribution. Melting points of ILs tend to decrease as the size of anion decreases or cation increases due to the weaker Coulombic interactions between cations and anions [11]. For example, the melting point of 1-ethyl-3-methylimidazolium salt decreases from 87°C to 7°C in the following order:  $\text{Cl}^- > \text{PF}_6^- > \text{AlCl}_4^- > \text{BF}_4^-$ . Since most ILs are nonvolatile, the thermal decomposition is the upper limit of the liquid range, which generally occurs between 350–450°C.

At room temperature ILs have viscosities of 10–500 cP, thus making them more viscous than common organic solvents. For comparison, water has a viscosity of 0.89 cP at room temperature [12]. Mainly, IL viscosities are dependent on temperature, but the structure of cation, anion and impurities have an affect also. For example, increasing the chain length of imidazolium cation while keeping anion the same gives rise to higher viscosities.

One of the exciting characteristics of room-temperature ILs is the wide variation of their solubility and miscibility properties [13]. It is possible to change the properties of ILs by changing their constituent ions. For example, the miscibility with water is significantly affected by the change of anion for imidazolium based ILs (Figure 1.).

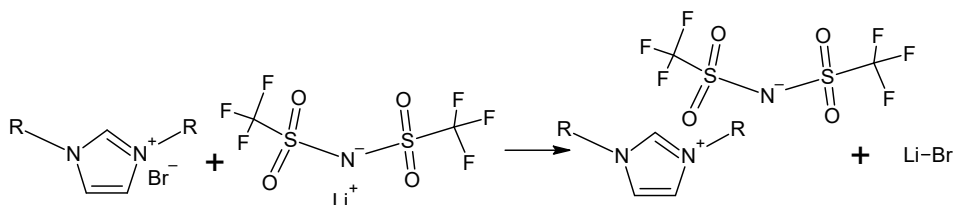


This following section will concentrate on the preparation of ILs based on 1,3-dialkylimidazolium cations and also protic ionic liquids. The alkyl cations of imidazolium ILs are widely prepared by quaternization with suitable haloalkanes. Quaternization reaction is favorable, because there are a variety of cheap haloalkanes available and the reaction occurs smoothly at reasonable temperatures. Additionally, the formed halide salts can be simply changed into salts with favorable anions.



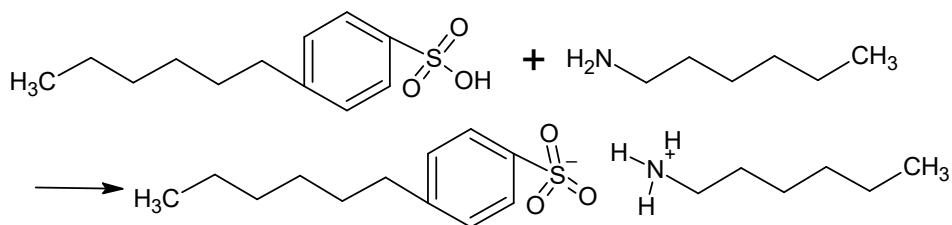
**Figure 3.** Synthesis of alkylimidazole by quaternization.

The formation of IL with favorable anion is achieved by anion metathesis, meanwhile direct treatment of halide salts with Lewis acids may also be used. Metathesis reaction involves the exchange of cations and anions from different salts. Salts are dissolved and solvated ions combine in a new way to form a more stable salt, which usually precipitates.



**Figure 4.** Metathesis reaction with metal salt.

Protic ionic liquids are relatively easy to synthesize, as Walden reported the first synthesis by mixing ethylamine with concentrated nitric acid. IL is prepared by mixing stoichiometric combination of a Bronsted acid and Bronsted base, where protonation of a starting material occurs [17].



**Figure 5.** Synthesis of protic ionic liquid

Although the synthesis of ILs is in general quite simple, the purification is difficult. Since distillation is not an option, due to their lack of vapor pressure, any volatile impurity can be removed by vacuum. Maximum care during the synthesis must be taken, e.g. purification of starting materials, avoidance of high temperature and oxygen and moisture exposure. Impurities in IL determine the color of the product, which often is yellow to brown. Moreover, impurities can influence some properties. For example, water can influence ionic conductivity or in some ILs highly corrosive HF may form.

### 1.1.4 Applications of ionic liquids

The unique combination of properties – nonvolatility, good electrochemical performance and stability make them excellent candidates for a broad range of applications. Since the early days, ILs have been used for their solvating properties, e.g. solvents for catalysis [18], synthesis [19] etc. Also, ILs have been replacing conventional organic solvents in numerous applications [20]. Replacing organic solvents in extraction and separation processes is fairly common, e.g. alkyylimidazolium-based ILs have been used as a stable stationary phase for gas chromatography [21]. The non-flammable, nonvolatile nature of ionic liquids makes them excellent candidates for the development of safer processes.

**Table 2.** Comparison of ionic liquids with organic solvents.

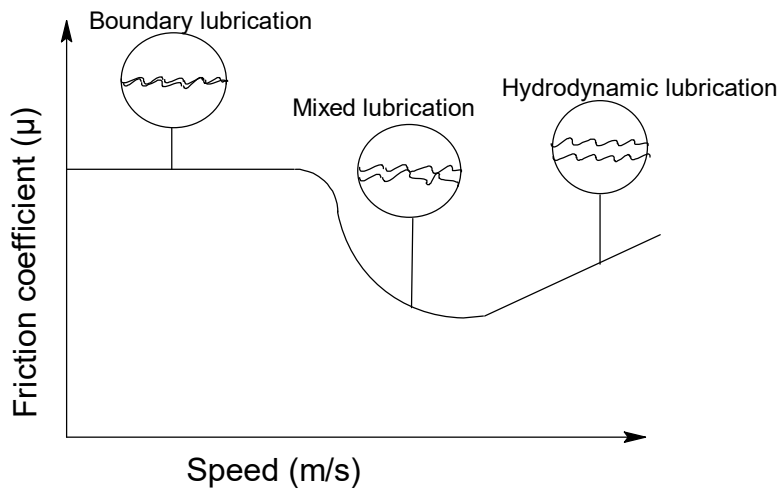
Property	Organic solvents	Ionic Liquids
Number of solvents	>1000	>100 000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tunable
Chirality	Rare	Common and tunable
Flammability	Usually flammable	Usually non-flammable
Vapor pressure	Usually remarkable	Negligible
Solvation	Weakly	Strongly
Viscosity/cP	0.2–100	22–40 000
Cost	Usually low	2–100 times higher
Thermal stability	Low	High

Electrochemical properties of ILs make them attractive for various applications. In lithium batteries, solar cells and fuel cells they are used as electrolyte [22]. Due to their large electrochemical window they can be used in electrodeposition of metals or semiconductors, where other organic solvents cannot be used. Morphology and crystal size of the product can be influenced by the choice of cation and anion [23].

## 1.2 Lubrication

Lubrication is a sub-topic in the science of tribology. The word ‘tribology’ is derived from Greek word *tribos* meaning rubbing and the exact translation would be “the science of rubbing” [24]. More coherently, the addressed phenomena are friction and wear. Friction is the resistance to motion during sliding or rolling, when two solid bodies in contact move relative to each other. Wear is the material loss due to the contact of working parts. Introducing lubricant in between the sliding surfaces prevents the direct contact between them, and thus results in decreasing wear and friction as well as the contact temperature. Friction and wear are measured with tribometers.

For various operating conditions different lubrication regimes occur. Boundary lubrication mostly occurs under high-load when lubricant between contacting surfaces is lacking and the friction coefficient is affected by the nature of surface and lubricant. Tribofilm on contact surface is generated by surface-active substances and by chemical reactions. Elastohydrodynamic lubrication is when contact surfaces are separated by lubricant and the lubrication efficiency is greatly influenced by lubricant viscosity. In mixed lubrication, load is supported both by surface asperities and lubricant [25]. Stribeck curve is fundamental concept of tribology and remarkably describes the lubrication mechanisms (Figure 6) [26].



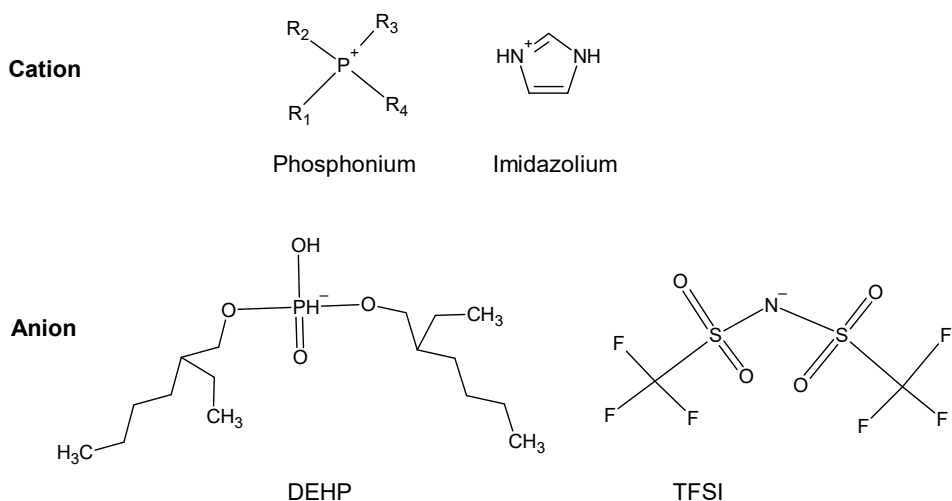
**Figure 6.** Stribeck curve [27].

Regardless of the operating condition, friction and wear between interacting surfaces are sufficiently decreased by lubricant. Lubricants may be liquids (oil, water), solids (molybdenum disulfide) or solid/liquid dispersion (grease). The most used lubricants are liquid and normally consist of 90% of base oil (mineral oil, vegetable oil) and 10% of additives (anti-wear, pour point, corrosion inhibitors, detergents etc.). In mid-1940s antiwear additives were developed to solve the problems in aviation applications, but fast became important in motor oils [28]. The most successful lubricant additive is zinc dithiophosphate, which has comparable antiwear performance at reasonable cost in engine oils.

