Friction **11**(10): 1939–1952 (2023)
https://doi.org/10.1007/s40544-022-0733-3
ISSN 2223-7690
CN 10-1237/TH
RESEARCH ARTICLE

Microencapsulated paraffin as a tribological additive for advanced polymeric coatings

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Received: 11 September 2022 / Revised: 27 November 2022 / Accepted: 20 December 2022

Abstract: Numerous tribological applications, wherein the use of liquid lubricants is infeasible, require adequate dry lubrication. Despite the use of polymers as an effective solution for dry sliding tribological applications, their poor wear resistance prevents the utilization in harsh industrial environment. Different methods are typically implemented to tackle the poor wear performance of polymers, however sacrificing some of their mechanical/tribological properties. Herein, we discussed the introduction of a novel additive, namely microencapsulated phase change material (MPCM) into an advanced polymeric coating. Specifically, paraffin was encapsulated into melamine-based resin, and the capsules were dispersed in an aromatic thermosetting co-polyester (ATSP) coating. We found that the MPCM-filled composite exhibited a unique tribological behavior, manifested as "zero wear", and a super-low coefficient of friction (COF) of 0.05. The developed composite outperformed the state-of-the-art polytetrafluoroethylene (PTFE)-filled coatings, under the experimental conditions examined herein.

Keywords: microencapsulated phase change material (MPCM); friction reduction additive; advanced polymeric coating

1 Introduction

Polymers are consistently growing as tribologically viable materials especially under dry sliding conditions, such as those experienced in space applications. They provide notably advantageous properties such as easy machinability, reasonable production cost, and light weight, as well as outstanding unique characteristics such as excellent corrosion resistance. Nonetheless, their poor wear resistance and friction properties hinder their more prevalent utilization in industrial applications. To tackle such shortcomings, three major approaches have been adapted, namely compounding polymers with other lubricious polymers/lamellar solids [1–3], adding fillers such as fibers, oxides, and metallic nanoparticles [4, 5], and incorporating encapsulated additives such as ionic liquids (ILs) and paraffins [6, 7]. The difference between ILs and other fillers is that they need to be properly encapsulated in a core–shell structure before blending with the polymer matrix. A brief description of the advantages and disadvantages of these categories is presented below.

Among lubricious polymeric additives [1, 8], polytetrafluoroethylene (PTFE) has been widely investigated and utilized by numerous researchers and industries. The unique molecular structure and chemical composition of PTFE result in minimal

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friction between its polymeric chains due to the fluorophilic polymer interchain interactions. In addition, PTFE can also serve as a polymeric matrix to accommodate other fillers, e.g., polyamide-imide (PAI) and polyether ether ketone (PEEK) [9, 10]. In fact, under certain conditions, dry sliding can yield a coefficient of friction (COF) of 0.06 in PEEK-filled PTFE composites, which epitomizes the frictional characteristics of PTFE [10]. However, it is sometimes neglected that obtaining such a low COF is limited to linearly reciprocating motion and certain experimental parameters. In addition, because PTFE is chemically inert, it cannot be cross-linked, yielding poor creep and wear resistance, and therefore a controlled amount of filler has to be incorporated to enhance the tribological performance [11]. When PTFE is being used as a filler, e.g., in advanced polymeric coatings, it exhibits enhanced tribological attributes, manifested as "zero wear" and low COFs, at ca. 0.2 under ambient conditions [3, 12, 13]. While the wear resistance of PTFE-filled composites can be tuned with the appropriate selection of the supportive polymeric matrix, e.g., aromatic thermosetting co-polyester (ATSP), a further reduction in COF (< 0.1) will require additional modifications of the additive composite. In general, the effective lubricating mechanisms of composite materials are based on lowering the shear resistance of the composite material and/or generating a lubricious transfer film on the countersurface.

Another category of fillers, which has been widely experimented and successfully implemented, is particulate additives, mostly in the form of non-organic fillers, including and not limited to metals, minerals, and oxides and graphitic compounds (e.g., copper, silicon carbide, and graphite oxide). These particles are generally used for fortifying the wear resistance of the polymers; thus, it is common to produce hybrid polymer–composite films, which include the polymer matrix in addition to particulate fillers. References [7, 8] have investigated the role of the chemical composition, particle size, volume fraction, shape, and specific surface area of these particles on enhancing the tribological performance of the polymer composites. In fact, the nanoparticles seem to be more effective in enhancing the mechanical and tribological properties of the polymers, since lower volume fraction results in better modifications when compared to similar microparticles [1, 9]. The lowest COF and wear rate were reported for bronze particles and carbon fiber fillers added into PTFE matrix, which yielded 0.39 and 2.25×10^{-6} $mm^3/(N\cdot m)$, respectively [1]. The emergence of hybrid composites has introduced novel fiber/particulate fillers, which could provide further tribological improvements [14, 15], yet at high raw material and production costs. The other shortcoming of such filled polymers is the weak interfacial interactions between the additives and the polymeric matrix, which result in inhomogeneous mechanical strength and consequently wear of the composite polymer.

