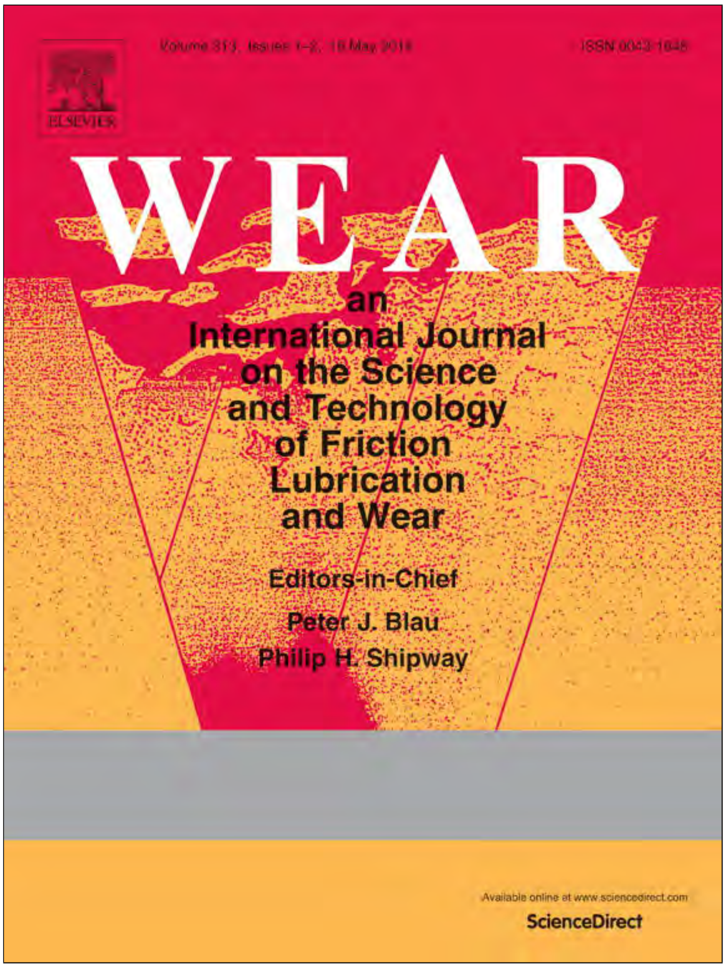
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Wear resistant epoxy composites with diisocyanate-based self-healing functionality

N.W. Khun, D.W. Sun, M.X. Huang, J.L. Yang *, C.Y. Yue

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

Hexamethylene diisocyanate (HDI) filled microcapsules were developed and incorporated in epoxy matrices to form a new type of wear resistant epoxy composites. The tribological properties of the epoxy composites were systemically investigated. The friction and wear of the composites slid against a Cr6 steel ball at different sliding speeds under various normal loads decreased with increased microcapsule content because of the lubricating effect of released HDI liquid from ruptured microcapsules during the wear test and the self-healing process of the released HDI liquid with the moisture to form new polyurea layers on the wear track. It can be concluded that the incorporation of microencapsulated HDI liquid is an effective way to lessen the wear of the epoxy composites during sliding via the self-healing process with a concurrent self-lubricating effect of the released HDI liquid.

1. Introduction

There are over 60 different types of commercially available polymer-based materials in the U.K. alone as bearing materials [1]. Polymers composites are widely used for tribological applications due to their tunable and designable properties. Investigation to improve the tribological performance of polymer composites is widely carried out over past years. Polymer composites could perform better than metals by incorporating solid lubricant fillers such as graphite, polytetrafluoroethylene (PTFE) and molybdenum disulfide into polymer matrices [1,2]. These solid lubricant fillers, which have self-lubricating function, have shown effectiveness in reducing the friction coefficient in many cases [1,2]. As the incorporation of solid lubricant fillers affects the mechanical properties of polymer composites, short fiber reinforcements are incorporated in many polymers to improve their mechanical strength [3]. Improvements in the mechanical and tribological properties of polymer composites have been achieved through the incorporation of glass fibers, carbon fibers and other reinforcements [4–6].

External liquid lubricants can be used to improve the tribological properties of polymer composites [7,8]. However, the use of liquid lubricants may limit the application since it is not applicable to oil-sensitive materials or oil-contamination-free operating condition. However, incorporation of microencapsulated liquid lubricant in polymer matrices can exclude the drawbacks of external liquid lubricants and provide ultra-low friction coefficient and wear rate due to the effective lubricating effect of released lubricant from ruptured microcapsules [9]. It was reported that epoxy and silicone composites filled with wax-containing microcapsules exhibited much lower friction and wear than pure epoxy and silicone, respectively [10,11]. Regardless of under dry or lubrication condition, repeated sliding or rolling contact under long-term tribological service easily causes surface damages in those materials in forms of surface wear or microcracks, which may bring significant failure risk to the whole structure. It was reported that a formation of microcracks was observed on the wear track of short carbon fiber and graphite flake reinforced poly (ether ether ketone) (PEEK) composites [12,13].