### 1.2.1 Ionic liquid lubrication

The demand for new lubricants due to application limits, durability, efficiency etc. are the reasons for sizing up ILs as the possible candidates. As said before, ILs have unique physical and chemical properties, e.g. high thermal stability, strong surface adsorption. In 2001, ionic liquids were firstly investigated as neat lubricant [29]. Imidazolium-based ILs are most investigated due to market availability and ease of synthesis. Due to high price, they are proposed to use in extreme tribological conditions (high load, vacuum and temperature) [30]. Qu *et al.* demonstrated that 1-ethyl-3-decylimidazolium-bis(trifluoromethylsulfonyl)imide reduced friction up to 36% and wear up to 34% compared to commercial engine oil [31].

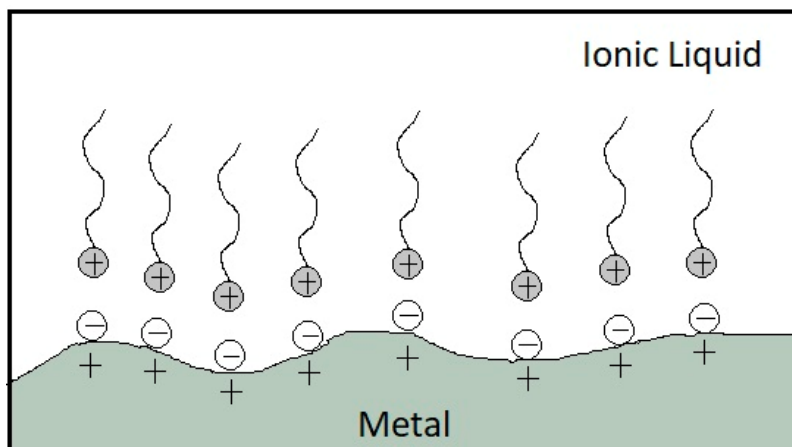
In 2012, a few oil-miscible phosphonium ionic liquids with promising anti wear properties were reported [32]. In order to be oil-soluble, long alkyl chains in IL are necessary and both anion and cation need to have oil-solubility. Barnhill et. al verified the significant wear reduction of base oil by adding 1% of phosphonium IL [33].



**Figure 7.** Common anions and cations used for lubricating ILs.

Ionic liquids have a high polarity, which makes them more preferred than synthetic oils, as a result of forming strong effective adsorption layer (Figure 8). During friction heat is generated and extreme pressure is applied, which causes the emission of low energy electrons of metal surface and positive charge is formed at the surface. Anions, with negative charge adsorb onto metal surface, while cations assemble by the electroneutrality principle [34]. In addition, under high sliding loads, adsorption layer might be damaged, leading to decomposition of ILs and formation of tribofilm. Moreover, ILs usually contain tribologically active elements such as boron, fluorine, nitrogen and phosphorus, which participate in formation of tribofilm. Phosphonium ILs contain phosphorus, which is an active element that is used in synthetic oil additive ZDDP.





**Figure 8.** A schematic representation of IL adsorption to metal surface [35].

Anion and cation of ionic liquid have great impact on lubrication performance and as a unique property of ILs, it is tuneable. The length of alkyl chains of cation has an effect on viscosity and therefore increase can reduce friction and wear. It is reported that the wear volume of [C1C8im]PF<sub>6</sub> was approximately 10 times higher than [C8C12im]PF<sub>6</sub> [36]. It is outlined that ILs with longer alkyl chains exhibited more advanced adsorption capacity and the formed tribofilm was thicker and more stable [37].

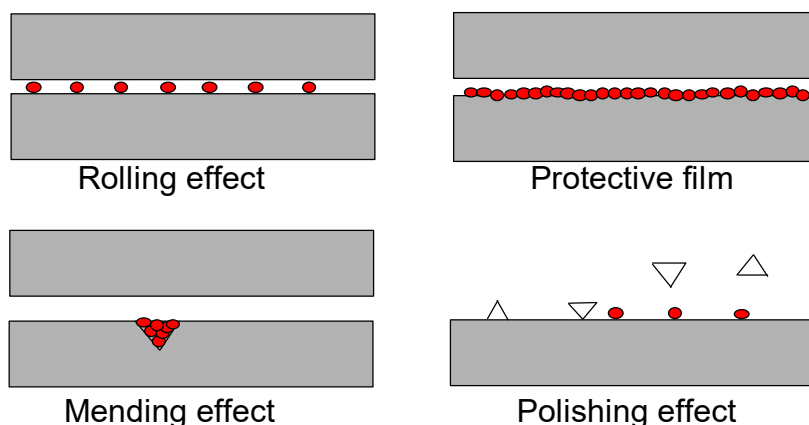
The anions have an impact on viscosity too. In addition, they may affect the formation of tribofilm via inducing specific chemical reactions. For example, coupled with the same cation, anions of tris(perfluoroalkyl) trifluorophosphate (FAP) and bis(trifluoromethane) sulfonimide (TFSI) exhibited better anti-wear properties than hydrophilic BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> anions [38,39]. Supposedly, the reasons behind this are the occurrence of complicated tribochemical reactions, as the surface analysis revealed different reaction products of fluoride. The precise mechanism of formation of tribofilm is not clear, but it has been proposed that ILs and/or their decomposition by-products react chemically with contact surfaces and/or wear residue, producing a protective tribofilm.

### 1.2.2 Nanoparticles lubrication

Failure of machineries and energy losses are significant tribological issues arising from high frictions and therefore additives to base oil are necessary. Recently, nanoparticles were implemented as friction and wear diminishing additives in oils due to their good thermal stability and suitable size (less than 100 nm), which allows them to adhere to the contact region. In literature different nanoparticles have been studied: metal [40], metal sulphides [41],

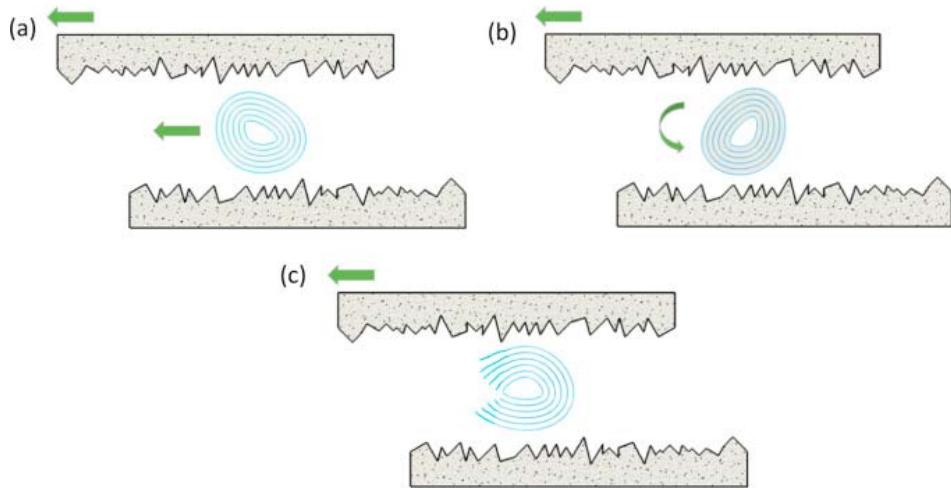
metal oxides [42], carbon materials [43] and borate [44]. Nanoparticles are believed to have several mechanisms including adsorption, tribo-chemical reactions, protective film etc.

Friction reduction mechanisms of nanoparticles are summarized in Figure 9. Direct effect of nanoparticles is seen in the rolling effect, where nanoparticles roll between surfaces and no chemical or mechanical interaction happens. Protective film forms from nanoparticles on the friction surfaces via interactions. Tribofilm may be formed in mending effect, where nanoparticles could deposit on wear scar. Moreover, hard nanoparticles could reduce the roughness of the frictional surfaces by polishing.



**Figure 9.** Lubrication mechanism of nanoparticles [45].

Nanoparticles' size determines their mechanical and chemical properties. For example, small size of nanoparticles lets them adhere to the contact surfaces for load bearing and high surface-to-volume ratio allows them to react with surface and base oil. The types of nanoparticles' morphologies investigated for tribology application in literature are granular, onion, sheet, spherical and tube [46]. Onion morphology has similar working mechanism to spherical, where nanoparticles roll or slide between surfaces, but at high loads it could exfoliate and be like sheet morphology and protective film is formed (Figure 10).

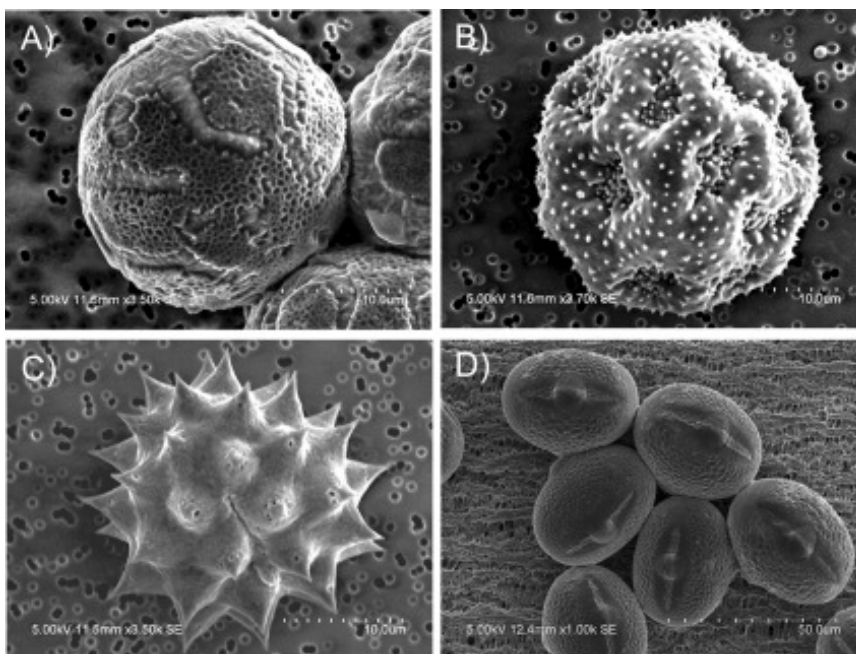


**Figure 10.** Between surfaces nanoparticle is a) sliding, b) rolling, c) exfoliating (adapted from ref [46]).

Metal nanoparticles have many applications, including magnetics, semiconductors and friction reducing agents. Environmentally friendly Cu nanoparticles have been reported to have outstanding self-repairing properties [47]. Nanoparticles have problems with dispersibility in base oil, but this could be resolved with surface modification. Adding surface active substances like surfactants or ionic liquids to nanoparticles allows their steric stabilization and limits aggregation in lubricant. TiO<sub>2</sub> and CuO nanoparticles exhibited uniform dispersion in oil and good friction and wear reduction [48]. Nanocarbon materials as graphite, diamond and carbon nanotubes have been studied as lubricant additive [49]. Carbon nanotubes are chemically inert, which makes their dispersibility in oil difficult. The solution is chemical modification, for instance with sulphuric, nitric and stearic acid [50]. Compared to microparticles, nanoparticles exhibit better tribological performance. It is believed that nanoparticles merge into wear scar asperities and create a protective film [51].