The last category of fillers, which has not been extensively investigated, is micro-/nano-encapsulated additives. Encapsulation of the additives facilitates their embedment in a polymeric matrix, which would have been impossible otherwise. This area of research initiated by implementing ILs as core materials, which are room-temperature stable molten salts, encompassed in a polymeric shell to embed this lubricious liquid lubricant in a solid polymeric matrix. ILs enhance tribological properties of a base lubricant in the form of friction and wear reduction. Such enhancements on a metallic surface were obtained via generating a tribo-film on the sliding surfaces through adsorption. Microencapsulated 1-hexyl-3-methylimidazolium bis(trifluoromethyl sulphonyl) imide ([HMIM][NTf_2]) IL was integrated into the top layer of a PTFE lubricious coating at 5 wt% [6]. Tests conducted under dry sliding conditions on both unfilled and filled polymer composites demonstrated lower wear and COFs. The obtained experimental data revealed that the IL could provide a 12% COF reduction, and up to a 70% decrease in the wear rate for hollow microcapsule IL cores. Reference [7] investigated the effect of the embedment of wax lubricant capsules into an epoxy on the tribological performance of the composite, and a dramatic decrease of the friction and wear with the increasing wax content was reported. Microencapsulated phase change materials (MPCMs) are another category of lubricious fillers that can be integrated in the matrix through an encapsulation process and has yet to be explored.

The objective of the present study is to introduce and preliminarily investigate the potential for MPCMs as effective and efficient additives for polymeric coatings in realistic operational conditions in dry contacts. We have demonstrated the enhancement in the tribological performance of an advanced bearing polymer, namely ATSP via implementing MPCM, and showed its superior performance compared to PTFE as a state-of-the-art industry-leading additive for solid lubrication.

2 Materials and methods

2.1 Materials

Shoe pins in the shape of half ellipsoids were made from SAE 52100 bearing steel. The exact chemical compositions of 52100 steel, as provided by the manufacturer, are shown in Table S1 in the Electronic Supplementary Material (ESM)). The flat side with a diameter (d_P) of 10.9 mm and root-mean-square (RMS) roughness of 0.1 μm was in contact with the disk. Disks with a diameter (d_D) of 50.8 mm and thickness of 5 mm were machined out of O1 tool steel, as shown in Fig. 1. They were then blasted with silicon carbide grit, with an average size of 250–300 μm, to enhance the bonding between the coating and substrate. The RMS roughness of the sandblasted substrates was 5.46±0.08 μm. The disks were coated with 0, 10, and 20 wt% MPCM filler in an ATSP polymeric matrix, resulting in Coatings A0, A2, and A3, respectively. Coating A1 was used to compare the effect of MPCM filler on reducing the friction and wear and the commonly used PTFE filler, as shown in Table 1. A composition of 5 wt% PTFE filler was chosen as this is the optimum concentration in ATSP+PTFE blends that yields the best tribological performance, as suggested by the vendor. Also, an increased PTFE concentration brings complexity to the deposition process with negligible favorable effects on the tribological performance.

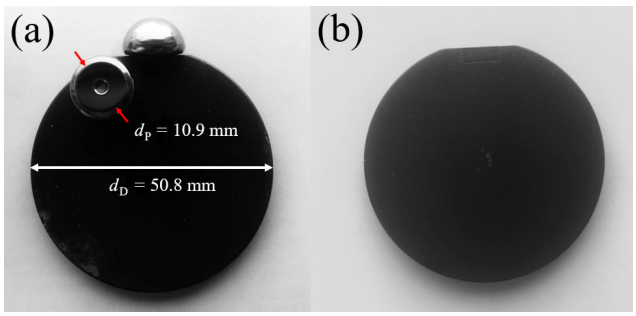

Fig. 1 (a) Neat ATSP-coated disk and shoe pin and (b) disk with a coat of ATSP+20% MPCM mixture.

Table 1 Compositions of the coatings under examination (unit: wt%).

Label	ATSP powder	MPCM powder	PTFE powder
Coating A0	100	0	0
Coating A1	95	0	5
Coating A2	90	10	0
Coating A3	80	20	0

ATSP is a thermoset polymer with a glass transition temperature of 238 °C, an onset degradation temperature of approximately 400 °C [3], and a curing temperature of 260 °C in the coating format [16]. ATSP has proven tribological performance in a wide range of operational conditions [12, 13, 16–18], and therefore it served as the polymeric matrix in the present study. The ATSP powder (NOWE C100) was purchased from ATSP Innovations Inc., and some of the mechanical properties provided by the vendor of neat ATSP (Coating A0) are presented in Table 2. The MPCM along with the corresponding PCM was purchased from Microtek Laboratories Inc. The used MPCM was Nextek 43D (melting point: 43 °C), which is a dry powder (> 97% solids) with an average particle size of 15–30 μm. The PCM was paraffin wax, and it was the same material as the core material of MPCM. Figure S1 in the ESM shows the scanning electron microscopy (SEM) images of the MPCM capsules dispersed on a double-face carbon tape, which they varied slightly in diameter. Figure S1(b) in the ESM shows a high-magnification SEM image of a capsule with a diameter of ca. 20 μm. The PTFE powder (Zonyl MP1300) with an average particle size of 12 μm was purchased from Chemours Company.

Table 2 Mechanical properties of Coating A0 provided by ATSP Innovations Inc.

Tensile strength (MPa)	Compressive strength (MPa)	Hardness (MPa)	Elastic modulus (GPa)
95	303.8	200.0	4.2

2.2 Physicochemical characterization of tested MPCM

Several characterization techniques were implemented to measure the physical and chemical properties of the microcapsules. The Fourier-transform infrared spectroscopy (FTIR) was used to detect the functional groups present in the microcapsule. The FTIR spectra were recorded on an infrared spectrometer (IR Prestige-21, Shimadzu) equipped with a diamond attenuated total reflection (ATR) lens.