Self-healing is a very common process in biological systems, which refers to an autonomous recovery process controlled by inherent physiological mechanism in the living bodies. Self-healing functionality in the synthetic materials has been well developed to autonomously repair damages and to restore functions of materials using healing agents inherently available to the system. Among the current self-healing systems, the major way to realize this process is through microencapsulation [14–19], hollow tubes [20], microvasculature [21,22] and molecular design [23–25] for various potential applications. Considering the time-dependent damaging feature of tribological process, one-part self-healing concept may find its valuable contribution to wear issues for materials working in the open environment. Liquid-phase diisocyanates, which are reactive with water and moisture in the environment, are one of the potential healing agents for one-part self-healing system. Leading-edge work on encapsulation of isophorone diisocyanate (IPDI) was carried out via interfacial

* Corresponding author. Tel.: +65 6790 6906; fax: +65 6792 4062.
E-mail address: MJLYang@ntu.edu.sg (J.L. Yang).

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polymerization in a stabilized aqueous emulsion by Yang et al. [14]. In order to realize instant healing, more reactive hexamethylene diisocyanate (HDI) filled polyurethane microcapsules were developed and incorporated in epoxy matrices to form a new type of epoxy composite coatings with an excellent anti-corrosion performance via self-healing functionality [15]. Recently, Keller et al. successfully applied epoxy coatings with one-part isocyanate-based healing chemistry for self-healing of the coatings subject to erosion damage [26]. Therefore, it is expected that incorporation of microencapsulated HDI liquid in epoxy matrices would improve the wear resistance of epoxy composites in the similar way. Pioneer work on the understanding and investigation of self-healing functionality in tribomaterials is greatly important and valuable to both academia and industry.

In this study, HDI filled microcapsules were incorporated in epoxy matrices to develop new wear resistant epoxy composites and their tribological properties were systematically investigated with respect to microcapsule content.

2. Experiment details

2.1. Materials

MDI prepolymer Suprasec 2644 was obtained from Huntsman. HDI, gum arabic and triethylenetetramine (TETA) were supplied by Sigma-Aldrich. Epolam 5015 and related hardener 5015 were purchased from Axson. All chemicals in this study were used without further purification unless otherwise specified.

2.2. Synthesis of microcapsules containing HDI

Suprasec 2644 and TETA were used to prepare microcapsules by interfacial polymerization in an oil-in-water emulsion system. 2.25 g of gum arabic surfactant was dissolved into 90 ml of deionized (DI) water in a 1000 ml beaker that was suspended in a temperature-controlled water bath on a programmable hot plate. The solution was agitated with a digital mixer (Caframo) at 550 rpm and heated to 50 °C. The oil phase was prepared by adding 13.5 g of HDI and 3 g of Suprasec 2644. After the aqueous solution was heated to the target temperature, the prepared oil solution was slowly added to form a stable emulsion. 10 g of diluted TETA solution was added into the emulsion. The reaction was ended after additional 2 h. The obtained microcapsules were cooled down to ambient temperature, rinsed with DI water, filtered and air-dried for 12 h for further analysis and testing.

2.3. Sample preparation

Pure epoxy and epoxy composites were prepared with epoxy resin (Epolam 5015) and hardener (Epolam 5015) at the recommended ratio of 100:30. The mixture was placed under vacuum to degas for about 15 min after well mixing and then poured into Teflon molds. For epoxy composites with HDI filled microcapsules, a certain amount of microcapsules was added into epoxy mixture and dispersed for about 5 min. The dispersion was degassed for 15 min and poured into Teflon molds. All the fabricated specimens in the molds were cured at room temperature (RT ~ 22–24 °C) for 24 h followed by post-curing at 80 °C for 2 h.

2.4. Characterizations

The thermalgravimetric analysis (TGA TA 2950) was conducted to characterize the thermal properties of the HDI filled microcapsules by ramping from about RT to 600 °C at a heating rate of 10 °C/min in a nitrogen (N_2) environment.

