

Ultralow friction polymer composites incorporated with mono-dispersed oil microcapsules

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Abstract: Ultralow friction polymer composites were prepared by adding oil-loaded microcapsules into epoxy (EP) resin. Mono-dispersed polystyrene (PS)/poly alpha olefin (PAO) microcapsules with a diameter of $\sim 2 \mu\text{m}$ and a shell thickness of $\sim 30 \text{ nm}$ were prepared by solvent evaporation method in an oil-in-water emulsion. The lubrication behaviors of the EP resin composites with oil-loaded microcapsules have been investigated under different loads and sliding speeds. As compared with the pure EP resin, the friction coefficient of the composite could be reduced to 4% (from 0.71 to 0.028) and the wear rate could be decreased up to two orders of magnitude. It was demonstrated that the released PAO oil from the microcapsules during the friction process produced a boundary lubricating film, which could prevent the direct contact of two rubbing surfaces, and thus leading to an extremely low friction coefficient and wear rate. Moreover, the composites with microcapsules could achieve comparable lubrication properties to the case under the external lubrication condition, while the former case could effectively minimize the lubricant leakage and improve the lubrication efficiency.

Keywords: polymer composite; microcapsules; solvent evaporation; ultralow friction; boundary lubrication

1 Introduction

In recent years, microcontainers, e.g., hollow microspheres, microcapsules, porous microspheres, and metal-organic frameworks (MOFs), with the ability to carry versatile core materials have attracted great interest for their variety of applications [1–6]. Representatively, the microcontainers encapsulated liquids can be employed to develop a new family of self-lubricating materials, because traditional external lubrication that lubricants are directly added into the interface of two rubbing surfaces could have some limitations under certain conditions. As compared with external lubrication, the release of liquid lubricants from microcontainers to the interface occurs when triggered by the friction processes (load or temperature), which could prevent lubricant leakage, and thus

increasing the durability of the effective lubrication process [7–10].

Recently, epoxy (EP) resin composites incorporated with MOFs microcontainers have been prepared and the improved lubricating performance of the composites was associated with the lubricating film produced by the chemical reaction between the released oleylamine from the capsules and the matrix [5]. Another type of wear-resistant material was prepared by adding microcapsules (hexamethylene diisocyanate (HDI) as the core and acacia gum as the shell material) into the epoxy resin matrix and the characterization results suggested the HDI reacted with the water vapor in the environment to form polyurea, effectively improving the wear resistance of the material [11]. The formation of cavities after the rupture of microcapsules could trap wear debris, which could consequently decrease

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the friction coefficient and the wear rate of the composite [12–14]. Microcapsules containing liquid lubricants were also prepared as reservoirs in thermally sprayed coatings with lubrication performances. The coatings containing thick wall microcapsules showed a better thermal input resistance, and nevertheless the microcapsules with the thick wall contained less liquid lubricant, resulting in less obvious enhancement of the lubricating performance of the coating [15]. In addition, a number of studies demonstrated that the increased content of microcapsules or the incorporation of larger microcapsules would optimize the lubrication behaviors of the microcapsule-containing composites due to the larger amount of lubricant released from the ruptured microcapsules during the friction process [16–20]. Nevertheless, it was suggested that the incorporation of more or larger microcapsules would degrade the mechanical properties [21–25]. Furthermore, most of the microcapsules with liquid lubricants inside reported in available literatures were relatively large (usually tens to hundreds of μm in diameter) or poorly dispersed [20, 26–28], giving rise to a negative effect on the comprehensive properties of the composites.

The microstructures of microcapsules depend largely on the preparation process technology, and the solvent evaporation method was considered as one of the commonly used processes for synthesizing microspheres in oil-in-water (O/W) systems [29, 30]. Parameters including the impeller speed, the surfactant concentration, and the viscosity of the organic phase, etc., strongly influence the size of the microspheres [31–33]. The average size of microcapsules generally decreases with the increasing stirring speed, owing to the fact that the stronger shear force and the increased turbulence facilitate the formation of smaller emulsion droplets [33]. The reduction in the viscosity of the emulsion could also improve the mixing efficiency, and thus enabling the formation of very small diameter ($\sim 1\mu\text{m}$) droplets [32]. In addition, the high surfactant concentration increases the diffusion rate of the stabilizer molecules at the droplet-aqueous phase interface in the emulsion, giving rise to a large number of stabilizer molecules adsorbed on the droplet surfaces, improving the formation of smaller emulsion droplets by preventing droplets from coalescence [31, 34].