To analyze the thermal stability and phase transition temperatures, the differential scanning calorimetry (DSC) analysis was conducted using a differential scanning calorimeter (DSC3/700/1190, Mettler Toledo). Three heating and cooling (10 °C/min) cycles were measured under an inert nitrogen atmosphere, where the heating cycle occurs first. The temperature range recorded was 0–200 °C. To obtain the degradation onset temperature (T_d) of the bulk PCM and MPCM, the thermogravimetric analysis (TGA) was implemented. The TGA was performed under an argon atmosphere using a thermogravimetric analyzer (TGA2/1100/464, Mettler Toledo) with a heating rate of 10 °C/min. The data were analyzed using STAR^e software (version 15.00a, Mettler Toledo).

A scanning electron microscope (JSM-IT200LA, JEOL) was utilized to obtain the morphologies of the coatings as well as the shapes and sizes of the microcapsules following tribological experiments. The composite coatings were sputtered with 5 nm of platinum and palladium to enhance the electrical conductivity of the samples. The same instrument was utilized to obtain the energy-dispersive X-ray spectroscopy (EDS) images.

The surface topographies of the coatings were obtained using a stylus profilometer (Dektak XD, Bruker). A 2 μm tip was used to obtain 150 parallel two-dimensional (2D) profiles with a scan length of 17 mm and an acquisition rate of 1 data point/μm. The profiles were acquired over a 3 mm width, resulting in a total scan area of 17 mm × 3 mm for each coating. The profiles were obtained on predefined locations on the untested and tested coatings. The roughness data of the untested coatings were measured, and the change in the surface topography was used to estimate the volumetric wear. The confocal imaging was conducted with an integrated three-dimensional (3D) optical profilometer (Lambda), and Gwyddion processing software was used to measure the thickness of each coating.

Note that the precise chemical compositions of the melamine shell and paraffin core of the MPCM used in the present study (Nextek 43D, Microtek Laboratories Inc.) are in proprietary possession of the manufacturing company. Nonetheless, the analyses herein provided critical and useful information about the physicochemical properties of the microcapsules and produced composite coatings.

2.3 Coating preparation

All coatings were prepared in the laboratory using the electrostatic spray coating technique. The ATSP powder and associated additive powders were mechanically mixed following the recipes, as given in Table 1. Using an electrostatic spray applicator, the mixture was deposited onto the metallic disk substrate. Five passes of spraying were applied to reach the desired coating thickness. The coatings were all cured at 260 °C for 30 min in a laboratory furnace and allowed to cool under ambient conditions afterwards. The thicknesses of the coatings were measured via the confocal microscopy (DSX500, Olympus), as shown in Fig. S2 in the ESM. Before the deposition process, a small piece of tape (Kapton, DuPont) was placed at the edge of the disk, and was removed after spraying each coating, leaving a small trace of the uncoated substrate. Note that material piled-up was formed right at the edge of the step (the red areas) due to coating accumulation between the coated surface and the tape, and therefore the thickness measurements were taken from places, where the coating was uniform. The thicknesses of the coatings ranged from ca. 25 to 55 μm and the exact values are given in Figs. S2(a)–S2(d) in the ESM. Figure 1(a) depicts a neat ATSP-coated disk and uncoated metal shoe pins. Figure 1(b) shows a disc with a coating of ATSP+ 20 wt% MPCM mixture. The presence of MPCM contributed to the grayish finish in color in contrast to the dark color of the neat ATSP coating.

2.4 Tribological tests

The experiments presented in this study were

conducted by a commercial tribometer (MFT-5000, Rtec). A flat pin-on-disk configuration was implemented to simulate the interfacial contact under industrial applications. All pins and disks were cleaned using isopropanol and dried under ambient conditions prior to testing. A constant normal load of 112 N was applied on the pin, which is equivalent to a nominal contact pressure of 1 MPa (calculated based on flat area of contact excluding the central hole). The disk was rotated at 637 r/min, and the center of the pin was 15 mm off the center of the disk that resulted in a sliding linear velocity of 1 m/s. Unidirectional rotating tests were conducted at room temperature and ambient pressure, where the relative humidity was 50%±3%. No external lubricant was used for any of the tests. The near contact temperature (NCT) was measured by a thermocouple that was positioned on the circumference of the pin approximately 1.5±0.5 mm above the contact interface. The *in-situ* friction force was measured, and instantaneous COF was recorded at 1,000 Hz of data acquisition rate. The obtained data were used to illustrate the changes of COF with time as well as calculating the average COF for each coating. A minimum of the two samples of each coating, as shown in Table 1, were produced and tested to assure the repeatability of the process.

3 Results and discussion

3.1 Differential scanning calorimetry (DSC)

The DSC experiments were conducted on both bulk PCM and MPCM for three cooling and heating cycles. The results obtained for the third cycle are illustrated in Fig. 2. It can be observed that the endothermic peak (i.e., melting temperature) of the bulk PCM is ca. 46 °C, which is approximately the same for the encapsulated MPCM (45 °C). This observation indicates that the effect of the encapsulating material on the melting temperature of the PCM is negligible. However, during the cooling cycle, the exothermic peak (i.e., crystallization temperature (T_c)) for the bulk PCM exhibited two well-defined separate peaks at the T_c = 33 and 38 °C, whereas the MPCM exhibited a single broader peak with two maxima occurring across a narrower temperature range at T_c = 29–32 °C. The presence of the two well-defined peaks for PCM could be attributed to the presence of different crystal forms and different dimensions of crystalline domains, or due to the mixed nature of the PCM used. In the case of MPCM, these peaks were merged forming minor humps. Most importantly to the present study is the observation of the effect of microscopic confinement, leading to changes in the crystallization behavior of MPCM versus that of PCM, yet with confirmation of the melting temperatures remaining comparable, which is the activation point, wherein the PCM undergoes a phase change and could potentially lubricate the interface.