The surface morphology and topography of the samples were studied using scanning electron microscopy (SEM, JEOL-JSM-5600LV)

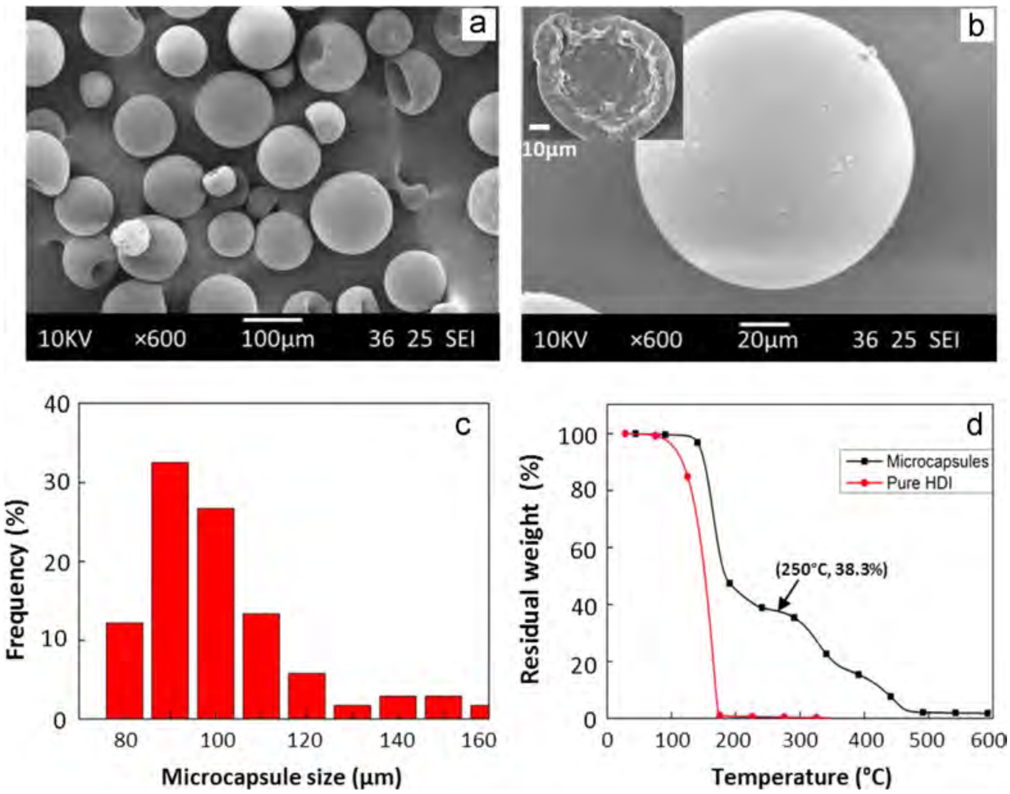


Fig. 1. SEM micrographs of (a) HDI filled microcapsules and (b) an individual microcapsule with smooth outer surface. (c) Size distribution and (d) TGA curve of HDI filled microcapsules. The inset in (b) shows a cross-sectional view of a ruptured microcapsule.

and surface profilometry (Talyscan 150) with a diamond stylus of 4 μm in diameter. For the SEM measurement, the samples were coated with a gold layer to avoid charging. Three measurements on each sample were carried out using surface profilometry to get an average root-mean-squared surface roughness (R_q).

The hardness and Young's modulus of the samples were measured using a micro-indenter (micro-CSM) with a pyramidal shaped diamond tip of 20 μm in diameter. The indentation test was performed in a load control mode with a total load of 3 N. In each indentation test, the loading and unloading rates and dwelling time at the peak load were 6 N/min, 6 N/min and 5 s, respectively. The hardness and Young's modulus of the samples were derived using Oliver and Pharr's method and average values were taken from sixteen indentation measurements carried out at different locations on each sample [27].

The tribological properties of the samples were investigated using a ball-on-disc micro-tribolometer (CSM) by sliding against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads. All the samples were pre-polished using 1200 grit papers prior to tribological test to stabilize the surface conditions. Three measurements per sample were carried out to get an average friction coefficient. The widths and depths of wear tracks were measured using surface profilometry to get average wear width and depth with 4 measurements per wear track.

3. Results and discussion

Fig. 1a shows the nearly spherical shaped microcapsules with a mean diameter of about 104 μm. The outer surfaces of the microcapsules are quite smooth as found in Fig. 1b as the inset in Fig. 1b shows the shell-wall structure of a ruptured microcapsule with roughly uniform thickness of about 7–8 μm. Fig. 1c illustrates the size distribution of the HDI filled microcapsules with a maximum frequency for 90 μm microcapsules.

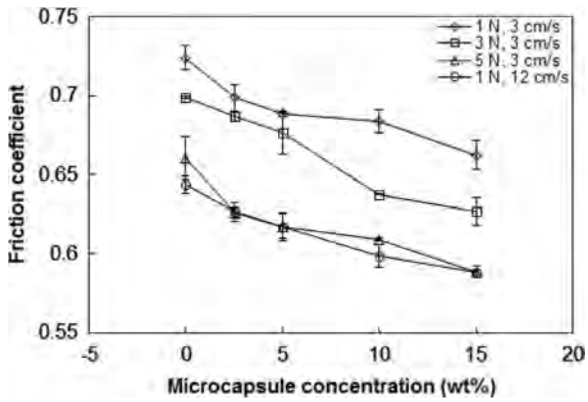


Fig. 2. Friction coefficients of epoxy composites, slid against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads, as a function of microcapsule content.