### 1.3 Ionic liquid inside SEM

Room-temperature ILs have unique physicochemical properties, including negligible vapor pressure, which means that they can be used in vacuum without any vaporization. Several instruments in sample analyses require vacuum conditions, which makes it difficult to use wet sample, but ILs can change it. In SEM observation, insulating specimens can be wetted by IL (Figure 11), which behaves as an electronically conducting material [52].



**Figure 11.** SEM images of pollen pre-treated with IL. A) *Primula juliae*, B) *Anemone coronaria*, C) *Leucoglossum paludosum*, D) *Lathyrus odoratus* (adapted from ref. [53]).

In addition, IL can be used as medium for synthesis of various structures by electron beam irradiation. Electron beam encouraged synthesis of Au nanoparticles in IL media have been reported by Imanishi et. al [54].

There is a demand for new microfabrication technologies and to satisfy all severe and complex requirements of microdevices, IL polymerization is a good option. Fabrication process contains controlled radiation of polymerizable ILs, resulting in controlled structures. IL monomers with an allyl substituent under high-energy radiation can polymerize. Recently, micro-electro-mechanical systems (MEMS) have been found increasing use and so there is a demand for new methods for fabricating the 3D micro/nano-scale structures. Minamimoto et. al reported the fabrication of three-dimensional micropolymer/nanopolymer structures by an electron beam from 1-allyl-3-ethylimidazolium bis((trifluoromethane)sulfonyl)amide [55]. Rola et. al fabricated microstructures from ILs with solvent free method in SEM. It concluded that the shape of microstructures is dependent on the patterning parameters and the type of IL anion, where smaller anion has a uniform thickness. The polymerization happens via free radical polymerization mechanism, where under high-energy electron beam exposure C=C bonds of IL degrade [56].

## 2. AIMS OF THE STUDY

The main focus of this study centres around the synthesis, characterization and application of ILs and ionic liquid/nanoparticle mixtures for lubrication. Alternatively, synthesis of IL and fabrication of microcantilever of it is investigated. More precisely, the objectives for the thesis were set as follows:

1. To synthesize task-specific imidazolium based ILs with -OH groups and their characterization.
2. To prepare and characterize protic ILs.
3. To covalently couple ILs to carbon nanotubes and to investigate the tribological properties of the composite.
4. To prepare ionic liquid/nanoparticle composites as lubricating oil additives and investigation of their tribological properties.
5. To fabricate microcantilevers from imidazolium based ILs by electron beam and measuring their mechanical properties.

### 3. MATERIALS AND METHODS

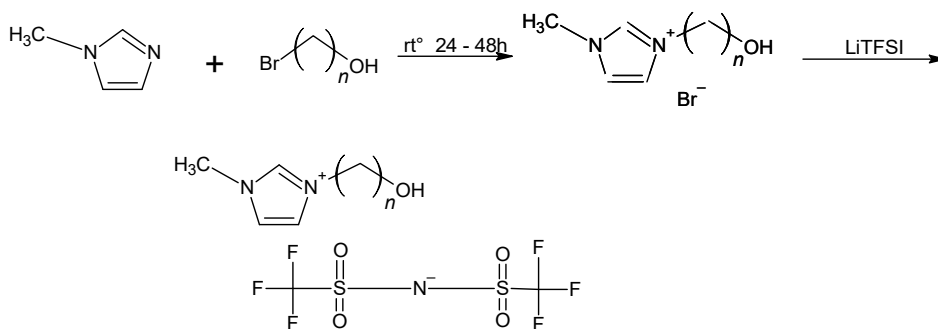
#### 3.1 Synthesis of ionic liquids

In the present work two different types of ionic liquids were prepared. The most common anions  $\text{BF}_4^-$  and  $\text{PF}_6^-$  were avoided due to their highly corrosive nature. The selection of ILs was made according to literature, keeping in mind the working temperature and thermal stability as the most important properties. The functional -OH group is important in nanoparticle functionalization, where the functional group forms a bridge between IL and nanoparticle. It is known that functional group of IL (-OH group) has a strong adsorption to metal surfaces [57].

All reactions were carried out in inert atmosphere. The reagents were commercially available.

##### 1. Synthesis of 1-(n-hydroxyalkyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $n=2; 6; 10$ ).

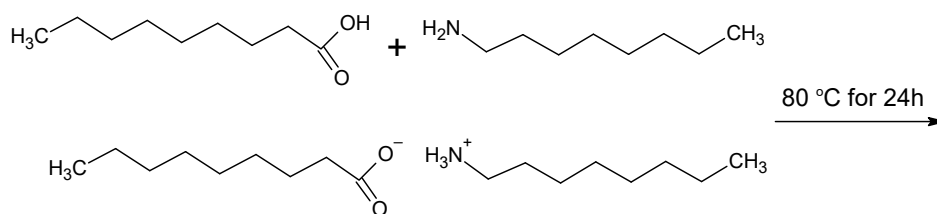
In a typical experiment at room temperature N-methylimidazole (0.1 mol) was added dropwise to  $\alpha,\omega$ -bromoalcohol (0.1 mol) under inert atmosphere and mixed for 24–48 h.



**Scheme 1.** Synthesis of imidazolium ILs.

##### 2. Synthesis of protic ionic liquid.

Standard procedure consists of warming octylamine (0.03 mol) and adding cautiously equimolar amount of nonanoic acid (0.03 mol), stirring for 24 h at 80°C under an inert atmosphere.



**Scheme 2.** Synthesis of protic ionic liquid.

### 3.2 Characterization of synthesized ionic liquids

Ionic liquids were characterized by NMR with Bruker Avance II 200 spectrometer at ambient temperature. The IR spectra were measured on all ionic liquids on a Bruker Vertex 70 FT-IR instrument. Thermogravimetric analysis at heating rate 10°C/min were carried out with Setaram Setsys Evo 1750 analyser.

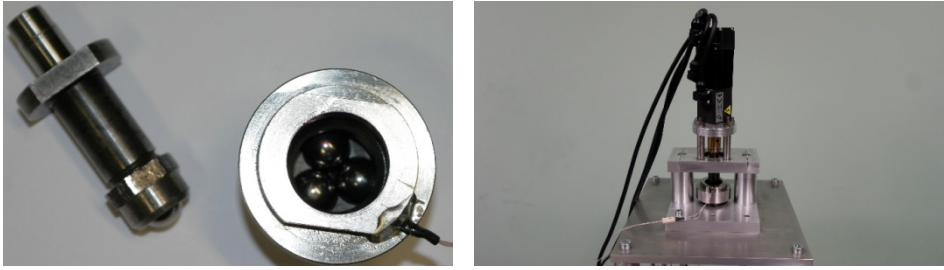
### 3.3 Microscopy and surface morphology

Scanning electron microscope (SEM) (Helios NanoLab 600) measurements were used to investigate nanoparticles' size and morphology. Moreover, obtained wear scars were analysed with SEM equipped with energy dispersive x-ray detector and also an optical microscope Olympus BX 51 was used. Covalently functionalized nanoparticles were analysed with x-ray photoelectron spectroscopy (XPS). Scienta SES-100 electron energy analyser and a non-monochromatic twin anode X-ray tube (Thermo XR3E2) with characteristic energies (1253.6 eV (Mg K $\alpha_{1,2}$  FWHM 0.68 eV) and 1486.6 (Al K $\alpha_{1,2}$  FWHM 0.83 eV)) were used.

Mechanical properties of polymerized ILs were analysed by SEM (TESCAN Vega-II SBU) equipped with 3D-nanomanipulator (Smartact) with connected silicon AFM cantilever (ATEC-CONT cantilevers, Nanosensors, C = 0. Nm<sup>-1</sup>, tip radius approx. 20 nm).

### 3.4 Tribological measurements

Four-ball tribometer was used to measure friction and wear according to ASTM standard D 4172 – 94 [58]. Steel balls (AISI E52100) with diameter 12.7 mm were used and the rotational speed for the top ball was 1200 rpm. 15 kg load was applied for 60 minutes, and the temperature was 75±2°C.



**Figure 12.** Four-ball tribometer.



## 4. RESULTS AND DISCUSSION

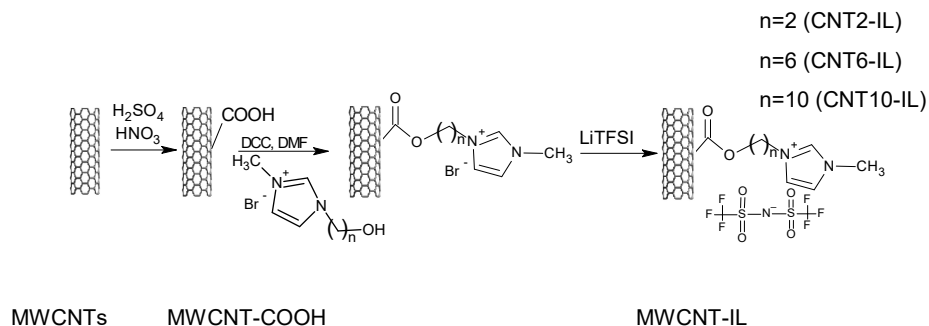
### 4.1 Synthesis of ionic liquids [Publication I, III]

The synthesis process, quaternization of N-methylimidazole, is depicted in Scheme 1. The process occurred in quantitative yield. The physical state of the formed ILs was different, depending on the alkyl chain length. The product was solid for  $n=2$  and  $10$ , and liquid for  $n=6$ . Through metathesis reaction the bromide anion was exchanged with bis(trifluoromethanesulfonyl)imide (TFSI), because TFSI anion has better thermal and chemical stability, and better lubrication properties [59].