3.2 Fourier-transform infrared spectroscopy (FTIR)

Figure 3 shows the FTIR spectra for both bulk PCM and MPCM. The purpose of the analysis was to obtain the information regarding the chemical composition in terms of functional groups presented in the shell and/or core constituent materials.

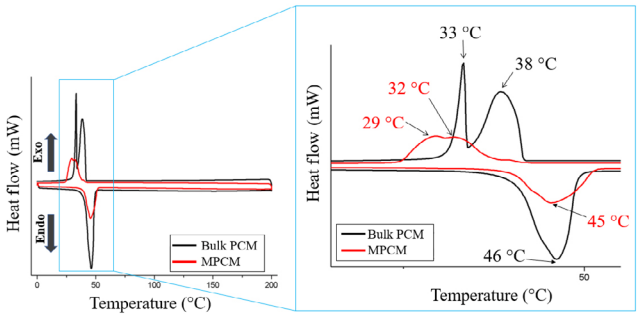

Fig. 2 DSC curves obtained in the third heating–cooling cycle on bulk PCM and MPCM.

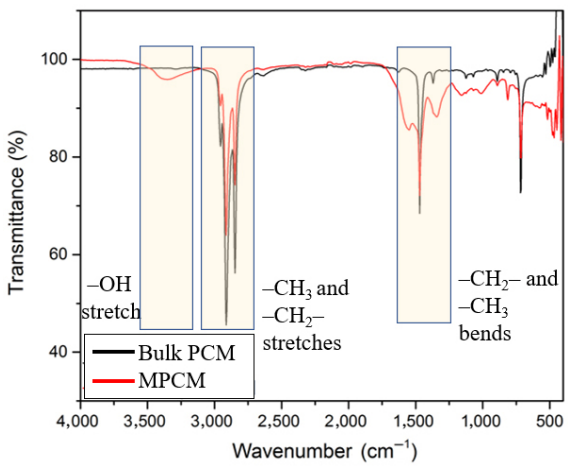

Fig. 3 FTIR spectra obtained for bulk PCM and MPCM.

Both spectra explicitly show strong peaks related to aliphatic methylene (–CH_2–) and methyl (–CH_3) bends and stretches (ca. 1,450 and 2,800–2,900 cm^{-1}, respectively). Peaks in these specific regions can indicate the presence of unsaturated alkyl chains commonly found in paraffins, waxes, and oils.

3.3 Thermogravimetric analysis (TGA)

The thermal stability of the MPCM is a key factor in the successful embedment of PCM in the form of microcapsules within the polymer matrix. The direct effective embedment of PCMs, such as paraffins in a polymer matrix, with a curing temperature higher than the evaporation/flash temperature of the PCM is impossible. Hence, the role of the encapsulating shell is to provide thermal and physical protection to the PCM to survive the curing process of the polymer matrix. More precisely, the thermal integrity of the encapsulation of the PCM allows for the integration of the PCM into the polymer matrix. The TGA results obtained for both bulk PCM and MPCM are shown in Fig. 4.

The T_d (i.e., 0.1% mass loss) of the bulk PCM is 81 °C, while encapsulation increases the onset temperature for the MPCM up to T_d = 156 °C. At the curing temperature of the ATSP coating, that is 260 °C, the vast majority of the bulk PCM mass had been lost; however, the MPCM had > 95% mass remaining at 260 °C. This result gives insight to the survival of the microcapsules during the curing process. Additional information that can be extracted from the TGA data is the amount of remaining mass of the MPCM at the ultimate degradation temperature of the bulk PCM. Approximately 18% of the initial mass of the MPCM remains at the complete degradation temperature of the PCM (T_f = 465 °C), which can be attributed to the shell mass. Thus, the core to shell mass ratio is about 4.6.

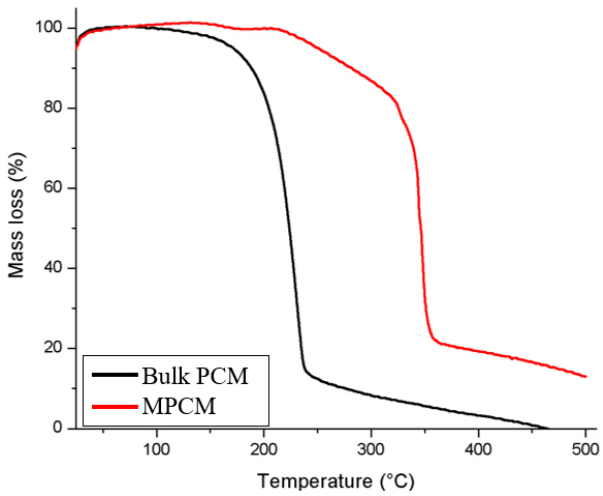

Fig. 4 TGA results obtained for bulk PCM and MPCM.

3.4 Surface topography

The surface roughness measurements of the coatings are obtained from the topographical images (Fig. 5) and are listed in Table 3. Figure 5 depicts the 3D topographical images of the as-deposited coatings. The color legend indicates the highest and lowest heights on each coating. All composites exhibit higher roughness compared to the neat coating (Coating A0), regardless of the blending ratio. Coatings A2 and A3 exhibit similar roughness, despite different MPCM contents. Both have increased surface roughness by almost 70%, compared to Coating A0. Knowing that the average size of the microcapsules is comparable to the coating thickness, such trend is expected as they create artificial peaks in the coating topography.