In the present study, an optimized solvent evaporation technique was adopted to prepare small ($\sim 2\mu\text{m}$ in diameter) and mono-dispersed microcapsules. The synthesized microcapsules were incorporated into the epoxy (EP) resin matrices and the lubrication behaviors of the prepared composites were investigated systematically on the basis of macroscopic ball-on-disc friction tests. Moreover, the lubrication properties of the cases where lubricants were directly added into the interface between the composite surface and the counterface were tested as control experiments. Multiple techniques, e.g., scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetry (TG) were employed for characterizing the microstructures, as well as the thermal, the mechanical, and the lubrication properties of samples. To further extend the application of the strategy proposed in this work, a series of small and mono-dispersed microcapsules were also successfully synthesized with the same method, and more details are given in the Electronic Supplementary Material (ESM).

2 Experimental

2.1 Materials

Lubricant oil PAO6 was supplied by Guangzhou Qijie Chemical Technology Co., Ltd. (China). PS, dichloromethane (DCM, >99.5 wt.%), polyvinyl alcohol (PVA) (degree of polymerization = 1750 ± 50), and Arabia gum were purchased from Beijing Lanyi Chemical Reagents Co., Ltd. (China). The epoxy resin and the curing agent were obtained from the Struers International Trade Co., Ltd. (Shanghai, China). All materials were used as received without any further purification.

2.2 Synthesis of PS microcapsules containing PAO oil

PAO-loaded PS microcapsules were prepared by the solvent evaporation method and the schematic diagram was shown in Fig. 1. PAO (4 g) and PS (2 g) were mixed with 50 mL DCM with magnetic stirring for a homogeneous solution. Subsequently, the mixture solution was added to a mixed solution (200 mL) of

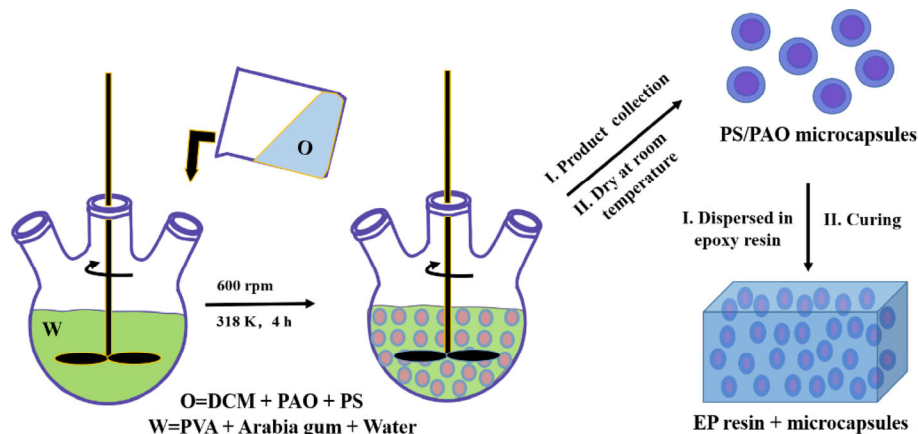


Fig. 1 Schematic diagram of synthesizing microcapsules and preparing epoxy-based composites.

0.1 wt.% Arabia gum and 0.5 wt.% PVA with mechanical stirring at 600 rpm. After reacting for 4 h at 318 K, the DCM evaporated completely and PS microcapsules containing the PAO oil were obtained. The synthesized microcapsules were collected after filtration, repeated rinse with deionized water, and finally being dried at room temperature for 24 h.

2.3 Preparation of epoxy-based composites

The synthesized microcapsules were incorporated into the epoxy matrices with different mass fraction for investigating the effect of the microcapsule concentration on the lubrication properties of the epoxy-based composites. As shown in Fig. 1, microcapsules of different mass fractions were added into 9 g EP liquid under stirring at room temperature for 20 min to form a good suspension. Then, 3 g curing agent was added into the above solution under stirring for 10 min and poured into a rubber mold after the removal of the bubbles in a vacuum drying oven. All the specimens were cured at room temperature for 24 h, producing a series of epoxy-based composites with microcapsules of different mass fractions (5 wt.%, 10 wt.%, 15 wt.%, and 25 wt.%).

2.4 Frictional tests of the epoxy-based composites

Frictional tests of pure EP resin and its composites with microcapsules were carried out with a universal microtribometer (UMT-3, CETR, USA) using the ball-on-disk mode. GCr45 bearing steel ball of $\Phi 4.68$ mm with a surface roughness of 5 nm (as provided by the supplier) was used as a counterface material. The ball

was thoroughly cleaned with alcohol before each test. As control experiments, the lubrication properties of the cases where lubricants were directly added into the interface between the composite surface and the ball surface were also analyzed under the same experimental conditions. The reciprocating friction stroke was 4 mm and tests were conducted at normal loads of 3, 6, and 12 N, and the average sliding speeds were 8, 16, and 32 mm/s.