In Fig. 1d, the microencapsulated HDI liquid experiences 5% weight loss at about 144.5 °C that is about 40 °C above the boiling point of the pure HDI liquid, indicating that the polyurea shell acts not only as a good barrier from leakage to provide enough protection during post-treatment of the samples but also as a good thermal barrier to greatly extend its application temperature scale.

The tribological properties of the epoxy composites were investigated by sliding against a Cr6 steel ball of 6 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads and their frictional results are presented in Fig. 2. The mean friction coefficient of the epoxy composites slid at a sliding speed of 3 cm/s under a normal load of 1 N decreases from about 0.72 to 0.66 with increased microcapsule content from 0 to 15 wt%. This can be explained by adopting the following self-healing mechanism of the epoxy composites during the wear test.

As shown in Fig. 3, the repeated sliding of the steel ball under a certain normal load gradually wears out the surface of the epoxy composite and ruptures the embedded HDI filled microcapsules accordingly. Then, the HDI liquid released from the ruptured microcapsules flows into the wear track and covers it. Before curing, the released HDI liquid plays a role in lubrication to reduce the friction of the composite because it serves as a lubricant to lubricate the rubbing surfaces and as a spacer to prevent a direct solid-solid contact between the steel ball and composite [9,11,28–31]. As the time goes on, the HDI liquid on the wear track of the composite and the steel ball reacts with moisture in the environment to produce new polyuria materials [15]. The reactive sites of the HDI (N=C=O) react with the hydroxyl group (OH^-) in moisture to produce polyuria materials via the reactions shown in Scheme 1.

It is therefore supposed that the rapid formation of polyurea layers on the rubbing surfaces decreases the friction of the epoxy composite by preventing a direct sliding of the steel ball on the composite [28–31]. It is clear that the released HDI liquid reduces the friction of the epoxy composites by lubricating the rubbing surfaces and forming the new polyurea layers on the rubbing surfaces as the increased microcapsule content results in the decreased friction of the composites by releasing more HDI liquid.

The effect of surface roughness on the friction of the epoxy composites should be taken into account since a rougher surface can give a higher friction in terms of mechanical interlocking between two mating surface asperities [32–35]. Fig. 4 shows the R_q value of the mechanically polished epoxy composites using 1200 grit papers as a function of microcapsule content. The R_q value of the epoxy is about 0.27 μm. The R_q value of the epoxy composites

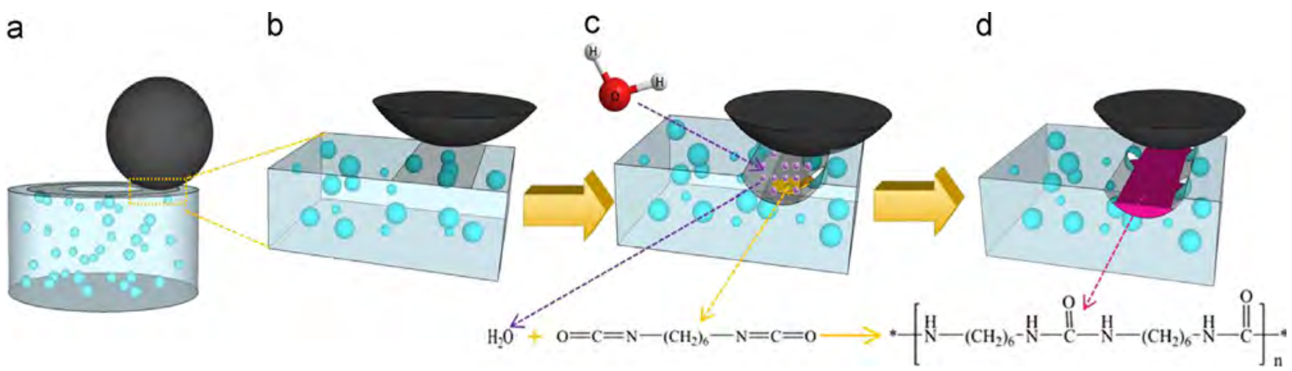


Fig. 3. Self-healing mechanism of epoxy composite during wear test. (a) Ball-on-disk, (b) sliding wear, (c) release and healing and (e) healed wear track.

increases from about 0.3 to 0.44 μm with increased microcapsule content from 2.5 to 15 wt%, which indicates that the higher microcapsule content gives rise to the higher surface roughness of the epoxy composites during the mechanical polishing although all the samples are mechanically polished under the same conditions. The reason is that the mechanical polishing ruptures the microcapsules via the surface wear and leaves single holes on the surfaces of the epoxy composites. Since the number of single holes on the surface increases with increased microcapsule content, the increased microcapsule content leads to the increased R_q value of the epoxy composites.

