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Tribological performance comparing different refrigerant–lubricant systems: The case of environmentally friendly HFO-1234yf refrigerant

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ABSTRACT

We report on the tribological performance of gray cast iron with different lubricants, namely PAG (Polyalkylene glycol), POE (Polyolester), and Mineral oil, in the presence of environmentally friendly HFO-1234yf refrigerant. Two operating temperatures (24 °C and 110 °C) were used to investigate the mutual solubility of lubricant/refrigerant systems. PAG/HFO-1234yf exhibited better tribological performance compared to the other systems. The better performance was attributed to lower solubility of PAG in HFO-1234yf refrigerant, thus allowing the lubricant and refrigerant to preserve their unique properties. Using Scanning Electron Microscopy, plastic flow associated with adhesive wear was revealed for PAG/HFO-1234yf, where an anti-wear film over the surface was also identified. X-ray Photoelectron Spectroscopy identified a fluorine enriched protective layer in the case of PAG/HFO-1234yf at 110 °C.

1. Introduction

Since the late 1990s, scientific consensus has been made to reduce/eliminate the use of high global warming producing refrigerants. Chlorofluorocarbon (CFC) and hydrofluoro-carbon (HFC)-based refrigerants cause either depletion of the ozone layer or increase the global temperature (i.e., they have a high index of Global Warming Potential GWP). Therefore, the atmospheric adversity of CFC and HFC based refrigerants has promoted countries throughout the world to pass legislation (according to Montreal and Kyoto Protocols) to phase out the use of such refrigerants [1–3]. In the European Union, regulation has already been enacted to substitute R-134a refrigerant in automotive air conditioning systems by a lower global warming potential (GWP) refrigerant [4]. Therefore, several low GWP refrigerants including natural refrigerants are being considered. Among natural refrigerants, carbon dioxide (R-744) is being investigated for possessing low toxicity along with low flammability [5,6]. Besides toxicity and flammability issues, material and tribological compatibility are also essential to deploy any alternative refrigerant in an air-conditioning/refrigeration automotive compressor system.

Tribological studies of R-744 refrigerant have been performed by several researchers [7–10], including lubricity effects at high operating pressures [11]. Implementation of R-744 involves higher cost for system mitigation as well as the likelihood of reduced safety.

Partly due to practical difficulties associated with R-744 refrigeration, refrigerant and air-conditioning industries are endeavoring towards the development of alternative environmental friendly refrigerants, which do not require any costly system modifications. In other words, the candidate refrigerant can be directly used, or is compatible with existing R-134a systems. In this framework of properties and applications, Honeywell® and DuPont® have developed a new refrigerant, namely 2,3,3,3-tetrafluoropropene (HFO-1234yf), which is considered a 'drop-in' solution to replace R-134a refrigerant. This refrigerant is proposed as a direct substitution for possessing similar thermo-dynamical properties [12–16] as R-134a. Note that, this newly developed refrigerant has lower GWP (namely 4 in 100 years) compared to the existing R-134a refrigerant (GWP is above 1200 in 100 years) [17]. The tribological compatibility of this new refrigerant is also essential prior to its implementation in compressor systems. In particular, lubricant compatibility plays a pivotal role in determining the tribological performance.

2. Background on compressor lubrication and HFO-1234yf refrigerant

The preferred lubrication regime in contacting interfaces is hydrodynamic lubrication to reduce friction and wear. In this regime of lubrication, the contacting surfaces are separated by a

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thick film of lubrication and surface properties of the interface are less important. However, interface components are often subjected to reduced lubrication, namely boundary or mixed/starved lubrication [18,19]. Specifically, contacting components experience this starved lubrication stage during the on or off state of the machine [20,21], as well as in many practical devices, such as air-conditioning and refrigeration compressors, where abundant lubricant is unable to reach all interfaces. Under starved lubrication conditions, lubricant viscosity and its surface interaction capacity are very important. Different surface layers are developed at this stage due to complex reaction between lubricant and surfaces in the sliding region [22,23]. This interaction is further complicated with the employment of a gaseous refrigerant in the contact zone. The reactions are very important because they determine the reliability and durability of moving components. The surface films are believed to be beneficial as they protect the interfacing surfaces from direct contact [23].

In regards to HFO-1234yf refrigerant, we have shown that a beneficial fluorine enriched tribolayer was formed over gray cast iron surface [24]. The development and growth of such films are strongly influenced by the mutual solubility of lubricant and refrigerant inside the compressor system. Excessive dissolution of lubricant in the refrigerant usually deteriorates the tribological performance due to degradation of the lubricant's viscosity and thus functionality. Thus, a compatible lubricant is necessary prior to implement an alternative refrigerant. Miscibility is prime concern to evaluate the thermodynamic performance in a lubricant/refrigerant mixture. This is important to avoid accumulation of lubricant in the system [25]. This miscibility issue triggered the development of synthetic lubricants, such as PAG (Polyalkylene glycol) and POE (Polyol ester). It is worth to note that mineral oil is not miscible with current HFC-based refrigerants [26].