2.5 Characterizations of the microcapsules and the epoxy-based composites

The thermal stability and the core content of the microcapsules containing PAO oil were evaluated using TG analysis from 298 to 873 K at a heating rate of 10 K/min under nitrogen atmosphere. The size distribution of microcapsules was determined by Zetasizer Nano ZSN nanoparticle size analyzer. The morphologies of the microcapsules and the wear tracks of the steel balls sliding against the pure EP resin and the composites with microcapsules were observed by SEM. The shell thickness of the microcapsule was measured by TEM. The mechanical properties (compressive strength and microhardness) of samples were tested by using a universal testing machine and a nanoindentation tester. The wear rate and the roughness of the worn composite were measured by three-dimensional white light interference surface topography device (ZYGO Nex View). X-ray photoelectron spectrometry (XPS) analyses were adopted to analyze the electronic states of elements on the transfer films from the composite surface to the steel ball surface.

3 Results and discussion

As shown in Fig. 2(a), monodispersed spherical PS/PAO microcapsules with the diameter of $\sim 2 \mu\text{m}$ were synthesized by the solvent evaporation method. Various factors such as the surfactant type and concentration, the stirring rate, and the volume of the dispersed phase could influence the synthesis process of microcapsules [30, 31]. A mechanical stirring of 600 rpm was efficient and enabled the formation of very small droplets ($\sim 1 \mu\text{m}$ in diameter) at a low emulsion viscosity owing to the large volume of the dispersed phase [32]. Nevertheless, the rapid precipitation of polymer shell could lead to the formation of large microcapsules [32]. When Arabia gum was used as the emulsifier, the hydrophilic polysaccharides on the molecule could form a viscous adsorption layer at the liquid-liquid interface [35]. On the one hand, the adsorbed layer can stabilize the formation of oil droplets in aqueous solutions, and thus minimizing the droplet coalescence. On the other hand, the viscous adsorption layer can reduce the deposition rate of nanoparticles on the surface of microcapsules, effectively avoiding the formation of larger microcapsules owing to too fast precipitation of shell particles. In addition, the synergistic adsorption of different emulsifier

molecules at the interface is more effective than that in a single surfactant system in reducing interfacial tension. It was deduced that the larger concentration of the dispersed phase, the co-emulsification of polyvinyl alcohol and Arabia gum mainly promote the formation of smaller monodisperse microcapsules in the present study. Monodispersed filler microparticles are beneficial to achieve good dispersion in composites and eventually to improve the homogeneity of the composites [36–38]. The magnified image of a microcapsule (Fig. 2(b)) suggested that the surface of the microcapsule was smooth and compact without obvious defects and holes, which could effectively improve the stability of the microcapsules. TEM characterizations were employed for obtaining the microstructural information of the microcapsules, and the shell thickness of the microcapsule was $\sim 30 \text{ nm}$, as shown in Fig. 2(c). The thermal stability of the microcapsules, the pure PAO oil, and the PS were analyzed, and the results are shown in Fig. 2(d). In the case of the microcapsules, two main weightless steps at 457 K and 663 K were observed from the TG profile, which were clearly assignable to the PAO oil and the PS shell decomposition, respectively. The calculated encapsulation capacity of the microcapsule was about 56 wt.%.

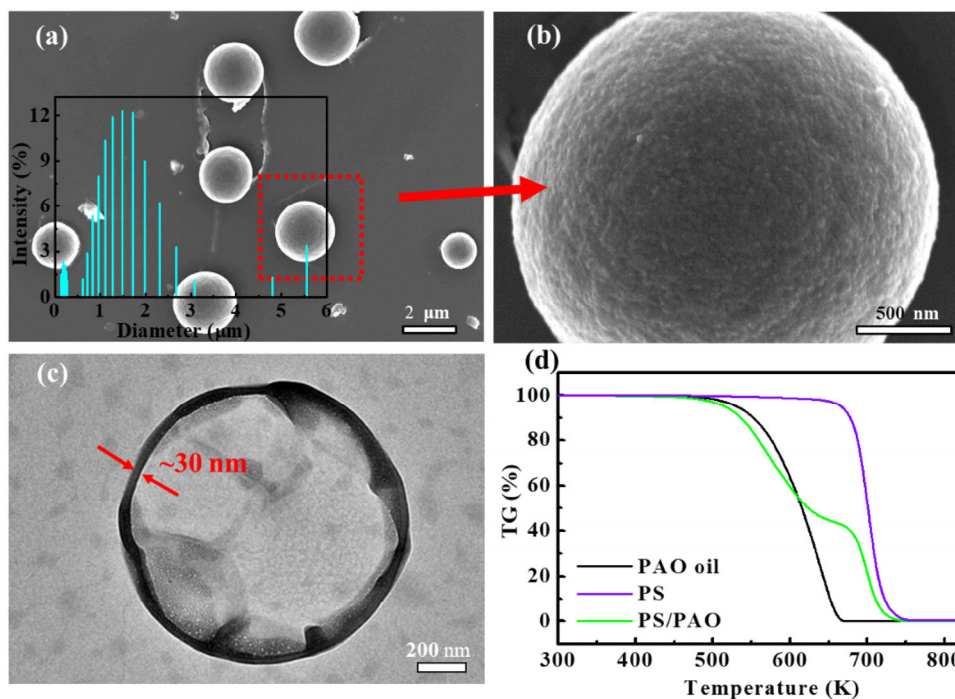


Fig. 2 (a) and (b) SEM images of size distributions, (c) TEM image of PS/PAO microcapsules, and (d) TG curves of the samples.