Imidazolium based ILs are a good choice for lubrication when the quantities are low and conditions are severe, but for everyday use they are too expensive and their solubility in oils is limited. Due to that, one part of the present thesis was to investigate protic ILs as additives to lubricant oil. Protic ILs are stoichiometric combination of Bronsted acid and Bronsted base. Imidazolium based ILs are highly polar, but oil has a low polarity, therefore it is a good idea to use long alkyl chains in synthesizing ILs. Different reactions with amines and carboxylic acids were carried out, but the best combination (nonanoic acid and octylamine) was chosen for tribological characterization. This IL was liquid at room temperature and was soluble in oil, moreover a clear solution in oil remained even for a month. The formation of IL was confirmed with IR, where were peaks assigned to  $\text{NH}_3^+$  of primary amine salt [60] and peaks assigned to carboxylate [61].

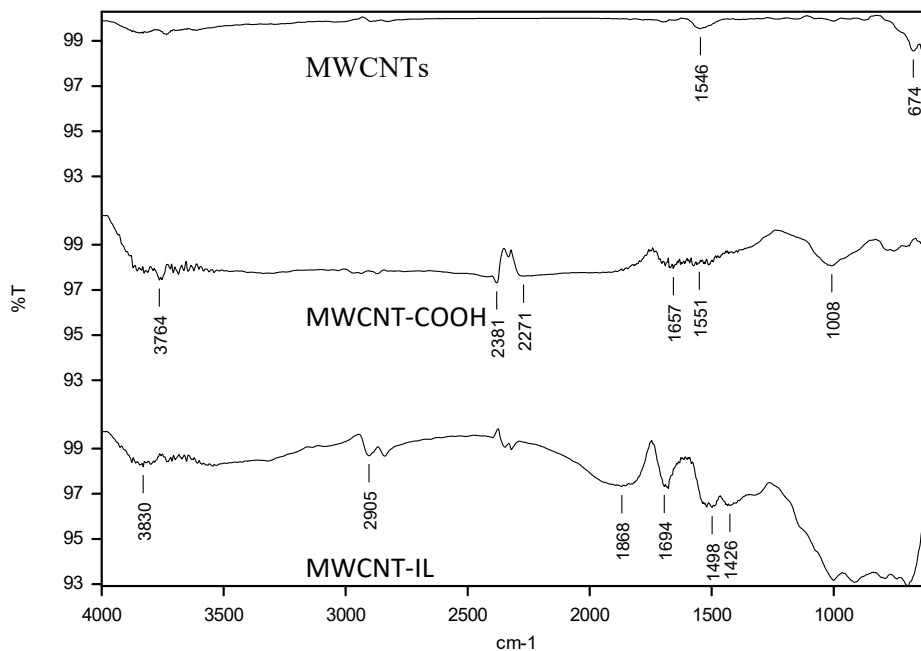
### 4.2 Preparation of ionic liquids nanoparticle combination [Publication II, III]

In this study a novel method for functionalizing oxidized multi-walled carbon nanotubes with hydroxylated imidazolium bromides via esterification reaction was reported and stable mixtures of nanoparticles in ionic liquids were obtained. Carbon nanotubes have poor solubility and tendency to form bundles, which significantly decreases their practical uses.  $\text{HNO}_3/\text{H}_2\text{SO}_4$  were used to chemically oxidize MWCNTs and to obtain carboxylic groups on nanotubes. In this work direct coupling reaction between COOH-functionalized MWCNTs hydroxyalkylimidazolium ionic liquids was used. Earlier methods operated with Cl(CO)-functionalized MWCNTs prepared by treatment of carboxyl group with thionyl chloride as an additional synthetic step [62, 63].



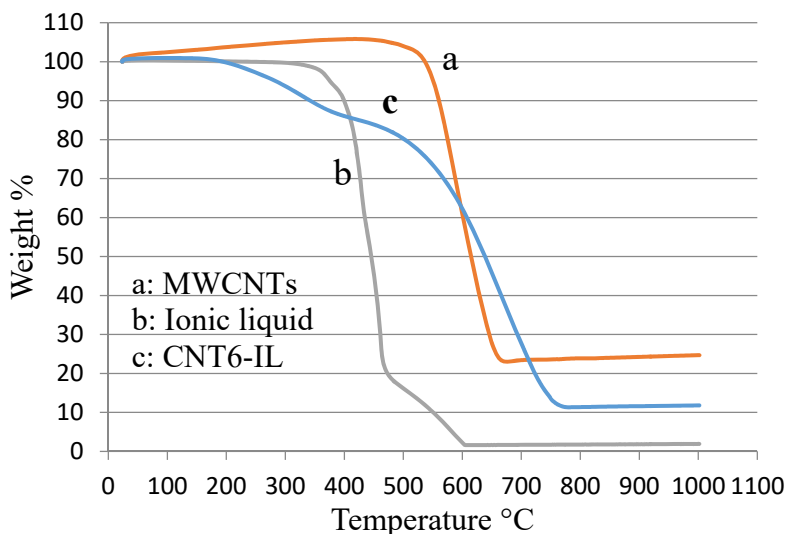
**Scheme 3.** Synthesis of the MWCNT-IL composites

Oxidation of MWCNTs and the appearance of carboxylic acid groups was confirmed with IR, where the C=O band appeared at  $1657\text{ cm}^{-1}$  and -OH band appeared at  $3764\text{ cm}^{-1}$  (Figure 13, MWCNT-COOH). The functionalization was approved by shifting C=O band at  $1657\text{ cm}^{-1}$  to  $1694\text{ cm}^{-1}$ , converting carboxylic acid group to an ester (Figure 13, MWCNT-IL).

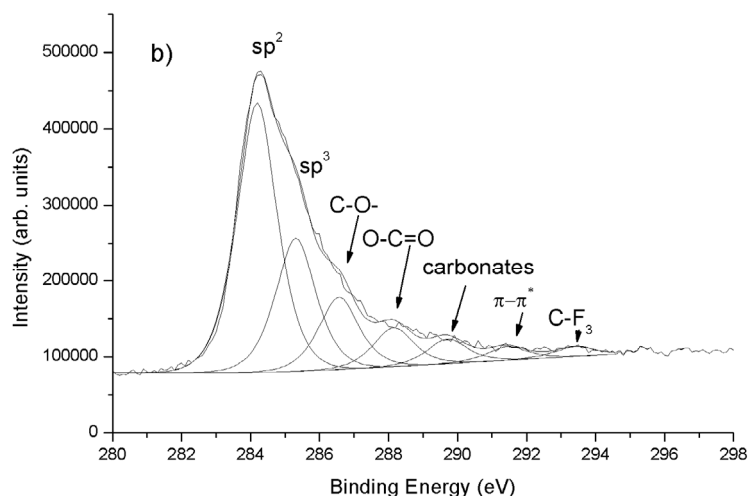


**Figure 13.** FT-IR spectra of MWCNTs, MWCNT-COOH and MWCNT-IL.

Moreover, pristine MWCNTs are insoluble in DMF and water, but our oxidized MWCNTs were soluble in water and DMF. Thermogravimetric analysis showed two weight losses for MWCNT-IL sample, first weight loss at 362°C is IL decomposition and second weight loss at 638°C is due to MWCNT decomposition (Figure 14). Energy dispersive X-ray spectroscopy also confirmed the covalent functionalization of MWCNTs, where carbon in the functionalized nanotubes was bound to different functional groups including ester functionalities (Figure 15).

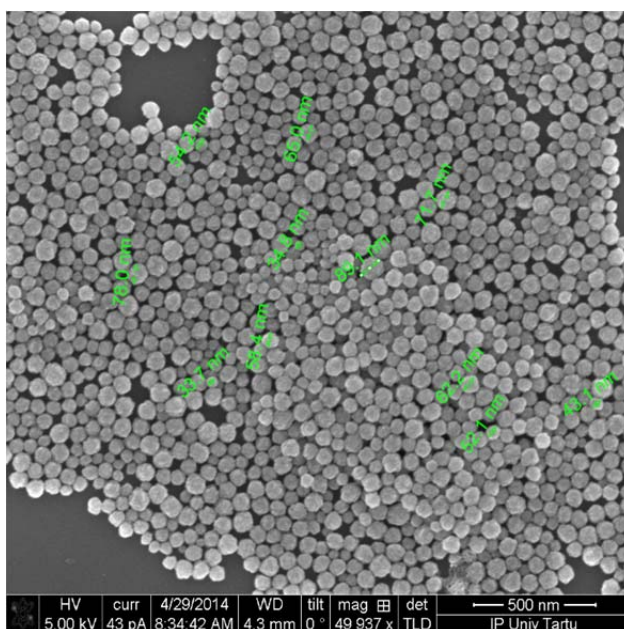


**Figure 14.** TGA curves of pristine MWCNT, IL and CNT6-IL.



**Figure 15.** C 1s spectra of MWCNT-IL.

Copper nanoparticles are widely used as lubricant additive due to their ability to decrease friction and wear, furthermore nanoparticles have self-repairing properties to worn surfaces [64]. In order to have good lubricating power, a stable mixture of nanoparticles in oil must be assured. Therefore, in our lab a simple thermal decomposition method for preparing functionalized nanoparticles was developed. To prevent agglomeration, in synthesis of copper oxide nanoparticles, monothiols were used to create an organic layer. Sample was analysed for all constituent chemical elements and molar ratio of copper to sulphur was 40.5:1. This indicated that nanoparticles were covered with approximately 1/3 of the organic ligands, because the molar ratio of starting materials was 13.0:1. To determine the size and morphology of the synthesized nanoparticles, SEM measurements were carried out. Results indicated that CuO nanoparticles diameters are in range of 30–90 nm, spherical and non-agglomerated.

