



The significance of tribochemistry on the performance of PTFE-based coatings in CO₂ refrigerant environment

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ABSTRACT

This work reports on the tribological performance of three commercially available PTFE-based coatings (PTFE/pyrrolidone (C1), PTFE/pyrrolidone (C2) and PTFE/MoS₂ (C3)) deposited onto engineered disk samples (substrates) made out of three different commonly used materials (gray cast iron, sintered iron and Al390-T6). Controlled oscillatory experiments were conducted to simulate the operating conditions of piston-type compressors in the presence of environmentally friendly CO₂ refrigerant. It was found that the substrate played a major role on the tribological performance of the coatings and one of the coatings (PTFE/MoS₂) was found to significantly improve the scuffing performance of Al390-T6 substrate. Furthermore, the tribological performance was found to improve with increasing CO₂ pressure since a thicker patchy PTFE transfer layer was formed at the substrate–pin interface. XPS analysis showed that metal fluorides have a beneficial role on the tribological performance of these coatings.

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1. Introduction

In recent years, the refrigeration industry has shown interest in the use of CO₂ as an environmentally friendly refrigerant in order to replace traditional environmentally harmful refrigerants like chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC). Not only CO₂'s ozone depleting potential is zero, but also as opposed to traditional refrigerants its global warming potential is thousands of times lower than that of traditional refrigerants [1,2]. The use of CO₂ refrigerant changes the conditions to which compressor contacts are subjected to, and in particular imposes a different environment and higher operating pressures. The interface might no longer be able to withstand harsh operating conditions caused by smaller clearances and higher speeds and loads found in compressors. Also, the air-conditioning and refrigeration industry has shown interest in oil-less compressors to eliminate the adverse thermodynamic effects of lubricants on the refrigeration cycle. Clearly, there is necessity for developing advanced surface treatments and coatings, capable of functioning under stringent operating conditions.

Due to the increasing importance of lightweight engineering and design driven by ecological and economical reasons, advanced composite coatings are needed to improve the surface properties of machine elements and system components made of light metals and their alloys (e.g., magnesium and aluminum), which in general exhibit

poor tribological properties [3]. Thus, there is a strong demand for coatings that are not only resistant to extreme operating conditions, but also exhibit long lifetime with minimal friction and wear. Environmental reasons are also driving the willingness to reduce or eliminate the use of oil in mechanical systems, which further increases the importance of high performance coatings.

Coatings are mainly produced through plasma vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. Among different categories of coatings, diamond-like-carbon coatings (DLC) [4], Ti–N [5], Cr–N [6] and WC/C [7] are some of the most widely used coatings. Their structure and mechanical properties can be tailored towards optimization of their tribological performance for a wide range of applications such as air-conditioning and refrigeration compressors and magnetic storage hard disk drives. A drawback of these coatings is their relative high cost, and the difficulty to apply them on substrates with low surface energy or high roughness [8–12].

Another coating category is polymeric-based materials, such as polytetrafluoroethylene (PTFE), high density polyethylene (HDPE), low density polyethylene (LDPE), and polyetheretherketone (PEEK) [13]. From these materials, PTFE presents many desirable properties for challenging tribological applications, such as chemical inertness, considerable thermal stability, low friction [14] and high melting temperature (327 °C), compared to other polymers [15]. In particular, PTFE sliding contacts exhibit friction coefficients lower than 0.1 and as low as 0.05 in different unlubricated tribological situations including PTFE sliding against metals and ceramics [16–20]. The low friction coefficient is explained by the ability of the extended chain molecules of PTFE, $-(CF_2-CF_2)_n-$, to form a low shear strength film upon its surface and mating counter-faces during sliding. This film is

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generally thinner and highly oriented than that found with other transferring polymers. The special nature of this film is believed to be connected with the low friction coefficient of PTFE. The major wear mechanism of PTFE is associated with the relative poor adhesion of its transfer film to the counter-face. Thus, the film transfer/film removal process becomes an effective mechanism for wearing away the polymer coating [17].

Despite the PTFE beneficial frictional properties described above, such as low friction, it suffers from weak mechanical properties, such as low hardness and poor tribological ones such as high wear and cold flow under prolonged load [14,21]. For example, PTFE exhibits the highest wear rate among all engineering plastics, with a value of $9.5 \times 10^{-4} \text{ mm}^3/\text{Nm}$ [17]. In order to overcome these drawbacks, PTFE-based blends have been developed and studied [22]. Demas and Polycarpou [12] presented a tribological study under compressor-specific conditions of commercially available PTFE-based coatings. Specifically, they have reported on three commercially available PTFE-based coatings, namely PTFE/pyrrolidone (trade name Dupont® 958-414 and coded as C1), PTFE/pyrrolidone (trade name Dupont® 958-303 and coded as C2) and PTFE/MoS₂ (trade name Whitford Xylan® 1052 and coded as C3), which exhibited good tribological behavior under a range of testing conditions when coated on cast iron substrates. These coatings were competitive when compared with a commercially-deposited hard DLC coating, showing high load carrying capacity and gradual failure. Under high contact pressures (corresponding to a normal load of 445 N), the PTFE-based coatings were fully penetrated. However, the wear debris generated acted as a third-body lubricant preventing catastrophic failure. Under lower loads (111 N), closer to typical compressor applications, the wear track could be distinguished from virgin areas only through burnishing of the surface, but no clear wear was observed.