Figure 3 presents the compressive strengths and the microhardnesses of the pure EP resin and the composites with different microcapsule contents. The compressive strength and microhardness of the pure EP resin matrix were about 83.5 MPa and 18.7 HV 0.1, respectively. The increased content of microcapsules in the EP resin composites from 5 to 25 wt.% decreased the compressive strength from 72.1 to 41.1 MPa, and the microhardness from 17.6 to 8.2 HV 0.1, owing to the increased liquid lubricant in the composite [18, 22].

The lubrication properties of the EP resin and the composites with microcapsules were investigated at different sliding speeds under 3 N. Figure 4 presents the relationship between the friction coefficients of the composites and the microcapsule contents under different sliding speeds. As shown in Figs. 4(a) and 4(c), when the sliding speed was 8 mm/s, the friction coefficient of the pure epoxy resin was relatively low in the beginning, and then it increased to 0.57 gradually. After the incorporation of microcapsules, the lubrication performance of the composite was greatly improved and the friction coefficient drastically decreased from 0.57 to 0.10. As for the composite with 15 wt.% microcapsules, the friction coefficient was as low as 0.06. When the microcapsule content was further increased to 25 wt.%, the lubricating property of the microcapsules decreased slightly and the friction coefficient increased to 0.07. It is inferred that, the rupture of microcapsules in the friction process followed by the lubricant flowing out, resulted in the formation of a lubricant film at the interface [33, 34]. Nevertheless, excessive microcapsules might cause

agglomeration in the composite, and poor dispersion of microcapsules would inevitably lead to inefficient lubrication at the interface between two rubbing surfaces. For comparison, the lubrication properties of the PAO oil were carried out under the external lubrication condition where PAO oil was directly added into the interface. As shown in Figs. 4(a) and 4(c), the friction coefficient of the EP resin decreased to 0.07 after adding 2 μ L PAO oil into the interface, presenting an excellent lubrication performance. The lubrication properties of the composites with different microcapsule contents were further investigated by increasing the sliding speed. As shown in Figs. 4(b) and 4(c), the general variation trend of the microcapsule effect on the lubricating properties of composites at the sliding speed of 16 mm/s was consistent with that of 8 mm/s. The friction coefficients of the composites at 16 mm/s were lower than those at 8 mm/s, owing to the fact that the higher sliding speed was more conducive to the formation of a uniform and stable lubricant film at the friction interface. In summary, the above results indicated that the composites with microcapsules could achieve comparable lubrication properties to the case under the external lubrication condition, while the former case could effectively minimize the lubricant leakage and improve the lubrication efficiency.

The lubrication properties of the composite with 15 wt.% microcapsules were further investigated at different loads and sliding speeds. As shown in Fig. 5, the friction coefficient of the composite decreases gradually with the increase of the load and the sliding

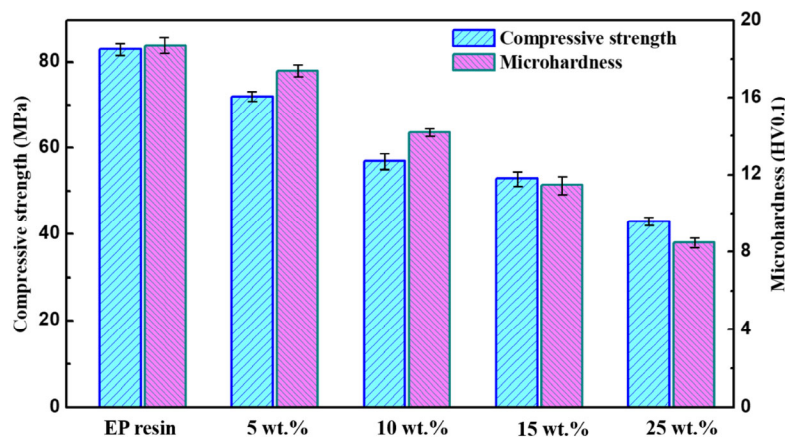


Fig. 3 Compressive strengths and microhardnesses of the pure EP resin and the composite with different microcapsule contents. The error bars indicate the uncertainty of the measured data.