Additionally, the PTFE composite (Coating A1) shows a slightly more uniform topography compared to the MPCM composites (Coatings A2 and A3), which can be attributed to the smaller particle size and potentially better chemical compatibility/miscibility between the matrix and additive. The pin countersurfaces featured a substantially smoother surface with an RMS roughness of 0.1 μm.

3.5 Tribological experiments and near contact temperature (NCT)

The *in-situ* COF vs. sliding time (*t*) for each coating is depicted in Fig. 6. The interfacial interactions of the 53100 steel pin against Coating A0 yielded severe fluctuations in the *in-situ* COF, whose amplitude gradually increased with *t*. Blending PTFE with ATSP (i.e., Coating A1) clearly altered the contact dynamics of the tribo-pair, demonstrated as a significant reduction in both the fluctuations of the COF as well as the instantaneous COF values. Despite the reduction in the *in-situ* COF, the moving average was increased as the test progressed. PTFE is one of the most commonly used friction reducing solid additives and is widely

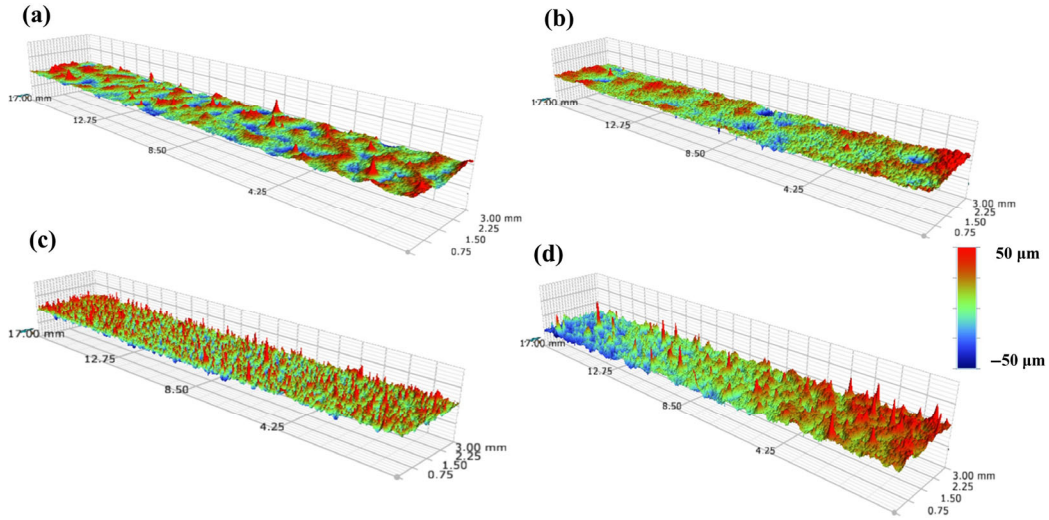

Fig. 5 3D topographical images (17 mm × 3 mm) obtained on untested Coatings (a) A0, (b) A1, (c) A2, and (d) A3.

Table 3 Arithmetic roughness (R_a) and RMS roughness of the as-deposited Coatings A0–A3.

Label	R_a (µm)	RMS roughness (µm)
Coating A0	1.71	2.22
Coating A1	2.25	2.92
Coating A2	2.87	3.76
Coating A3	2.87	3.80

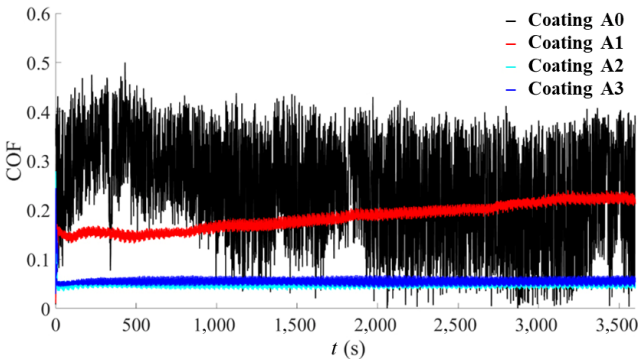

Fig. 6 Typical *in-situ* COF vs. *t* for the coatings produced for the present study.

utilized in polymer composites. Coatings A2 and A3 exhibited the most dramatic changes in the frictional behavior with the presence of MPCM; there was a decrease in the COF, and undesired fluctuations in the *in-situ* COF were substantially suppressed. Moreover, the stability of the COF is striking and resembles a frictional behavior of a fully hydrodynamic contact rather than a dry contact in boundary lubrication.

The average value±one standard deviation of the *in-situ* COF values of identical experiments are shown in Fig. 7. The average COF of Coating A0 was 0.285, which was reduced by 35% in Coating A1 that was leveraged by the presence of PTFE as the additive lubricant. The friction reduction obtained by the MPCM-filled ATSP composites were 82% and 80%, represented by Coatings A2 and A3, respectively, compared to that of the neat ATSP coating. Therefore, the maximum friction reduction efficacy obtainable by this MPCM was already achieved by the 10 wt% blending ratio, and doubling the MPCM concentration to 20 wt% did not further reduce the COF. The COF oscillations were also reduced by 74%, 95%, and 95% for Coatings A1, A2, and A3, respectively, when compared to COF oscillations measured for Coating A0.