While miscibility studies are important, tribological studies along with mutual miscibility are critical in order to select an appropriate lubricant for a specific refrigerant. For example R-744 carbon dioxide exhibits better tribological performance with PAG-based lubricants, compared to POE lubricants [27,28]. These studies demonstrated that in the case of lower mutual solubility of PAG lubricants and refrigerant gas, better performance was achieved. Note that, tribological experiments could be used as a predictive tool for understanding the solubility limit of a lubricant at the interface. Thus, high solubility results in reduction in viscosity, implying a weaker interface, which in turn leads to higher friction. Detailed analysis of the solubility limit requires thermo-dynamical and chemical analysis, which was out of the scope in the present study. To date, there is no significant scientific work available in the literature, focusing on how the tribological properties of certain lubricants are influenced by their solubility in the presence of HFO-1234yf refrigerant. In this work, we examine the tribological performance of gray cast iron with different lubricants for a fundamental understanding of the lubricant compatibility with the environmental friendly refrigerant HFO-1234yf.

The tribological performance of cast iron in the presence of HFO-1234yf refrigerant was previously studied [24,29]. Our earlier studies showed better tribological performance over gray cast iron interface for HFO-1234yf refrigerant compared to R-134a. The better results were attributed to the formation of an inorganic fluoride layer on the surface in the presence of HFO-1234yf. Note that, this refrigerant has an unsaturated carbon bond (–C=C–) in its chemical structure, which facilitates the formation of a wear preventive (or triboprotective) layer. The tribo-layers are usually formed during the tribological experiments, which can be revealed through tribochemical analysis. An oxidative layer over the surfaces was found to protect the substrate in a CO_2 environment (demonstrated using Auger Electron Spectroscopy (AES)) [8]. A fluorine-enriched layer has a beneficial contribution, in terms of wear, as revealed from X-ray photoelectron Spectroscopy (XPS) analysis [24,30,31]. Similar tribo-beneficial layers were found by Dascalescu et al., while working with PTFE-based coatings in R-744 environment [32].

In this work, we conducted a comparative study to evaluate the compatibility of different lubricants (PAG, POE and mineral oil) with the environmentally friendly refrigerant HFO-1234yf. Two sets of controlled tribological experiments were performed to determine the friction behavior and the maximum interfacial scuffing loads. Wear mechanisms were analyzed through Scanning Electron Microscopic (SEM) analysis and XPS was utilized to identify the chemical species on the surface and their subsequent changes following the tribological experiments. In addition, XPS was used to identify the different levels of lubricant solubility at the interface in the presence of HFO-1234yf refrigerant.

3. Experimental procedure

3.1. Controlled tribological experiments

Scroll type compressor conditions (where the main tribological interface can be simulated with a nominally flat pin-on-disk unidirectional motion) were experimentally simulated using a specialized high-pressure tribometer (HPT). The question of compressor lubrication conditions (in the field) and laboratory conditions to simulate aggressive compressor conditions is an important one. It is well understood that even though most air-conditioning/refrigeration compressors have an abundant amount of oil in a sump, critical tribocontacts do not experience fully flooded conditions and typically experience boundary/mixed lubrication conditions, as mentioned earlier. It has been shown that under fully flooded conditions, scuffing is usually not experienced and thus our laboratory experiments (using a small predetermined amount of lubricant at the contact) simulate aggressive compressor conditions. Such aggressive experiments are used to determine the overall lifecycle and reliability of critical tribo-components. The HPT is a customized tribometer and capable of controlling versatile environmental chamber and loading conditions. The lower fixture of the machine is mounted to a 6-axis force transducer, which measures the forces in three orthogonal directions to measure in-situ friction coefficient. The normal load is controlled with the vertical movement of the lower fixture while the upper rotating spindle is held fixed along any linear motion in all directions. The pin is mounted at the lower fixture with a self-aligning holder. The disk was mounted at the upper spindle, which can rotate up to 4.8 m/s. The test chamber is enclosed and thus able to maintain a constant environmental pressure during the experiments: it consists of a special housing capable of 27 Pa vacuum, while it allows for a pressurized environmental pressure up to 1.72 MPa. In addition, the test temperature can be controlled from $-20\ ^{\circ}C$ to $140\ ^{\circ}C$. Further details of the HPT can be found in [29].

Fig. 1(a) shows a photograph of a typical cast iron disk and Fig. 1 (b) and (c) of a typical cast iron flat pin (stand-alone and inside a self-aligning holder respectively). Gray cast iron components are widely used in sliding operation for having excellent wear resistance [33,34], which is attributed to the presence of graphite flakes found in pearlitic matrix, as can be seen from the SEM image in Fig. 2 (its chemical composition is also provided). The samples were machined using a grinding operation, resulting in a roughness of about 0.7 μm (rms) for the disk samples. A single drop of lubricant was directly used at the interface before performing the experiment in order to develop boundary/mixed lubrication conditions. A series of experiments under different sliding velocities [Fig. 1(c)] were conducted, confirming mixed/ boundary lubrication conditions. Note that, these experiments were performed in the presence of PAG/HFO-1234yf system at room temperature. Earlier studies