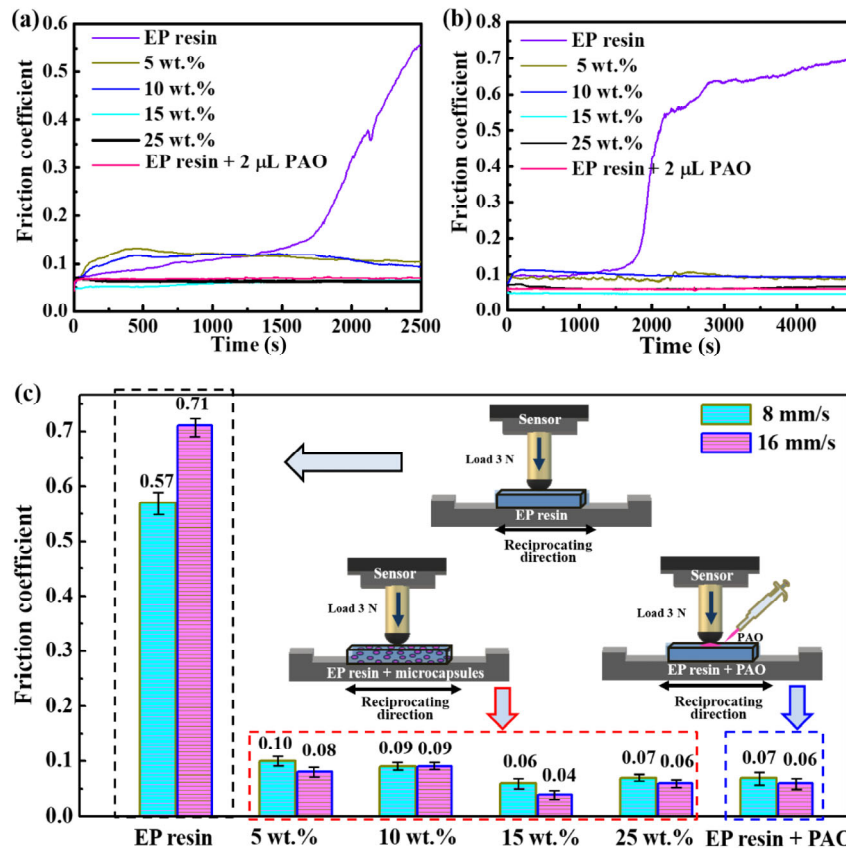


Fig. 4 Friction coefficients of the samples at different sliding speeds under 3 N. (a) and (c): 8 mm/s, (b) and (d): 16 mm/s. The error bars indicate the uncertainty of the measured data.

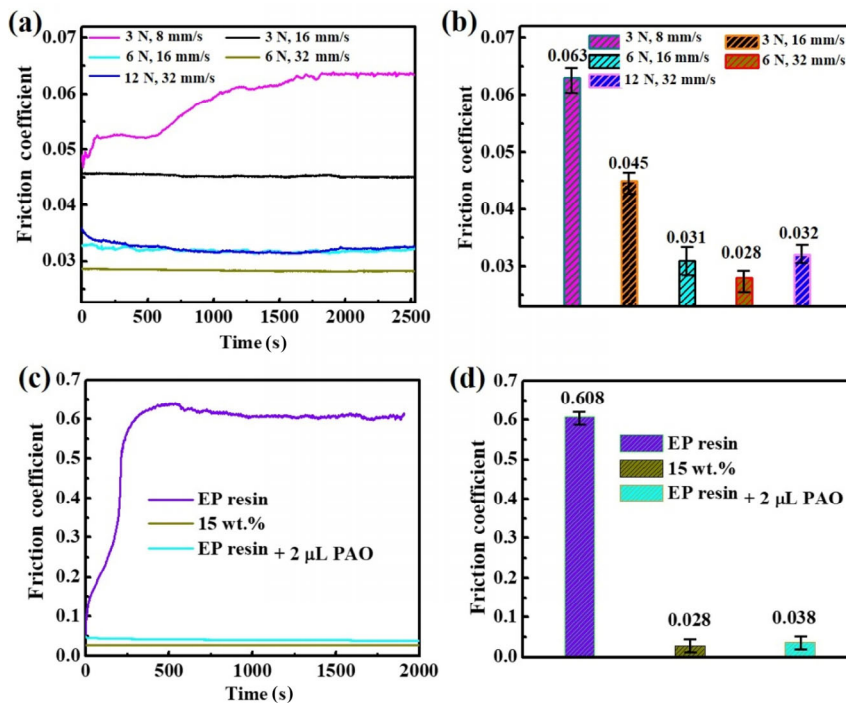


Fig. 5 (a) and (b): friction coefficients of the composites with 15 wt.% microcapsules at different loads and sliding speeds; (c) and (d): friction coefficients of the EP resin and EP resin + 2 μL PAO under 32 mm/s and 6 N. The error bars indicate the uncertainty of the measured data.