Normally, the rupture of microcapsules with a mean diameter of about 104 μm should give the much larger R_q values of the epoxy composites by forming large single holes on the surfaces. However, no dramatic increase in the R_q value of the epoxy composites with increased microcapsule content implies that the surfaces of the epoxy composites are not covered by the large number of single holes. Comparison of Fig. 5a and b clearly shows that the mechanical polishing forms single holes on the surface of the epoxy composite with 15 wt% microcapsules via the rupture of microcapsules, which is responsible for the larger R_q value of the epoxy composite than that of the epoxy (Fig. 4). However, the number of single holes on the surface of the epoxy composite (Fig. 5b) is apparently small even at the highest microcapsule content of 15 wt%. It is clear that the surface wear of the epoxy composite releases the HDI liquid during the mechanical polishing and the rapid reaction of the released HDI liquid with moisture allows healing of the ruptures with newly formed polyurea materials. The further mechanical polishing can result in smoothening or wearing of the formed polyurea layer so that the epoxy composite with 15 wt% microcapsules possess a smooth surface with a few single holes as found in Fig. 5b. Therefore, the increased microcapsule content does not dramatically increase the R_q value of the epoxy composites by healing the ruptures with the newly formed polyurea materials.

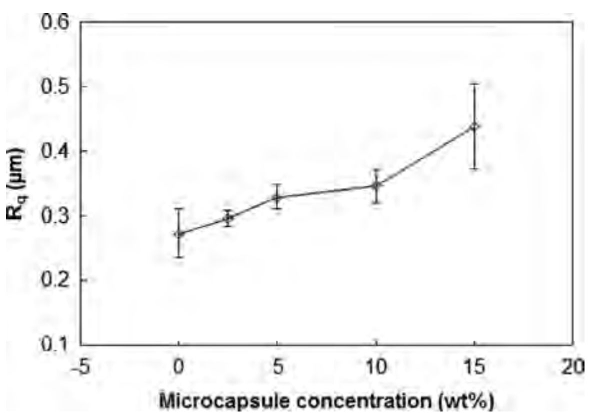
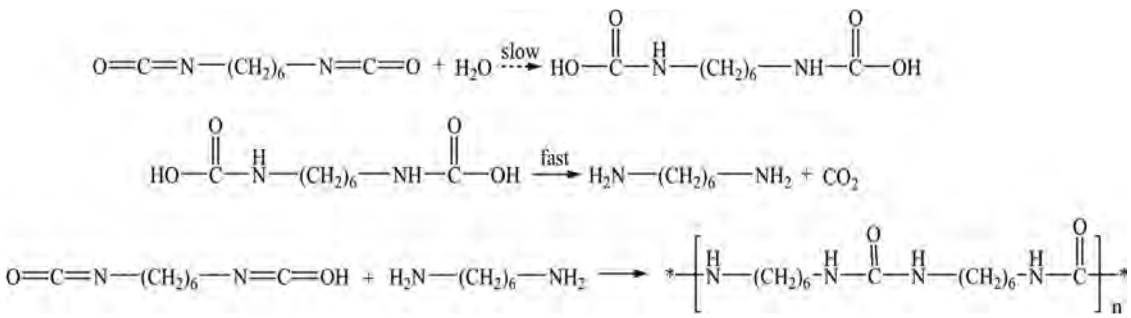


Fig. 4. Root-mean-squared surface roughness (R_q) of epoxy composites as a function of microcapsule content.

No correlation between the increased R_q value (Fig. 4) and decreased friction (Fig. 2) of the epoxy composites clearly indicates that the surface roughness of the epoxy composites does not have a significant influence on their friction in terms of mechanical interlocking between two mating surface asperities because the higher R_q values of the epoxy composites result from the larger number of single holes left on the surfaces by the rupture of microcapsules during the mechanical polishing. On the other hand, the increased surface roughness of the epoxy composites contributes to their decreased friction by reducing a real contact area between the rubbing surfaces [32–35].

Generally, the high mechanical strength of a polymer can prevent the wear and reduce the friction of the polymer during sliding [36,37]. It is therefore necessary to diagnose the hardness and Young's modulus of the epoxy composites with respect to microcapsule content. Fig. 6 shows the hardness and Young's modulus of the epoxy composites as a function of microcapsule content. The hardness and Young's modulus of the epoxy composites significantly decrease from about 237.5 MPa and 4.6 GPa to about 172.2 MPa and 3.3 GPa, respectively, with increased microcapsule content from 0 to 15 wt% as a direct consequence of the much lower hardness and elastic modulus of the microcapsules than those of the epoxy matrix [14]. The decreased hardness and elastic modulus of the epoxy composites with increased microcapsule content (Fig. 6) should increase the friction of the composites by increasing the wear of the composites. However, the decreased friction of the epoxy composites with their decreased mechanical strength clearly indicates that the effect of the mechanical strength of the epoxy composites on their tribological properties is not significant in this study probably due to the self-lubricating and self-healing of the composites with released HDI liquid.