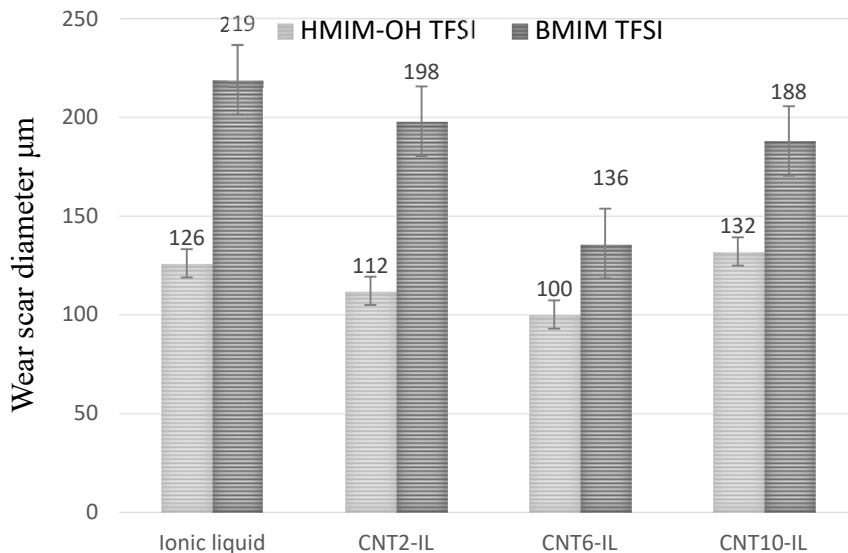


**Figure 16.** SEM micrograph of copper oxide nanoparticles.

## 4.3 Tribological measurements

### 4.3.1 Carbon nanotubes functionalized with ionic liquid [Publication II]

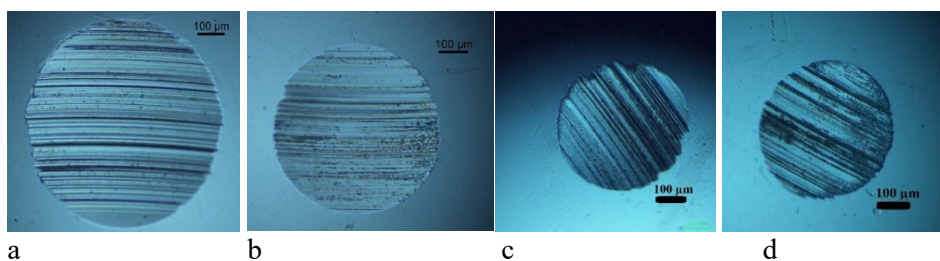
Tribological properties of this compound were measured with a UMT-2 (CETR) nano and micro tribometer on ball-on-disc configuration. The specific test parameters were: ball diameter (AISI 52100) 3 mm, load 2.9 N, time 555 minutes, sliding distance 5000 m. Average values of triplicate measurements were reported and for wear scar measurement an optical microscope was used. The imidazolium ionic liquids with TFSI anion have shown good lubrication [65], therefore this ionic liquid was used and 0.5 wt.% MWCNT-IL was added. Functional groups have been reported enhancing the antiwear properties of ILs [66], therefore hydroxyl groups on cations were used. In Figure 17 it can be seen that IL with hydroxyl moieties has smaller wear scar diameters, as compared to the IL without hydroxyl groups. Obviously, this could be because of the hydroxyl groups facilitate the adsorption of the IL molecules to metal surface and thereby the formation of a protective film [67]. MWCNT-IL composites in ionic liquid exhibited better antiwear properties than IL alone. The best optimum alkyl chain length of IL was concluded to be six according to wear scar diameter.



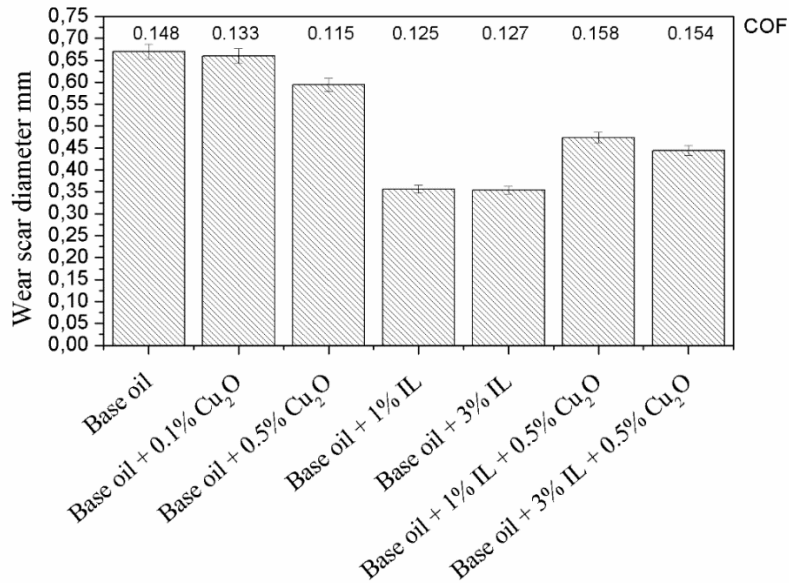
**Figure 17.** Wear scar diameters.

### 4.3.2 Ionic liquids and nanoparticles as oil additives [Publication III, V]

By visual inspection, protic ILs and copper nanoparticles were completely miscible with base oil. The solution appeared clear yellowish without any aggregation or phase separation, even after one month. The lubricating performance was evaluated by four-ball tribometer. In Figure 18 wear scar diameters and coefficients of friction (COF) are shown. The addition of 1% of protic IL to base oil reduced wear by 47%. Ionic liquid is reported to physically adsorb to wear surface [68], furthermore, carboxyl group of IL has an affinity towards steel surfaces. Copper oxide nanoparticles as additive to base oil reduced wear up to 12%. It is interesting to note that the wear reduction of protic IL and copper oxide nanoparticle combination was slightly lower than protic IL only. This might be due to the competition and interaction between protic IL and copper oxide nanoparticles over the adsorption centres on the wear surface. As mentioned before ILs have strong physical adsorption towards metal surface and thus their molecules shelter most of the wear surfaces, interfering copper nanoparticle wear reduction mechanism.



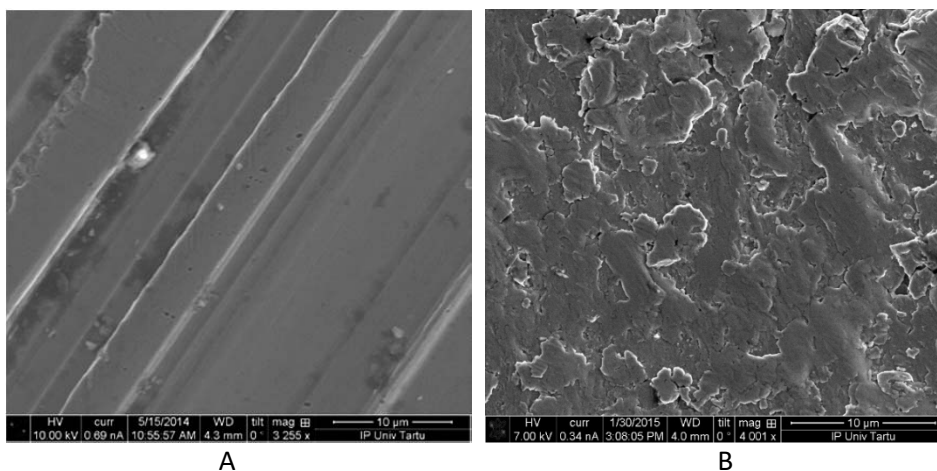
**Figure 18.** Wear scar images of a) base oil, b) base oil + 0.5%  $\text{Cu}_2\text{O}$ , c) base oil + 1% IL, d) base oil + 1% IL + 0.5%  $\text{Cu}_2\text{O}$



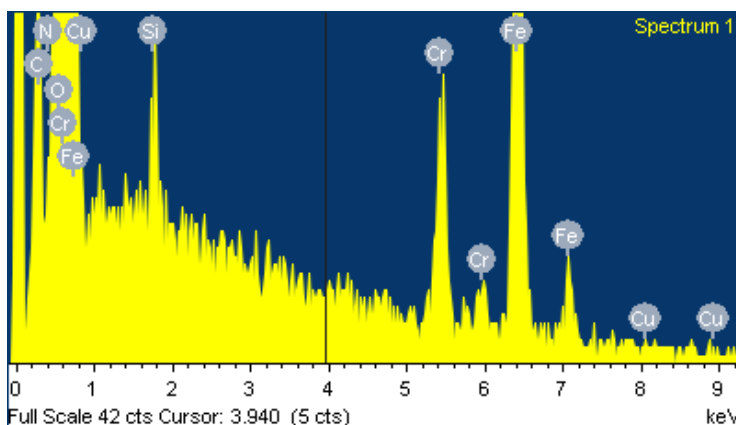
**Figure 19.** Wear scar diameters and coefficients of friction of base oil with various additives.

The coefficient of friction of base oil was reduced by adding protic IL or copper oxide nanoparticles, which agrees well with the wear scar data. When protic IL and copper oxide nanoparticles were used together, the increase of COF was seen, while wear was decreased. Nanoparticles may form particulate network and when there is also protic IL with long alkyl chain, it may adhere to this nanoparticle network and increase COF. In case of high loads, the capacity between nanoparticles/IL network may disappear, leading to better lubrication [69].

Copper oxide nanoparticles have been reported to form a protective layer on rubbing surfaces [70]. During tribological measurements, metal surfaces are being rubbed, depending on the load the contact temperature and pressure might be raised. Copper oxide nanoparticles are softened and protective layer on steel is formed. In Figure 20, SEM images of wear scar of base oil and base oil with protic ionic liquid and copper oxide is seen. In case of additives, the wear scar was flake-like surface and it was further analysed by EDX (Figure 21). The presence of copper and nitrogen were confirmed, originated respectively from copper oxide nanoparticles and protic ionic liquid, confirming the formation of tribofilm.



**Figure 20.** Wear scar images obtained with SEM from a) base oil and b) base oil + 1% IL + 0.5% Cu<sub>2</sub>O mixture.