Figure 8 shows the average NCTs measured on the

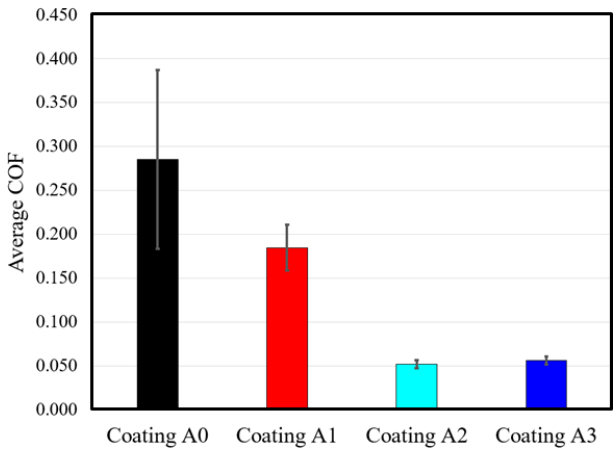

Fig. 7 Average COF values obtained for the coatings produced in the present study.

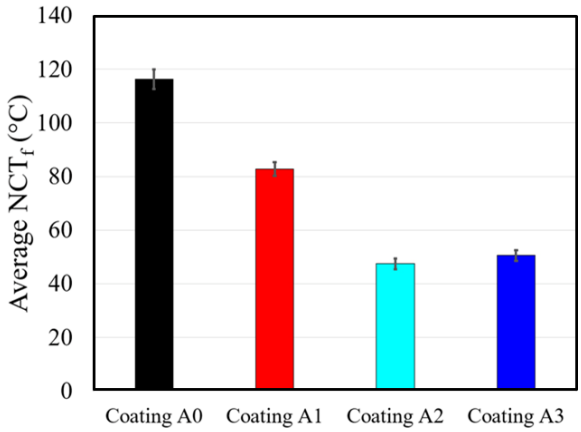

Fig. 8 Average NCTs obtained from the pins used against Coatings A0–A3.

pins for each tribo-pair. The error bars indicate ±1 standard deviation. Lower NCT promises lower thermal softening of the polymer and hence the reduction of hardness degradation of polymers. Hardness is a key parameter in abrasive wear, and therefore Coatings A2 and A3 are expected to exhibit better wear performance.

The 3D topographical images of the wear track of Coatings A0–A3 after the tests were obtained and depicted (Fig. 9), which is the slice of the coatings that straddle the wear track. The wear was uniform on the coatings; thus, this slice is a good representative of the whole wear track. The obtained topographies vividly display the role of the additives in reducing the wear intensity of the neat polymer. Due to excellent wear resistance of MPCM-filled ATSP coatings, it was not possible to obtain a reliable wear coefficient for the composite coatings, that is, the interface only exhibits mild asperity burnishing and "zero" wear. However, for the neat ATSP and PTFE-filled ATSP (Coatings A0 and A1), the volumetric wear rate [19] was calculated as $8\times10^{-5}\pm2\times10^{-7}$ and $3\times10^{-6}\pm3\times10^{-7}$ mm^3/(N·m), respectively. PTFE provided excellent wear resistance to neat ATSP coating; however, the wear protection that the buffer layer of partially liquid paraffin in the MPCM-filled coatings outperformed that of the PTFE filler.

3.6 Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS)

The PTFE friction reduction mechanism in composite polymers has been extensively studied. PTFE generates a thin tribo-film on the counter metallic surface under certain operating conditions, which reduces adhesion and provides low shear at the sliding interface. Subsequently, provided that a uniform and stable film prevails at the interacting surfaces, the frictional force and COF reduce. However, such enhancements are limited by operating conditions and can diminish as the test continues. The lubrication mechanism provided by Coating A1 is through film transfer, which is rich in fluorine and is documented in Refs. [2, 13, 16].

As shown in Fig. 10, the microcapsules were distributed in the coatings and were also exposed on the surface. The SEM images were obtained on the top surface of the wear track of Coating A2. Intact microcapsules were positioned on lower topographies,

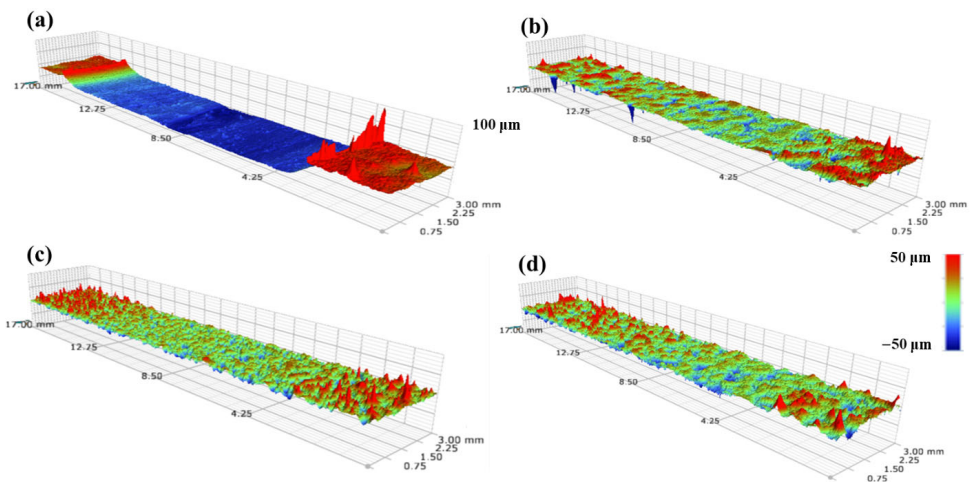

Fig. 9 3D topographical wear scans of Coatings (a) A0, (b) A1, (c) A2, and (d) A3 straddling the wear tracks obtained after each test.