It is consistently found in Fig. 2 that the mean friction coefficients of the epoxy composites tested at a sliding speed of 3 cm/s under normal loads of 3 and 5 N also decrease from about 0.7 and 0.66 to about 0.63 and 0.59, respectively, with increased microcapsule content from 0 to 15 wt%. The increased microcapsule content to 15 wt% does not give rise to a dramatic decrease in the friction of the epoxy composites, which implies that the released HDI liquid cannot effectively reduce the friction of the epoxy composites because the rapid reaction of the released HDI liquid with moisture to form polyuria martials provides only a short lubrication period during the sliding. In Fig. 2, the friction coefficients of the epoxy and epoxy composites with different microcapsule contents decrease with increased normal load. Roughening of the rubbing surfaces can give lower friction via a smaller real contact area between them as wear debris can also result in lower friction through their free-rolling or free-sliding under a lateral force and a reduced direct contact between the two rubbing surfaces [28–31,38,39]. It is supposed that the increased



Scheme 1. Reactions between released HDI and moisture in environment.

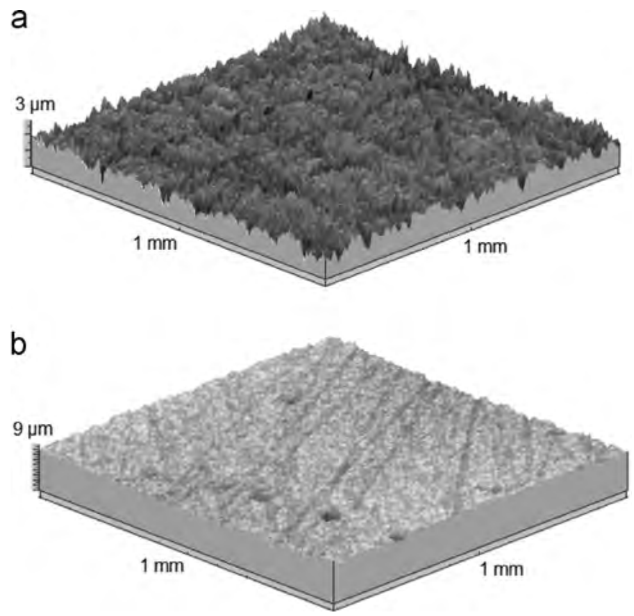


Fig. 5. Surface topographies of (a) epoxy and (b) epoxy composite with microcapsule content of 15 wt%.

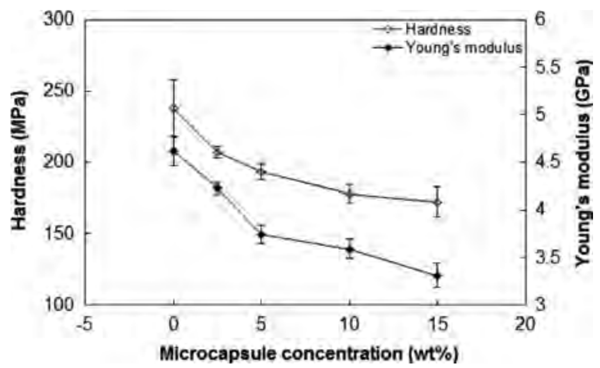


Fig. 6. Hardness and Young's modulus of epoxy composites as a function of microcapsule content.

normal load apparently decreases the friction of the epoxy and epoxy composites by promoting the surface roughening and the production of wear debris.

The repeated sliding of a counter ball on a polymer can generate high frictional heat which in turn causes localized softening or melting of the polymer so that the molten materials transfer onto the counter ball surface to form a transfer layer [40,41]. The transfer layer can reduce the friction by preventing a direct contact between the counter ball and polymer. Therefore, the promoted frictional heat associated with increased normal load pronounces the transfer of materials onto the counter ball and lowers the friction of the epoxy and composites as found in Fig. 2.

Increasing the normal load at the same sliding speed decreases the friction of the epoxy composites by releasing more HDI liquid via the higher surface wear. In addition, the higher normal load generates the higher frictional heat, which in turn results in the lower viscosity of the HDI liquid and its faster curing velocity. The lower viscosity of the released HDI liquid can lead to the lower friction of the epoxy composites by spreading over more places and better lubricating the rubbing surfaces. The faster curing of the released HDI liquid on the rubbing surfaces can help to lower the friction of the epoxy composite by accelerating the formation of polyurea layers which lessen the direct contact between the steel ball and composite. As a result, the increased normal load apparently decreases the friction of the epoxy and composites as found in Fig. 2.