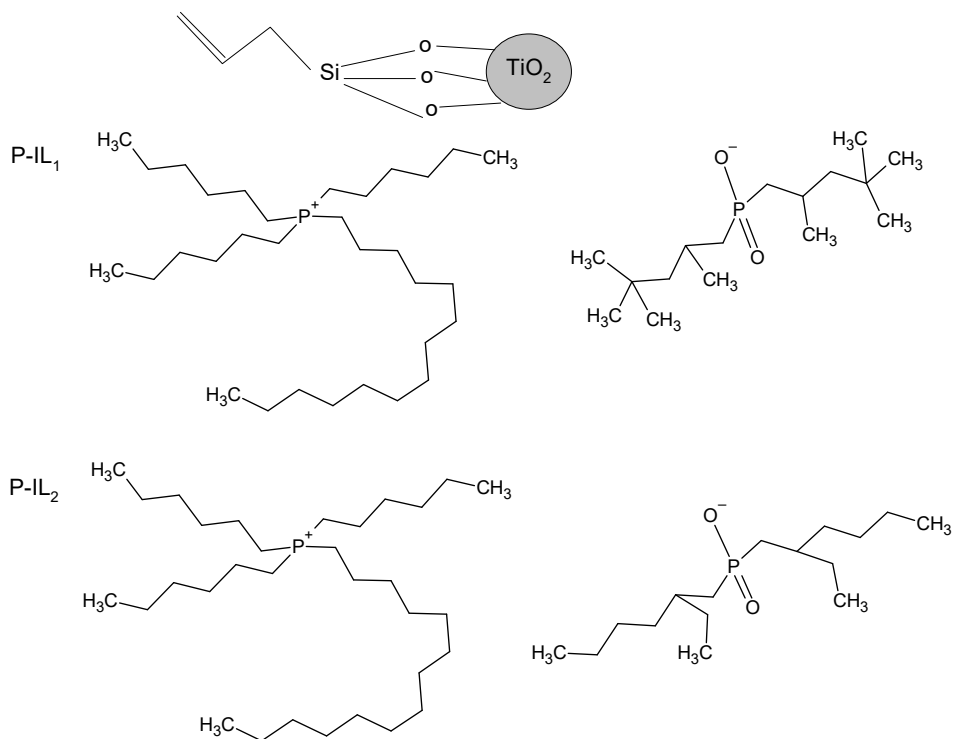


**Figure 21.** Base oil + 1% IL + 0.5% Cu<sub>2</sub>O mixture EDX analysis results.

Since alkyimidazolium ILs are mostly polar, there are some problems with their miscibility with oil. Our synthesized protic ILs with long alkyl chain are a good option, but according to literature phosphonium ILs can also be synthesized with long alkyl chains to make them soluble in oil [71]. Phosphorus is an active element, which is present in additives used in lubricant oil, e.g. ZDDP, furthermore, phosphonium ILs exhibit high stability and wide liquid-phase temperature range [72]. In our lab phosphonium ILs were synthesized (Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate (P-IL<sub>1</sub>)) or commercially available (trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate

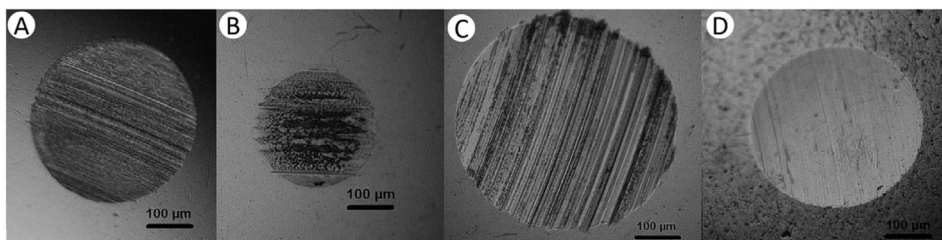


(P-IL<sub>2</sub>) were used to prepare nanoparticles in IL media (Figure 22). The part of this thesis was to investigate the tribological performance of this new composite.



**Figure 22.** Molecular structures of P-IL<sub>1</sub> trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [THTP][TMPP] and P-IL<sub>2</sub> trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [THTP][DEHP].

Both ionic liquids P-IL<sub>1</sub> and P-IL<sub>2</sub> were fully miscible with base oil and by visual inspection no phase separation was observed. 0.1% nanoparticles (TiO<sub>2</sub>) and 1% ionic liquid as additive to base oil was used. Optical pictures of wear scars are shown in Figure 23. The addition of 1% P-IL<sub>2</sub> and TiO<sub>2</sub> nanoparticles to base oil reduced wear significantly. According to literature CuO nanoparticles exhibited better antiwear properties than TiO<sub>2</sub> as additives to oil [73]. CuO nanoparticles may deposit on the worn surface, leading to decreasing shearing stress and therefore improving tribological properties. In our work, both TiO<sub>2</sub> and Cu<sub>2</sub>O nanoparticles as additives to base oil with ILs decreased wear significantly. Based on wear scar images (Figure 18 and Figure 23) Cu<sub>2</sub>O nanoparticles exhibited slightly better wear reduction, which may be attributed to formation of tribofilm.

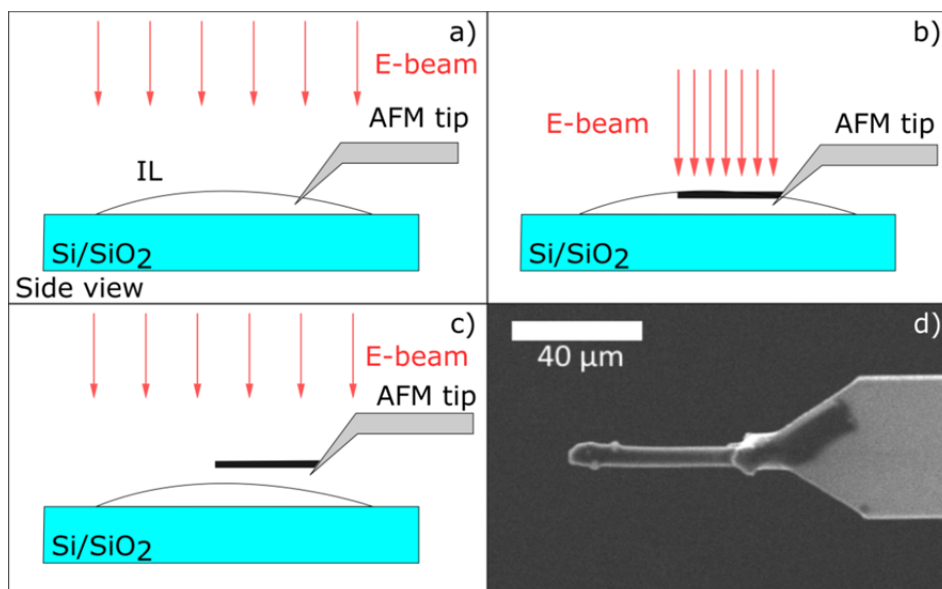


**Figure 23.** Optical microscope images of the wear scars: a) synthetic motor oil, b) synthetic motor oil + 1% P-IL<sub>2</sub> + nanoparticles additive, c) base oil, d) base oil + 1% P-IL<sub>2</sub> + nanoparticles additive.

#### 4.4 Formation and characterization of microcantilevers [Publication IV]

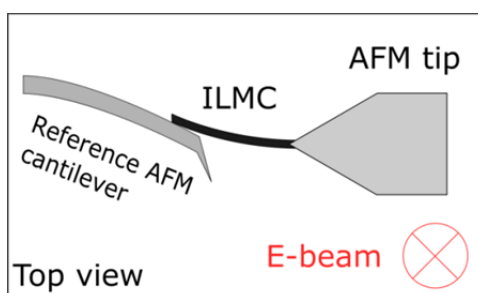
Since ILs have several applications, because of their exceptional combination of chemical [74], electrical [75], thermal [76] and tribological [77] properties, their behaviour in SEM needs to be studied additionally. ILs have been reported to serve as functional reaction medium under electron beam (e-beam) radiation [78], furthermore, ILs themselves can undergo polymerization, which open up many applications. The polymerization of ILs can be achieved by exposure to radiation (e.g. e-beam), which interacts with ionic liquid and yields reactive species, for instance radical ions and solvated electrons [79]. Including IL polymerization, several fragmentations, modifications and chemical reactions are initiated by these reactive species. Polymerized ILs have been used in micro- and nanoscale lithography, to prepare positioned patterns on substrates, but direct writing of suspended and cantilevered domains is also possible. Previously synthesized 1-(6-hydroxyhexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-OH TFSI) and commercially available 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM TFSI) were used to construct freestanding microcantilevers (MC) connected to a silicon AFM tip.

IL was drop-casted onto untreated silicon wafer inside the SEM, and the AFM tip was immersed and held in the IL droplet (Figure 24a). Low current density was used to avoid unintentional structural changes in the IL. Then, much higher current density was used to locally irradiate with the e-beam the rectangular area adjacent to the AFM tip. The irradiated areas in the SEM images appeared darker and polymerization/solidification process was saturated when no changes in the contrast were observed. As seen in Figure 24b, a solid rectangular structure connected to the AFM tip was formed.

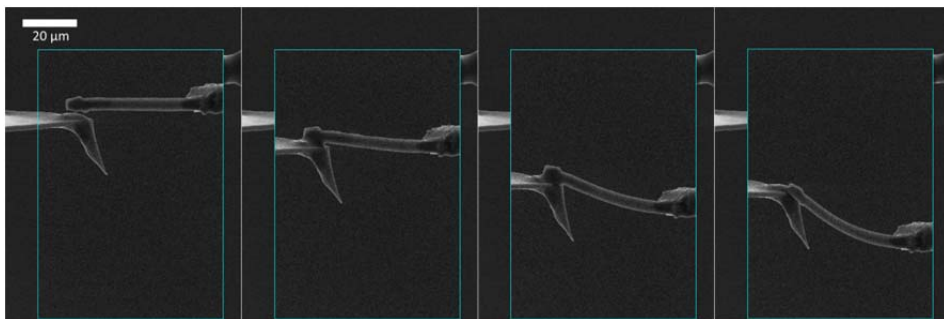


**Figure 24.** Formation of ionic liquid microcantilever (ILMC) inside SEM: a) AFM tip flooded in IL under the low current density, b) high current density was used to irradiate rectangular area adjacent to AFM tip, causing local polymerization/solidification of the IL, c) free-standing ILMC is visible by lifting AFM tip, d) image of the ILMC attached to the AFM cantilever

For better understanding of ILMC mechanical and chemical characterization was performed. Young's moduli was measured with the bending test, where a fixed reference AFM cantilever with known stiffness was used (Figure 25). The measurements were performed on 9 HMIM-OH TFSI and 13 HMIM TFSI ILMCs, while average length remained 40 microns and width 4 microns. The values of Young's moduli were in the same range as that of a well-known polymer (polystyrene) [80],  $7.2 \pm 0.9$  GPa and  $3.5 \pm 1.3$  GPa for HMIM-OH TFSI and HMIM TFSI, respectively.