speed, and the lowest value reached 0.028 at 6 N and 32 mm/s. Presumably, microcapsules were more easily ruptured under large loads with more lubricating oil released. Basically, the lubrication state can be determined by the ratio (λ) of the film thickness (h) to the combined surface roughness (σ) ($\lambda > 3$: elastohydrodynamic lubrication; $\lambda < 1$: boundary lubrication; $1 < \lambda < 3$: mixed lubrication) [39–42]:

$$\lambda = \frac{h}{\sigma} = \frac{h}{\sqrt{\sigma_1^2 + \sigma_2^2}},$$

where σ_1 ($\sigma_1 = 123$ nm) and σ_2 ($\sigma_2 = 82$ nm) are the surface roughnesses of the wear spot on the ball surface and the wear scar area on the composite surface, respectively. The h can be theoretically calculated by Hamrock-Dowson formula [43]:

$$H = 3.63 \frac{U^{0.68} G^{0.49}}{W^{0.073}} (1 - e^{-0.68k}),$$

$$H = \frac{h}{R}, \quad U = \frac{\eta v}{E'R}, \quad G = \alpha E', \quad W = \frac{F}{E'R^2},$$

where R ($R = 0.0023$ m) is the ball radius, η ($\eta = 0.0242$ Pa·s) is the lubricant viscosity, v ($v = 0.032$ m/s) is the sliding speed, E' ($E' = 1.16 \times 10^9$ Pa) is the effective elastic modulus, F ($F = 6$ N) is the normal load, α ($\alpha = 1.58 \times 10^{-8}$ Pa $^{-1}$) is the viscosity-pressure coefficient, and k ($k = 1.03$) is the ellipticity parameter. According to the given experimental parameters, the calculated h and λ are 9.49 nm and 0.064, respectively, and thus it can be inferred that the lubrication state was boundary lubrication [40–43]. In this case, it can be reasonable to expect that the thicker lubrication film was established with the increasing sliding speed, giving rise to the reduction of the friction coefficient owing to the decrease of the direct contact ratio of the asperities at the friction interface. Nevertheless, the friction coefficient of the composite increased when the load was increased further to 12 N, and it is inferred that the larger load destroyed the lubricant film at the friction interface. In contrast, the lubrication properties of the EP resin and the PAO under the external lubrication condition (EP resin + 2 μ L PAO) were also tested under 32 mm/s and 6 N, as shown in Figs. 5(c) and 5(d). In contrast to the high friction coefficient (0.608) of the pure epoxy, both the composites with

microcapsules and the case under the external lubrication condition achieved ultra-low friction coefficients. It is basically consistent with the reported result in Ref. [44] that the PAO oil could exhibit the excellent lubrication performance (friction coefficient: 0.02) under the boundary lubrication condition. As for the composites with microcapsules, lubricating oil appeared at the friction interface in the form of many tiny droplets along with the rupture of microcapsules, which could effectively avoid the drag and energy dissipation caused by lubricating oil spreading in the sliding process under the external lubrication.

The 3D surface morphologies of the wear scars on the surfaces of the pure EP resin and the composites after friction tests and the corresponding wear rates are presented in Fig. 6. As can be seen in Fig. 6(a), the wear scar of the pure epoxy was wide and deep. After adding 5 wt.% microcapsules, the width and depth of the wear scar decreased significantly, and the wear rate (6.7×10^{-7} mm 3 ·(N·m) $^{-1}$) was much smaller, only 0.25% that of the pure EP resin (2.7×10^{-4} mm 3 ·(N·m) $^{-1}$). Nevertheless, as the microcapsule content increased, the wear rate of the composite increased gradually, owing to the reduced mechanical properties of the composite as well as the more vacancies left after the release of the lubricating oil from the microcapsules. To gain more insights into the friction mechanisms, the morphologies and the roughnesses of the worn surfaces were further analyzed. The worn surface of the pure EP resin was very rough, with an average roughness of 744 nm. After adding microcapsules into the matrix, the worn surface became smooth and the roughness was greatly reduced. As for the composite with 15 wt.% microcapsules, the roughness of the worn surface was the lowest (82 nm), being conducive to realizing a good lubricating state.