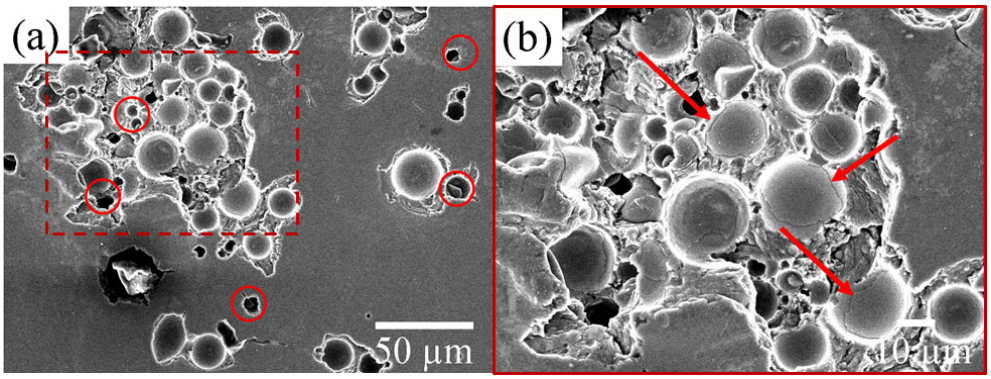

Fig. 10 (a) SEM image of intact and broken (shown with circles) microcapsules obtained on the wear track of Coating A2 and (b) magnified SEM image showing the cracks (shown with arrows) on the MPCM shell.

while the broken microcapsules (indicated by the circles) had been in contact with the sliding countersurface, resulting in breakage and subsequent releasing of the PCM material, yielding a low COF. The higher magnification image (Fig. 10(b)) clearly exhibits the crack generated on the shell of several microcapsules (shown with the arrows), which could potentially break open and release the PCM, and therefore the lubrication mechanism of the MPCM-filled coatings is uncoupled.

It is hypothesized that the shell of the microcapsules on the interface breaks under contact pressure, resulting in exposure of the lubricious paraffin (i.e., PCM core). Paraffin absorbs the frictional thermal energy and undergoes a phase transition from solid to liquid phase. Liquid paraffin is shown to be an effective lubricant especially for polymeric interfaces [20, 21]. The melted paraffin generates a thin lubricious film that hinders the solid–solid contact and transforms the contact dynamic to a mixed lubrication regime, which otherwise would operate in a dry boundary regime. Hence the outstanding 82% and 72% COF reduction are obtained for Coating A2 compared to those of neat ATSP and ATSP/PTFE composites, respectively. Another advantage that the tested MPCM provides as an additive is the absorption of the frictional heat generation, thus preventing the degrading of the mechanical properties of the polymer matrix, as a result of the increasing temperature [22]. It is well-known that most polymers have weak thermal conductivity [23] and subsequently suffer from accumulation and localization of frictional heat generated at the sliding interface. MPCMs distributed in the polymer matrix can absorb a fraction of the frictional heat or the environmental heat to undergo phase transition from the initial solid state to a liquid state. More importantly, the markedly lower friction due to enhanced lubrication results in lower frictional heat generation, which is directly correlated to the COF [24].

To investigate the wear mechanisms further, the SEM images of the wear tracks of Coatings A0, A1, and A2 were obtained, as shown in Fig. 11. Coatings A2 and A3 yielded similar tribological behavior, and therefore only the images of Coating A2 were included. The obtained images show that the wear mechanism in neat ATSP is mostly abrasive and fatigue wear, as indicated by crack propagation across the surface (Figs. 11(a) and 11(d)). In case of ATSP/PTFE, localized fatigued zones, where subsurface cracks have reached the surface, are dominant. Further propagation of such cracks can readily generate wear debris, as shown in Figs. 11(b) and 11(e). These observations confirm the findings of Refs. [2, 3, 25] on the wear mechanisms of neat ATSP and ATSP/PTFE composite. In the case of the MPCM-filled composites, the presence of a protective paraffin layer minimized the direct contact of solid asperities, and abrasive wear was prevented (Figs. 11(c) and 11(f)). Weakened areas of the coating, as a result of consumption of the core paraffin, could potentially trigger abrasive wear; however, within the scope of the present study, no such wear was observed.

The EDS analyses on the sliding surface of the 52100 pin countersurfaces provided critical information to support the described lubrication mechanisms. The