In Fig. 2, the friction coefficients of the epoxy and composites slid at the higher sliding speed of 12 cm/s under the normal load of 1 N are apparently lower than those of the ones tested at the lower sliding speed of 3 cm/s under the same normal load although the mean friction coefficient of the epoxy composites tested at 12 cm/s consistently decreases from about 0.64 to 0.59 with increased microcapsule content from 0 to 15 wt%. During the wear test, the sliding of the steel ball at the higher sliding speed gives rise to the larger interaction between the steel ball and epoxy composite via the higher vibration of the sliding system and results in the higher wear of the composite [42]. Therefore, the higher wear of the epoxy and composites slid at the higher sliding speed of 12 cm/s results in their lower friction through the higher surface roughening and the larger quantity of wear debris. In addition, the higher frictional heat generated at the higher sliding speed can help to lower the friction by producing the less viscous HDI liquid with the faster curing velocity and promoting the transfer of materials onto the counter steel ball [39–43]. It can be deduced that the normal load and sliding speed have significant influences on the friction of the epoxy and composites.

Fig. 7a shows the friction coefficients of the epoxy and epoxy composites with different microcapsule contents, slid against a Cr6 steel ball for about 170,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N, as a function of the number of laps. The epoxy and composites exhibit a relatively stable friction during the entire sliding probably due to their stable wear although the friction of the epoxy composites with respect to the number of laps decreases with increased microcapsule content. In addition, the cyclic increase and drop in the friction coefficient during the prolonged sliding indicate the repeated formation and detachment of tribolayers on the wear track [11,31]. The repeated sliding of the steel ball under a high normal load compacts wear debris and forms a tribolayer on the wear track. Since the compacted tribolayer is somewhat harder, the formation of the tribolayer dramatically lowers the friction by lessening the contact between the rubbing surfaces and preventing the further removal of surface materials. However, the further rubbing of the steel ball wears out the tribolayer so that the friction turns to increase with increased laps. Therefore, the repeated formation and detachment of tribolayers result in the cyclic increase and drop in the friction of the epoxy and composites during the prolonged sliding. This phenomenon becomes less with higher microcapsule content, which is confirmed by the longer cyclic periods on the trends of friction coefficient versus laps of the epoxy composites as found in Fig. 7a, because the released HDI liquid and the subsequent formation of polyurea layers prevent the wear of the epoxy composites during the sliding.

In Fig. 7b, The friction coefficients of the epoxy and composite with 2.5 wt% microcapsules tested under the higher normal load of 5 N apparently increase with increased laps, which is indicative of the promoted wear of the epoxy and composite with prolonged sliding. However, the further increased microcapsule content to 15 wt% further depresses the trends of friction coefficient versus laps of the epoxy composites as a result of the decreased friction of the composites (Fig. 7b).

In Fig. 7c, the friction coefficients of the epoxy and epoxy composites slid at the higher sliding speed of 12 cm/s are relatively unstable compared to those of the ones slid at the lower sliding speed of 3 cm/s (Fig. 7a and b) due to the unstable wear behavior of the epoxy and composites at the higher sliding speed. Nevertheless, the increased microcapsule content still can reduce the friction of the epoxy composites, especially for the longer run, as found in Fig. 7c.

Fig. 8a and b shows the wear widths and depths of the epoxy and epoxy composites with different microcapsule contents,