For polymer-on-metal sliding interfaces, there is a natural propensity for the polymer material to be transferred onto the metallic counterface [45, 46]. The presence of a uniform and thin transfer film is beneficial to the sliding process, because the film protects the relatively soft polymer bulk from the abrasive action of the hard asperities on the metallic surface [47, 48]. The SEM micrographs of the surfaces of the steel balls after sliding against the EP resin and the composites with microcapsules are presented in Fig. 7. The obvious scuffing on the ball surface against the pure EP resin

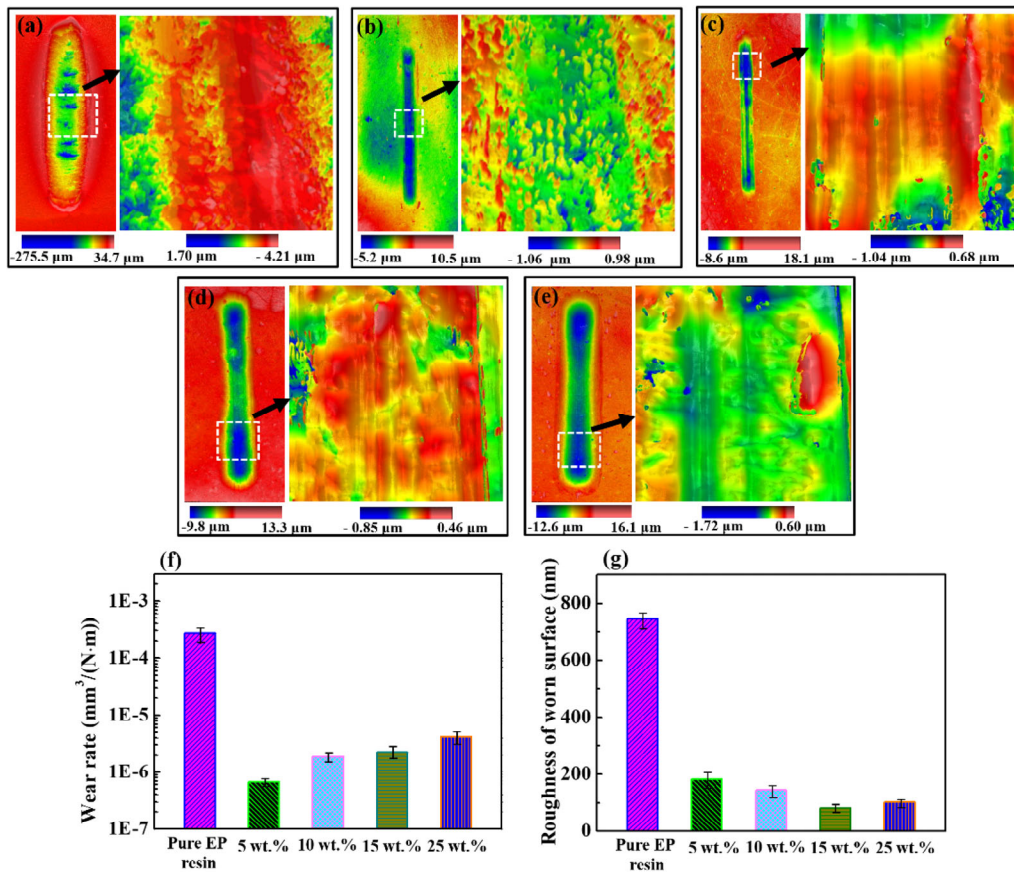


Fig. 6 Surface morphologies of the worn surfaces of the pure EP resin and the composites: (a) the pure EP resin, (b) the composite with 5 wt.% microcapsules, (c) the composite with 10 wt.% microcapsules, (d) the composite with 15 wt.% microcapsules, and (e) the composite with 25 wt.% microcapsules, (f) the wear rates of the samples, and (g) the worn surface roughnesses of the samples. The error bars indicate the uncertainty of the measured data.