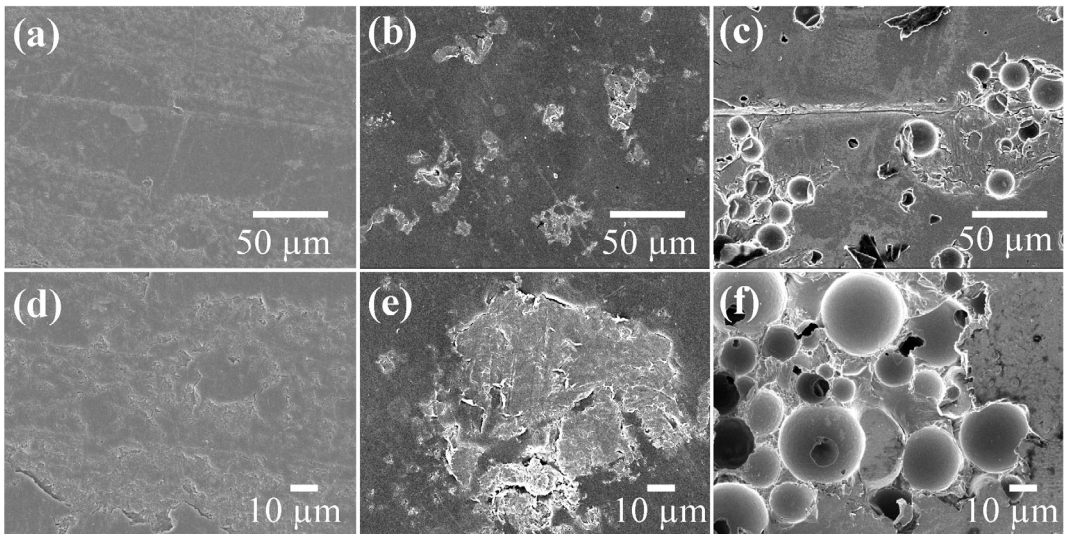

Fig. 11 SEM images of Coatings (a) A0, (b) A1, and (c) A2 obtained on the wear track and respective higher magnification images showing the surface damage of Coatings (d) A0, (e) A1, and (f) A2.

pin that was tested against neat ATSP was covered by a thick layer of wear debris, which deteriorated the sliding condition by generating excessive heat and adhesion. The effect of the gradual accumulation of compacted wear debris was best demonstrated in the *in-situ* COF behavior of A0 Coating vs. *t*, as depicted in Fig. 6. The EDS mappings on a streak of such layer are shown in Fig. 12.

Pins tested against Coatings A1–A3 show no sign of abrasive wear or material compacted on the surface. The EDS analysis of the surface showed a 3.5 at% of fluorine on the pin tested against Coating A1, as shown in Table S2 in the ESM. The presence of fluorine is attributed to the material transfer from the PTFE soft phase of Coating A1. Nevertheless, the amount of material transfer and thereby the wear from the coated surface were not adequate to form compacted stripes or a uniform film on the countersurface. Finally, the pins tested against Coatings A2 and A3 showed an increase in the carbon atomic percentage of approximately 10% compared to a clean, untested 52100 pin sample, for which the EDS results are also provided. Note that only the main elements of 52100 steel were detected from the EDS. Considering the visually unaffected surface of these pins and their coated countersurfaces (Coatings A2 and A3), the origin of such increase could be attributed to the paraffin film that was transferred to the pin surface during sliding.

4 Conclusions

We have studied the role of MPCM (paraffin core) as a novel additive for ATSP-based coatings. The MPCM was characterized physically and chemically to obtain the information about its size distribution, chemical composition, and thermal stability. The MPCM was mixed at 10% and 20% mass ratios

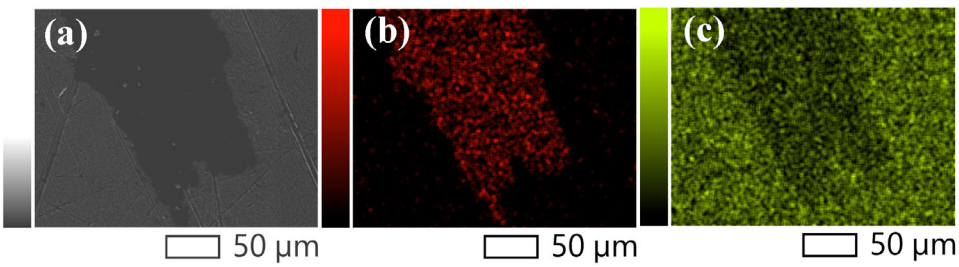

Fig. 12 (a) SEM image and EDS mappings of (b) carbon and (c) iron on a streak of compacted layer on top of the pin tested against Coating A0.

with ATSP and coated on steel substrates. Coated composites were tested against steel pins under industrial-relevant conditions. To provide a baseline for evaluating the role of MPCM on the tribological performance of the composite, neat ATSP was also coated on steel substrate and subjected to identical tribological testing. Additionally, to demonstrate the superior performance of the MPCM compared to that of the current state-of-the-art industrial additives, PTFE was blended with ATSP at an optimum ratio and was tested under the same conditions. The friction and wear performance of the produced coatings were analyzed and compared, yielding the following conclusions:

1) The COF of the MPCM-filled ATSP (Coating A2) was lower than those of the neat ATSP and PTFE-filled composite by 82% and 72%, respectively.

2) The wear resistance of MPCM-filled coatings within the short duration of the present study was higher than that of ATSP/PTFE coating.

3) The origin of such dramatic enhancement in the tribological performance of the MPCM-filled coatings is attributed to the paraffinic film produced on the metallic countersurfaces, as a result of breakage of the shell and release of the core material of the MPCM.

Acknowledgements

Fundings of the present study were provided by Texas A&M University X-Grant and by Strategic Transformative Research Program (STRP) Grant, College of Science. The authors also acknowledge the use of the Texas A&M Materials Characterization Core Facility (RRID: SCR_022202). We gratefully acknowledge the financial support from the Robert A. WELCH Foundation through the W.T. Doherty-WELCH Chair in Chemistry (A-0001). Mariela VAZQUEZ appreciates the support by the National Science Foundation Graduate Research Fellowship Program (Grant No. M1703014). Insightful discussions with Ms. Yidan SHEN are also greatly appreciated.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40544-022-0733-3.

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