The present work reports on the effect of substrate material and CO₂ refrigerant pressure on the tribological performance of the above mentioned PTFE-based coatings, as well as their tribochemical interfacial interactions. Three different substrates (gray cast iron, sintered iron and Al390-T6 aluminum alloy) and two different CO₂ pressures (25 and 200 psi) were examined. Tribochemical analysis using Scanning Electron Microscopy interfaced with Energy Dispersive X-ray analysis (SEM/EDS) and X-ray Photoelectron Spectroscopy (XPS) was used to investigate the wear mechanisms.

2. Experimental procedure

2.1. Samples and contact geometry

The substrates used in this study were aluminum alloy (Al390-T6), sintered iron, gray cast iron (Durabar® G2), whereas the pins (counter-part) were 52100 steel. The PTFE-based polymeric coatings applied on the substrate disks were the aforementioned coatings coded as C1, C2 and C3 and were deposited by an authorized applicator, using a spraying technique. Before application, the substrates were cleaned according to the manufacturers' specifications to be free of dirt, oil and other soils in order to achieve good adhesion and a defect free coating. The coatings were applied in 2 or 3 passes of the spray gun to obtain a uniform full wet appearance. To completely cure the coatings, the substrate temperature was kept constant for the entire bake schedule. Table 1 shows the curing and in-use temperature for all coatings along with various physical properties. General information on the application method for these coatings can be found in Refs. [15,23]. The 8 mm diameter pins were cut to length of 8 mm and machined out of 52100 steel pins to sit flat. As illustrated in Fig. 1a, the semi-cylindrical pins were oriented to create a line contact and also had a 1 mm diameter hole to accept a miniature thermocouple that recorded temperature during tests, 2 mm below the surface. This contact geometry simulates the wrist pin contact in a piston-type compressor. A self-aligning pin-holder ensured uniform contact between the pin and the disk (Fig. 1b).

Table 1

Processing and physical properties of the coatings used in this work: C1, C2 and C3 deposited on cast iron, Al390-T6 and sintered iron substrates.

Coating	DuPont® 958-303	DuPont® 958-414	Whitford Xylan® 1052
Designation	C1	C2	C3
Chemical composition	PTFE/pyrrolidone	PTFE/pyrrolidone	PTFE/MoS ₂
R _a , rms roughness (μm) (cast iron substrate)	3.3 ± 0.3	1.2 ± 0.2	2.3 ± 0.3
Hardness (VHN)	38	25	32
Curing temperature min–max (°C)	250–340	255	220–345
In-use temperature (°C)	260	200	260
Color	Black	Dark green	Black
Weight solids (%)	26.3	25.7	32.6
Theoretical coverage (m ² /kg/25 μm)	7.8	5.9	7.2

2.2. Tribological performance evaluation

A custom-made High Pressure Tribometer (HPT) was used to perform controlled tribological experiments. The HPT is a fully enclosed, controlled environment tribological testing machine capable of simulating the tribological conditions encountered in air-conditioning and refrigeration compressors. Further details of the HPT and test procedures can be found elsewhere, e.g., [24]. Basically, a pin-on-disk arrangement consisting of a disk mounted to a rotor and a pin placed in a self-aligning fixture is used. Traditional pin-on-disk testing utilizes either a cylindrical flat pin or a spherical pin, for convenience. In this research, however, cylindrical connecting rod-piston wrist pins, obtained from a piston-type reciprocating compressor, were used and oriented in the tribometer to create a line contact, as found in a typical compressor. Using this configuration, desired contact pressures were readily applied. To accommodate this pin orientation, a special holder was designed which allows the pin to self-align (Fig. 1b) to the disk surface ensuring a uniform contact pressure. The chamber temperature can be controlled from –20 to 120 °C (Fig. 1a). The chamber can be vacuum evacuated up to 27 Pa, while it allows pressurized environment up to 1.72 MPa (250 psi). The HPT is computer controlled and data is acquired, plotted automatically, and can be exported for further processing. The data acquired includes in-situ normal force, friction coefficient and near-contact temperature.

A normal load of 445 N, corresponding to a mean contact pressure of 460 MPa (representing aggressive compressor conditions) was used to investigate the performance of the coatings. Lower loading conditions representing mild compressor operating conditions were unable to cause detectable coating wear within the finite time duration of the experiments, in agreement with Ref. [12]. A preload of 44.5 N was applied before test initiation (to enable run-in and avoid abrupt failures) and the tests were performed under oscillatory conditions at a frequency of 4.5 Hz, amplitude of 30°, and an average wear track diameter of 47.6 mm to produce average and maximum linear velocities of 0.21 m/s and 0.33 m/s, respectively. The tests were realized in a CO₂ refrigerant environment at 23 °C. In order to directly compare with earlier results [25,26], a CO₂ pressure of 25 psi was used for the majority of the experiments. Experiments at a higher chamber CO₂ pressure of 200 psi using the sintered iron coated surfaces were also performed to study the effect of pressure (higher CO₂ pressure was consequently introducing more CO₂ molecules (mass) in the chamber). The nominal duration of the experiments was 30 min and tests were stopped earlier when the friction coefficient and temperature increased sharply, indicating abrupt catastrophic failure. The experiments showed good repeatability based on multiple experiments under identical conditions.

Before testing, the non-coated samples were immersed in a pool of acetone and ultrasonically cleaned, then rinsed with isopropanol (IPA)

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