The Effect of Phosphonium- and Imidazolium-Based Ionic Liquids as Additives in Natural Oil: An Investigation of Tribological Performance

Abstract
Natural oils have been known to be viable lubricants since the emergence of lubrication and have regained their prominence due to new eco-friendly initiatives. Recently, environmentally benign ionic liquids (IL) have been proposed as a new class of green lubricants. In this study, the effects of phosphonium- and imidazolium-based ILs as additives in natural oils on tribological performance are investigated using a pin-on-disk apparatus. The results indicate that the effects of both ILs as additives in natural oils enhance the tribological properties of the lubricant mixtures. As the amount of the IL additive increase within the natural oil, the tribological properties continue to improve. Among the two types of ionic liquid mixtures investigated, the phosphonium-based ionic liquids had the superior performance.

Introduction
Recently, there has been a resurgence of biolubricants due to increased environmental efforts to reduce the use of petroleum-based lubricants in addition to the depletion of oil reserves, increases in oil price, and rises in lubricant disposal costs [1, 2]. When compared to petroleum-based oils, biolubricants have a higher lubricity, lower volatility, higher shear stability, higher viscosity index, higher load carrying capacity, and superior detergency and dispersancy [1], therefore, they are excellent alternatives to petroleum-based oils. Despite, these favorable attributes, the largest drawbacks to many bio-based oils are their poor thermal-oxidative stability, high pour points, and inconsistent chemical composition, which have led to the development of chemically modified synthetic biolubricants and the use of stabilizing additives [3, 4]. Ionic liquids (ILs), particularly those that are fluid at room temperature, represent a promising new class of biolubricants that show potential to minimize the ecological concerns associated with petroleum-based oils, and overcome the drawbacks to many bio-based lubricants [4].

Room Temperature Ionic Liquid Lubricants
In this study, imidazolium- and phosphonium-based ILs are investigated. Room temperature ionic liquids (RTILs) have lamellar liquid crystal structure, where anions and cations form ionic bonds that create layers. These layers are held together with the weak van der Waals force [2, 3]. The appeal of ILs as lubricants becomes even more evident when one considers their many potential advantages over other lubricants including: (1) a broad liquid range (low melting and high boiling point); (2) negligible vapor pressure; (3) non-flammability and non-combustibility; (4) superior thermal stability; (5) high viscosity; (6) miscibility and solubility; (7) environmentally-benign (non-toxic); (8) lamellar-like liquid crystal structure; (9) long polar anion-cation molecular chains; and (10) economical costs [3, 4]. Additionally, ionic
liquids have consistent physicochemical properties and an easily tailorable chemical composition that affords them the ability to provide the level of thermal-oxidative stability, lubricity, and reproducibility required for a variety of applications. Furthermore, they can be designed to be environmentally friendly by selecting both the cationic and anionic constituents to be non-toxic [3, 4].

Experimental Details

To assess the potential of using ILs as additives in lubricants, a series of experiments were conducted with two conventional ionic liquid cations. They are (a) a phosphonium-based cation, trihexyl(tetradecyl)phosphonium, denoted as $\text{P}_{666,14}^+$ and (b) an imidazolium-based cation, 1-decyl-3-methylimidazolium denoted as $\text{C}_{10}\text{mim}^+$. Both the cations were mixed with a bis(trifluoromethylsulfonyl)imide anion, denoted as $\text{Tf}_2\text{N}^-$. The anions and cations were combined to form two ionic liquids: $\text{P}_{666,14}\text{Tf}_2\text{N}$ and $\text{C}_{10}\text{mimTf}_2\text{N}$. Each ionic liquid was mixed with avocado oil, a natural oil due to its high concentration of oleic acid. The ionic liquids were mixed in the lubricant mixture in the following percentages 0%, 25%, 50%, 75%, and 100%, to investigate the use as additives and as a base fluid in an effort to replace traditional plant-based oils. In the investigation, pin-on-disk tests were conducted to characterize the tribological performance of the hybrid lubricants.

The tests materials consisted of 2024 aluminum hemispherical pins sliding on 440C stainless steel disks with a normal load of 10N, sliding velocity of 36mm/s, and for a test duration of 13 hours. Additionally, scanning electron microscopy and energy dispersive X-ray spectroscopy were conducted to analyze the surface damage and potential for transfer layer formation after the pin-on-disk testing.

Results and Discussion

Figure 1(a) shows the variation of the coefficient of friction (COF) for different mixtures of the phosphonium- and imidazolium-based hybrid lubricants. It can be seen that for both lubricant mixtures as the IL percentage increases, the COF decreases. Figure 1(b) shows the variation of the wear volume for the different IL lubricant mixtures. In a similar manner to the trends of friction, the wear volume decreases with an increase in the amount of the IL in the lubricant mixtures. There is a clear trend between an increase in the amount of IL in the lubricant mixtures and an improvement in the tribological performance. The phosphonium and imidazolium-based lubricant additives showed reductions in friction of 69% and 67% respectively as well as reductions in wear of 73% and 59% respectively. For both the phosphonium- and imidazolium-based lubricant mixtures a correlation coefficient was calculated to be over 98%, indicating a strong relationship between the amount of IL and the tribological performance.
between an increase in the IL percentage and the enhancement in the tribological performance.

Scanning electron micrographs of the worn pin surfaces lubricated with different mixtures of the phosphonium-based IL are shown in Fig. 2. It can be seen in Figs 2(a)-(c) that worn surface transitions from a relatively smooth unabraded surface when lubricated with 100% IL to a severely abraded surface when lubricated with 100% natural oil. The SEM images substantiate the positive effects of the ILs when present in the lubricant mixtures. Similar results were found for the imidazolium-based lubricant mixtures.

The friction and wear results indicate that the presence of either IL as an additive improves the tribological performance. More still, the use of ILs as base fluids further enhances the tribological performance. The low friction and minimal wear caused by the ILs are due to (1) their liquid crystal lamellar structure that affords them low internal resistance, (2) their anion-cation moiety that inherently adsorb on to charged worn metal surfaces; and (3) their ability to establish monolayers that effectively minimize the amount of asperity contact [3]. The properties of the ionic liquids clearly exhibit improved boundary lubrication properties when compared to those of fatty acids (e.g. oleic acid), which are present in the natural oils.

This study demonstrates that RTILs have the potential to serve as a new class of biolubricants. It has been shown that their lamellar-like liquid crystal dipolar structure allows the cations and anions to more effectively adsorb onto charged worn metal surfaces. This phenomenon promotes self-assembling monolayers that create boundary films that minimize wear, reduce friction, and can lead to improved component operation. Environmentally friendly ILs were presented and demonstrated to be feasible in design and provide superior tribological properties. The effect of ILs in the natural oils as additives reveals that ILs have a tremendous effect on promoting the life of mechanical components by reducing friction and wear.

Conclusions
The major findings of the current investigation of ionic liquid-based hybrid lubricants revealed the following conclusions:

- RTILs outperform natural oil-based lubricants due to their lamellar-like liquid crystal structure and self-assembling monolayers, which improve lubricity and wear resistance.
- As the percentage of the IL increases in the lubricant mixture, the tribological performance increases as well.
- Phosphonium and imidazolium-based ionic liquids can serve as effective boundary lubricant additives or as base-fluids for lubricant mixtures.
- The phosphonium-based ionic liquid lubricant has the greatest enhancement to the tribological performance.

References