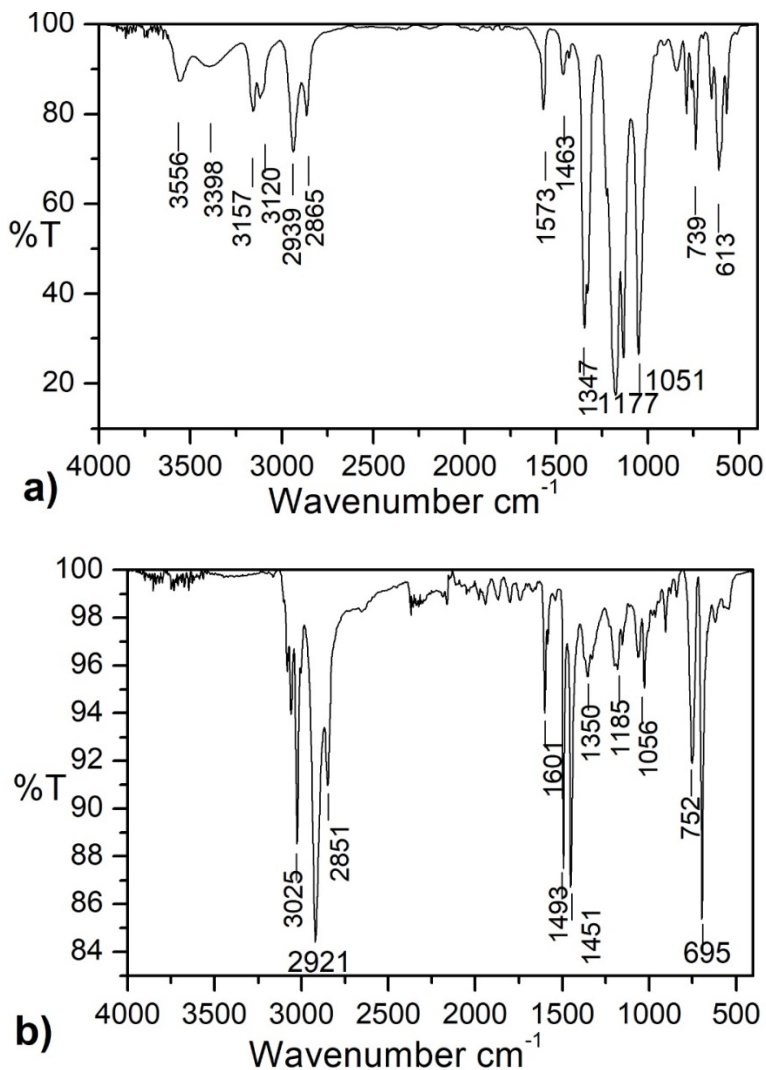


**Figure 25.** Graphic of the bending test: ILMC is bent against a reference AFM cantilever with fixed stiffness.



**Figure 26.** Bending test of ILMC produced from HMIM-OH TFSI

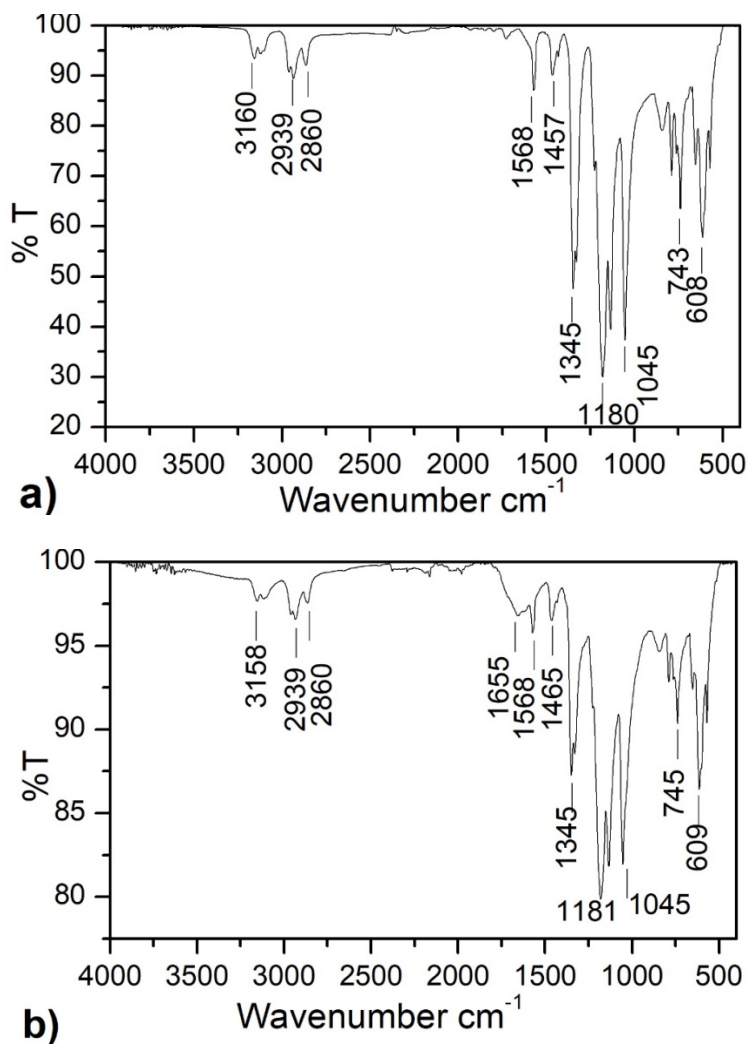
Larger areas of ILs in SEM were irradiated in order to gain insight into the processes that happen in ILs. Irradiated HMIM-OH TFSI formed a solid film, which was able to be detached from the Si wafer. In Figure 27a the spectra of HMIM-OH TFSI is shown, where the -OH band appeared at  $3555\text{ cm}^{-1}$  and  $3398\text{ cm}^{-1}$ . The signals of C-H stretching and  $\text{C}^+=\text{N}$ - bond of imidazolium cation is shown at  $3100\text{ cm}^{-1}$  and  $1463\text{ cm}^{-1}$ , respectively [81]. Imidazolium side chain C-H stretching signals are at  $2930\text{ cm}^{-1}$  and  $2865\text{ cm}^{-1}$ . TFSI anion has absorption bands around  $1400\text{--}100\text{ cm}^{-1}$  [82]. In Figure 27b, the IR spectra of irradiated HMIM-OH TFSI is shown. The absorbance bands of -OH group disappeared, suggesting that hydroxyl group has been removed and an aromatic ring has been organized [83]. Furthermore, the absorbance bands of TFSI anion are significantly lower, but still visible. Suggesting that methyl group of the imidazolium cation may be attacked by anion [81]. Weak absorbance bands at  $2000\text{--}1700\text{ cm}^{-1}$ ,  $752\text{ cm}^{-1}$  and  $695\text{ cm}^{-1}$  may be attributed to monosubstituted aromatic ring, made by recombination of cations that are transformed into radicals. Hydroxyl group of IL could be favourable by directing the deprotonation from methylene. The IR spectrums of polymers with aromatic group, for example polystyrene, are very similar to spectrum of the e-beam irradiated HMIM-OH TFSI [84].



**Figure 27.** FTIR spectra of HMIM-OH TFSI (a) before and (b) after irradiation with e-beam.

At ambient conditions, irradiated HMIM TFSI transformed into soft gel-like material and was measured on the Si wafer. In Figure 28a, the spectrum of HMIM TFSI before radiation shows multiple signals around  $3100 \text{ cm}^{-1}$ , attributed to C-H stretching of the imidazolium cation.  $\text{C}^+=\text{N}$ - bond of imidazolium cation has a peak at  $1463 \text{ cm}^{-1}$  and peaks at  $2939$  and  $2860 \text{ cm}^{-1}$  are assigned to C-H bond of imidazolium side chain. Furthermore, TFSI anion absorption bands are at  $1400$ – $1000 \text{ cm}^{-1}$ . Irradiated spectrum (Figure 28b) revealed minor changes including new absorption band at  $1655 \text{ cm}^{-1}$ , which may confirm the presence of alkyl amine. Commonly nucleophilic anion attack

to the cation leads to IL decomposition. TFSI anion is a weak nucleophile, while decomposing to a more nucleophilic atom or group (F and NH<sub>2</sub>), it attacks the hexyl or methyl chain of the cation, leading to generating alkyl amine [85]. While the real mechanism of polymerization of ILs needs to be further studied, it is remarkable that the mechanism of double-bond ILs polymerizations are essentially different.



**Figure 28.** The IR spectra of HMIM TFSI (a) before and (b) after irradiation with e-beam.

HMIM-OH TFSI microcantilever had a higher elastic modulus (7.2 GPa), which associated well with the IR measurements, where the formation of polymer is shown. Furthermore, the irradiated film could be peeled off, while HMIM TFSI exhibited lower elastic modulus (3.5 GPa) and melted in ambient environment. E-beam exposure to IL resulting with slight or no intermolecular bonding opens up new applications as temporary adhesives in lithography.

## CONCLUSIONS

New lubricants and improved antiwear additives are in need, because of increased service intervals, extreme conditions and regulations to reduced emissions. Ionic liquids are molten salts, which have unique properties (low volatility, high thermal stability) and recently have shown many advantages in this area. Nanoparticles have also been reported as lubricant additives due to their high-load tolerance and self-repair function to wear surface.

In the present thesis the synthesis of different ionic liquids was investigated. Task-specific imidazolium based ionic liquids with -OH groups were synthesized and characterized. 1-(n-hydroxyalkyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (n=2; 6; 10) was chosen according to literature, keeping in mind thermal stability and lubricating performance. Functional -OH group is important for nanoparticle functionalization and IL adsorption to metal surfaces.

Multi-walled carbon nanotubes were chemically oxidized using HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> and then carboxylic acid groups were covalently coupled with -OH group of IL. The difference between earlier methods was the absence of hazardous thionyl chloride and fewer synthetic steps. The success of functionalization was confirmed with XPS, TGA and IR. Moreover, functionalized MWCNTs formed a stable dispersion in ILs, which opens up new applications, e.g lubricants. Tribological properties of MWCNT-IL dispersions were measured with ball-on-disc tribometer. Compared to neat IL, the addition of 0.5 wt% functionalized MWCNT-IL reduced wear volume up to 60% and friction up to 30%.