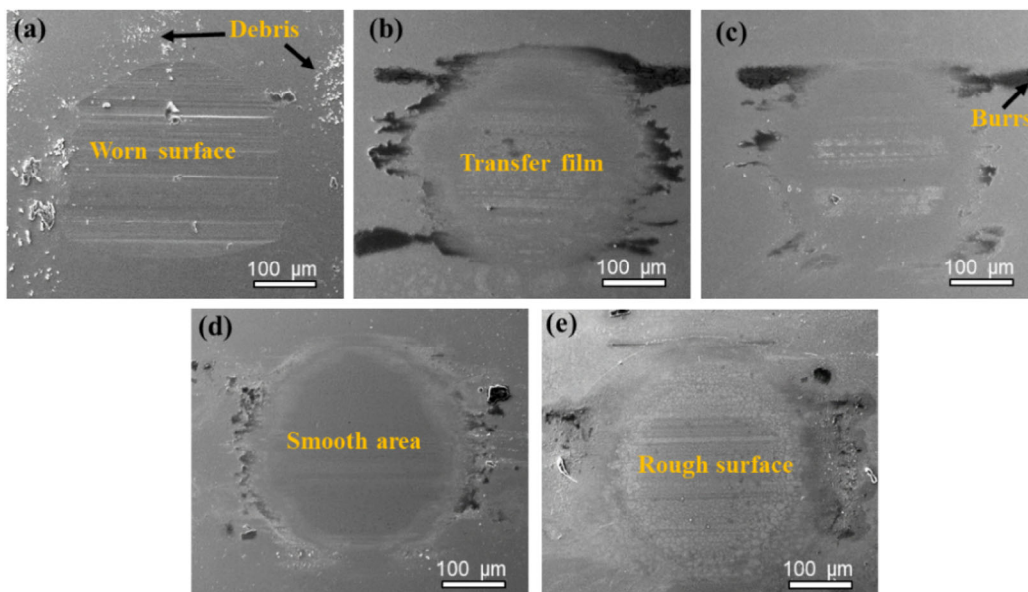


Fig. 7 SEM images of the ball surfaces sliding against different composites: (a) the pure EP resin, (b) the composite with 5 wt.% microcapsules, (c) the composite with 10 wt.% microcapsules, (d) the composite with 15 wt.% microcapsules, and (e) the composite with 25 wt.% microcapsules.

indicated severe plowing of the ball by the resin surface occurred during the friction process. In this case, the transfer film from the resin surface was of poor quality, or no transfer film formed. In contrast, no obvious scuffing was observed on the ball surface against the composite with microcapsules, and it could be ascribed to the tenacious character of the transfer film formed on the ball surface. As shown in Fig. 7(d), the ball surface sliding against the composite with 15 wt.% microcapsules was relatively smooth. Nevertheless, the surface became rough when the microcapsule content was increased to 25 wt.% in the composite. After the formation of a smooth, uniform, and tenacious transfer film, the subsequent sliding occurred under the lubrication of the boundary oil film on the composite surface and the transfer film covering the ball surface, and therefore a lower friction coefficient and wear rate was obtained.

XPS analyses of the ball surfaces were performed to verify the surface compositions after friction tests. In the XPS spectra of C1s (Fig. 8(a)), the peaks observed at 284.6 and 286.1 eV were attributed to the carbons in hydrocarbon C-C/C-H and C-O, respectively [49]. After microcapsules were added into the composite, the peak moved towards the low binding energy. In the friction process, the rupture of microcapsules and the flow out of the lubricant to form a lubrication film on the ball surface contained a large number of C-C and C-H bonds, resulting in the shift to the low binding energy. As can be seen in the XPS spectra of Fe2p_{3/2} (Fig. 8(b)), there were obvious characteristic peaks of Fe element, indicating that the transfer film was of poor quality or no transfer film formed. Nevertheless, it was noteworthy that after adding microcapsules in the composite, the characteristic peaks of Fe2p_{3/2}

detected on the surface were extremely weak or even disappeared completely when the mass fractions of microcapsules were 10 wt.% and 15 wt.%. It was inferred that the lubricant flew out of the microcapsule during the friction process and a dense lubricant film formed to cover the ball surface, and thus the characteristic peaks of the Fe element could not be detected.

4 Conclusions

Monodispersed PS microcapsules containing the PAO oil were successfully prepared using the solvent evaporation method. The diameter and the shell thickness of microcapsules were approximately 2 and 30 nm, respectively. Self-lubricating composites were also fabricated by incorporating the microcapsules into the EP resin. The lubrication properties of the epoxy composites could be greatly improved by the addition of oil microcapsules. As compared to pure EP resin, the friction coefficient and the wear rate of composites with microcapsules reduced to 4% and 0.25%, respectively. It was demonstrated that the PAO oil released from the microcapsules during the friction process produced a boundary lubricating film, which could prevent the direct contact between two sliding surfaces, leading to the lower friction coefficient and wear rate. In addition, properly increasing the load and the sliding speed could effectively promote the release of the lubricating oil and form a more uniform lubricant film at the friction interface. The strategy proposed in this work is expected to be a general solution which can be extended to other composites with excellent lubricating performances by adding

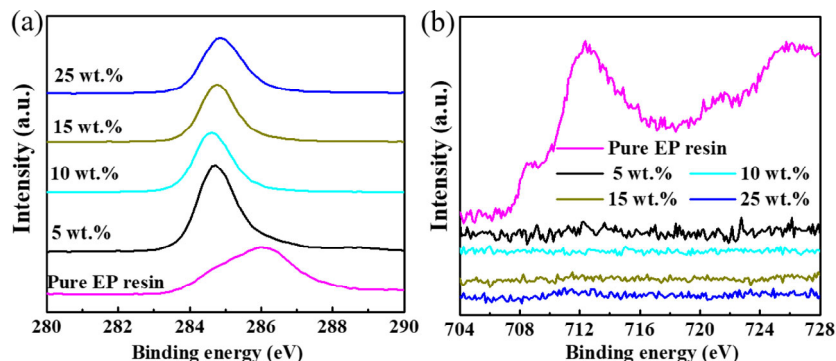


Fig. 8 XPS spectra for the ball surfaces after friction testing: (a) C1s and (b) Fe2p_{3/2}.

microcapsules with different kinds of lubricants into the matrix.

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