Imidazolium based ILs show good antiwear reduction properties, but commonly they show poor miscibility with low polarity oils. Therefore, imidazolium based ILs can be used as neat lubricants. For lubricant additives, protic ionic liquids with combination of Bronsted acid and base are a good and inexpensive choice. Synthesis of protic IL with octylamine and nonanoic acid was carried out and characterized with IR and TGA. Four-ball tribometer was used to determine the fact that 1% protic IL to base oil can reduce wear up to 47%. To make even more effective lubricant additive, copper oxide nanoparticles covered with thiol molecules were synthesized by thermal decomposition method. XRF and XRD were used to confirm thiolization of copper oxide nanoparticles and SEM showed that nanoparticles were non-agglomerated and spherical with diameters of 30–90 nm. It is interesting to note that SEM images of wear scars after tribological measurements showed the difference between base oil and base oil with IL and copper nanoparticles. Wear scar of IL and nanoparticle additive was a flake-like surface, where copper from nanoparticles and nitrogen from protic IL were detected, confirming the formation of tribofilm.

Another tested IL type for lubricant additive were phosphonium-based ionic liquids. They are thermally stable, non-corrosive and relatively cheap. Both ILs, trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [THTP]



[TMPP] was commercially available and trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate [THTP][DEHP] was synthesized, showed great antiwear properties as lubricant additive to oil. Moreover, titanium oxide nanoparticles were prepared via the sol-gel process in ILs and a stable, homogeneous dispersion was achieved. Tribological measurements showed up to 61.7% wear scar reduction by adding 1% IL-nanoparticle dispersion.

Another interesting new application of -OH functionalized IL can be production and manipulation of microcantilevers *in situ* in SEM. 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (HMIM TFSI) and 1-(6-hydroxyhexyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-OH TFSI) were used to produce well-defined microstructures by electron beam. For mechanical characterization *in situ* in SEM, the cantilever beam bending technique was applied, where Young's moduli of HMIM TFSI and HMIM-OH TFSI were  $3.5 \pm 1.3$  GPa and  $7.2 \pm 0.9$  GPa, respectively. These microcantilevers are good candidates for Si-based MEMS technologies, while they withstand high mechanical stresses without fracture and remain strongly bonded to the Si tip.

For conclusion, several ionic liquids were synthesized and characterized in this thesis. They were investigated as lubricants and lubricant additives. Moreover, different nanoparticles were synthesized and characterized, and the synergistic effect of IL-nanoparticle lubrication was examined. In addition, ILs were investigated as precursors in lithography to produce microcantilevers.

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## SUMMARY IN ESTONIAN

### Ioonseed vedelikud: Süntees ja rakendused lubrikatsioonis ja litograafias

Vajadus uute lubrikandite ja kulumisevastaste õlilisandite vastu on suurenenud, kuna masinatel on pikemad hooldusintervallid, ekstreemsemad kasutustingimused ning uued regulatsioonid emissioonide vähendamiseks. Ioonseed vedelikud on sulas olekus soolad, millel on unikaalsed omadused (madal lenduvus, kõrge termiline stabiilsus) ja hiljuti on nad näidanud häid omadusi lubrikantidena. Nanoosakesi on samuti uuritud kui lubikandi lisandeid nende suure koormustaluvuse ja hõõrdepinda parandavate omaduste tõttu.

Antud doktoritöös uuriti erinevate ioonsete vedelike sünteesi. Sünteesiti ja karakteriseeriti OH-rühmaga imidasoolimkatiooniga ioonseed vedelikud. Toetudes kirjandusele, valiti 1-(n-hüdroksüalküül)-3-metüülimidiasoolium bis(trifluorometüülsulfonüül)imiid ( $n=2; 6; 10$ ) tänu selle termilisele stabiilsusele ja triboloogilistele omadustele. Ioonse vedeliku funktsionaalne -OH rühm mängib olulist rolli nanoosakeste funktsionaliseerimisel ja ioonse vedeliku adsorptsioonil metalli pinnale.

Süsinkinotorud oksüdeeriti keemiliselt, kasutades  $\text{HNO}_3/\text{H}_2\text{SO}_4$  segu, mille tulemusel tekitati karbüksüülrühmad nanotorude pinnale ja seoti need kovalentselt ioonse vedeliku -OH-rühmadega. Antud meetodil puudus ohtlik tionüülkloriid, võrreldes eelmiste kirjanduses olevate meetoditega. Funktsionaliseerimise edukus kinnitati XPS, TGA ja IR-ga. Funktsionaliseeritud süsinkinotorud moodustasid stabiilse dispersiooni ioonseed vedelikus, mis võimaldab neid kasutada erinevates rakendustes. Dispersiooni triboloogilised omadused mõõdeti tribomeetriga. 0.5% süsinkinotorude-ioonse vedeliku dispersiooni lisamine ioonsele vedelikule vähendas kulumist kuni 60% ja hõõrdumistegurit kuni 30%.

Tavaliselt imidasoolium ioonseed vedelikud segunevad halvasti mittepolaarsete õlidega, ning seetõttu kasutatakse neid puhaste lubrikantidena. Õlilisandiks sobivad prootilised ioonseed vedelikud on enamasti odavad ja neid on lihtne toota stöhhiomeetrilise seguna Bronstedi alusest ja happest. Prootilise ioonse vedeliku sünteesi oktüülamiinist ja nonaanhappest viidi läbi ja produkt karakteriseeriti IR ja TGA-ga. Nelja-kuuli tribomeetriga mõõdeti, et 1% prootilist ioonset vedelikku õlis võib vähendada kulumist kuni 47%. Vasenanoosakesed kaetud tioli molekulidega sünteesiti termilise lagunemise meetodiga ning XRF ja XRD kinnitasid tiolatsiooni edukust. SEM pildid näitasid, et vasenanoosakesed ei ole aglomereerunud ning on ümarad diameetriga 30–90 nm. Pärast prootilise ioonse vedeliku ja vasenanoosakeste dispersiooni triboloogilisi mõõtmisi hõõrutud kuule uuriti SEM-ga. Pildid näitasid helbe-laadset pinda, kus tuvastati vaske nanoosakestest ja lämmastikku ioonseed vedelikust, kinnitades tribokihi tekkimist.

Fosfaat ioonseed vedelikud on termiliselt stabiilsed, mittekorrodeeruvad ja suhteliselt odavad, seetõttu uuriti neid antud töös õlilisandina. Triheksüültetra-deküülfosfoonium bis(2,4,4-trimetüülpentüül)fosfinaat [THTP][TMPP] oli

kommertsiaalselt kättesaadav ning triheksüültetradeküülfosfoonium bis(2-etüülheksüül) fosfaat [THTP][DEHP] sünteesiti meie laboris. Stabiilne ja homogeenne titaanoksiidi nanoosakeste dispersioon ioonsetes vedelikus saavutati soolgeel meetodiga. Triboloogilised mõõtmised näitasid, et kulumine võib väheneda kuni 61,7%, kui lisada õlile 1% ioonse vedeliku ja titaanoksiidi nanoosakeste dispersiooni.

Veel üks huvitav rakendus -OH rühmaga ioonsetele vedelikele oleks mikrofiibrite valmistamine *in situ* SEM. 1-heksüül-3-metüülimidasoolium bis(triflorometüülsulfonüül)imiidi (HMIM TFSI) ja 1-(6-hüdroksüheksüül)-3-metüülimidasoolium bis (triflorometüülsulfonüül)imiidi (HMIM-OH TFSI) kasutati, et valmistada elektronkiirega mikrostruktuure. HMIM TFSI ( $3.5 \pm 1.3$  GPa) ja HMIM-OH TFSI ( $7.2 \pm 0.9$  GPa) mikrofiibrite Youngi moodulid saadi *in situ* SEM neile painutamise tehnikat rakendades. Mikrofiibrid kannatasid suuri mehaanilisi koormusi ilma purunemata ja jäid tugevalt seotuks Si tipuga, andes neile potentsiaalselt palju rakendusi MEMS tehnoloogiates.

Kokkuvõtteks, antud töös sünteesiti ja karakteriseeriti mitmed erinevad ioonsetes vedelikud ning neid uuriti kui lubrikante ja kui õlilisandeid. Mitmed erinevad nanoosakesed sünteesiti ja karakteriseeriti, veelgi enam uuriti ka ioonsetes vedelike ja nanoosakeste sünergilist efekti triboloogias. Peale selle, ioonseid vedelikke kasutati mikrofiibrite lähteaineteks litograafias.

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2007–2010 B.Sc. in material science, University of Tartu  
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2015–2016 MATECC, specialist  
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1. Välbe, R.; Tarkanovskaja, M.; Mäeorg, U.; Reedo, V.; Lõhmus, A.; **Taaber, T.**; Vlassov, S.; Lõhmus, R. Phosphonium-based ionic liquids mixed with stabilized oxide nanoparticles as highly promising lubricating oil additives. *Proc. Est. Acad. Sci.* **2017**, *66*, (2), 174–183.
2. **Taaber, T.**; Antsov, M.; Vlassov, S.; Mäeorg, U.; Dorogin, L.; Järvekülg, M.; Saal, K.; Lõhmus, R. Formation and Characterization of Microcantilevers Produced from Ionic Liquid by Electron Beam Radiation. *J. Mol. Liq.* **2017**, *229*, 45–50.
3. **Taaber, T.**; Enok, A. E.; Joost, U.; Oras, S.; Järvekülg, M.; Lõhmus, R.; Mäeorg, U.; Saal, K. Tribological properties of protic ionic liquid and functionalized copper oxide nanoparticles as additives to base oil. *Mechanika.* **2015**, *21* (2), 148–153.
4. **Taaber, T.**; Põhako-Esko, K.; Joost, U.; Külasalu, K.; Antsov, M.; Antonov, M.; Veinthal, R.; Saal, K.; Lõhmus, R.; Mäeorg, U. Covalent coupling of ionic liquid to carbon nanotubes: preparation and tribological properties. *MRS proceedings.* **2014**, *1707*, 1–6.

5. Põhako-Esko, K.; **Taaber, T.**; Saal, K.; Lõhmus, R.; Kink, I.; Mäeorg, U. New Method for Synthesis of Methacrylate type Polymerizable Ionic Liquids. *Synth. Commun.* **2013**, 43, 1–7

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1. Välbe, R.; Tarkanovskaja, M.; Mäeorg, U.; Reedo, V.; Lõhmus, A.; **Taaber, T.**; Vlassov, S.; Lõhmus, R. Phosphonium-based ionic liquids mixed with stabilized oxide nanoparticles as highly promising lubricating oil additives. *Proc. Est. Acad. Sci.* **2017**, 66, (2), 174–183.
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