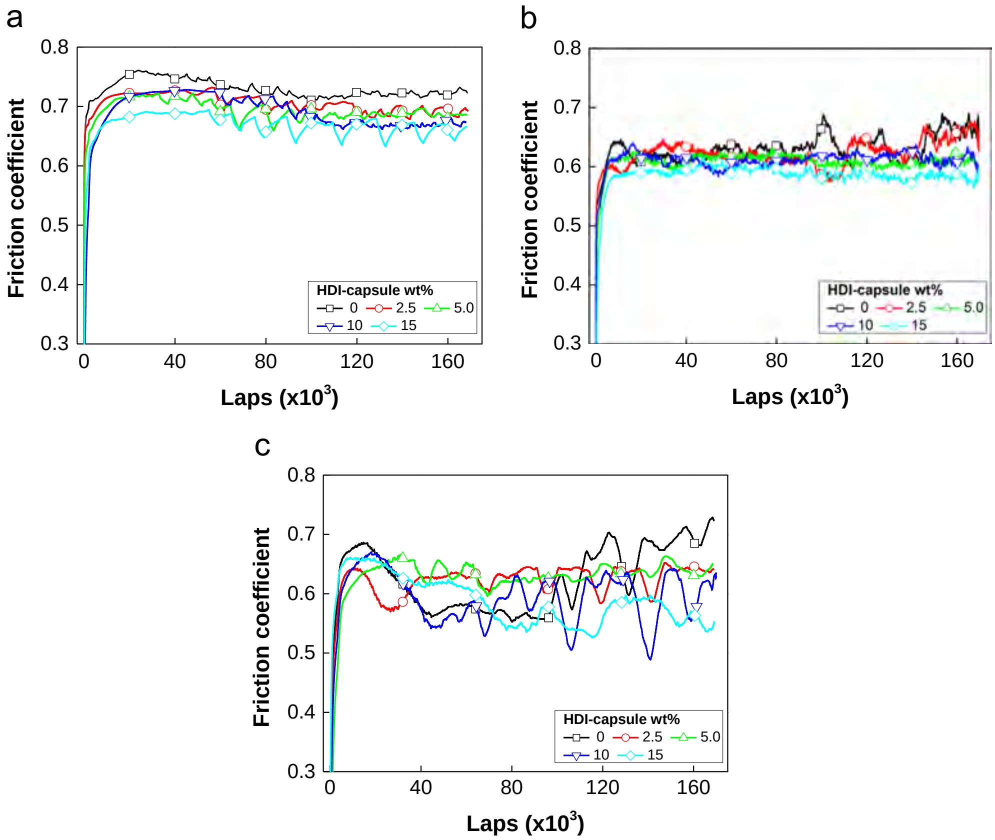


Fig. 7. Friction coefficients of epoxy composites with different microcapsule contents, slid against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads: (a) 1 N, 3 cm/s, (b) 5 N, 3 cm/s and (c) 1 N, 12 cm/s, as a function of the number of laps.

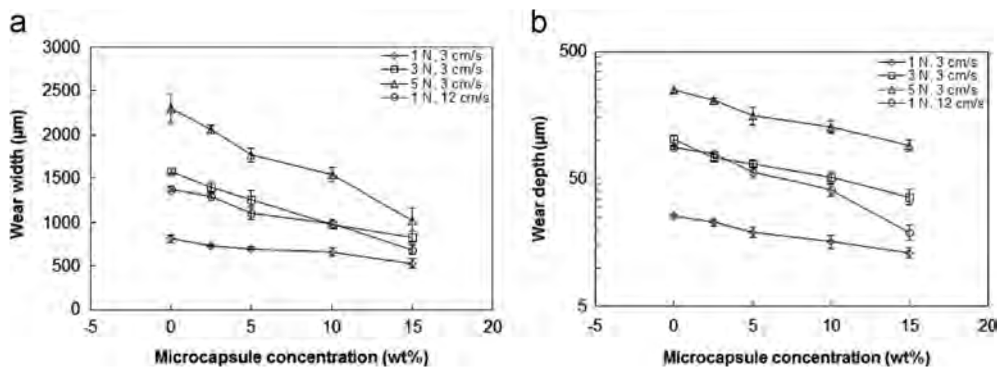


Fig. 8. (a) Wear widths and (b) depths of epoxy composites, slid against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads, as a function of microcapsule content.

respectively, slid against a Cr6 steel ball at different sliding speeds under different normal loads. In Fig. 8b, the wear depths are presented in log axis to clearly show the trends of wear depth versus microcapsule concentration. The wear width and depth of the epoxy composites significantly decrease with increased microcapsule content because the released HDI liquid lessens the wear of the composites by lubricating the rubbing surfaces and the newly formed polyurea layers on the rubbing surfaces via the rapid reaction of the HDI liquid with moisture lower the wear of the composites by changing the rubbing mode from the steel-on-polymer to the polymer-on-polymer during the sliding [9,11,15,28–31]. The wear widths and depths of the epoxy and composites increase with increased normal load due to the promoted wear of the composites. Although the friction coefficients of the epoxy and composites slid at the higher sliding speed of 12 cm/s under the normal load of 1 N are apparently lower than those of the ones tested at the lower sliding speed of 3 cm/s under the same normal load (Fig. 2), the wear widths and depths of the epoxy and composites slid at the higher sliding speed of 12 cm/s are significantly larger (Fig. 8), confirming that the higher sliding speed gives rise to the lower friction of the epoxy and composites via their higher wear.

After the tribological test, the worn surfaces of the epoxy and composites were observed using SEM. Fig. 9a and b shows the worn surfaces of the epoxy slid against the steel ball for about 170,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N on which a significant wear track is found. In Fig. 9a, the most severe wear is found in the center of the wear track where the contact pressure is highest. In addition, micro-wave features are apparetently found in the center of the wear track as shown in

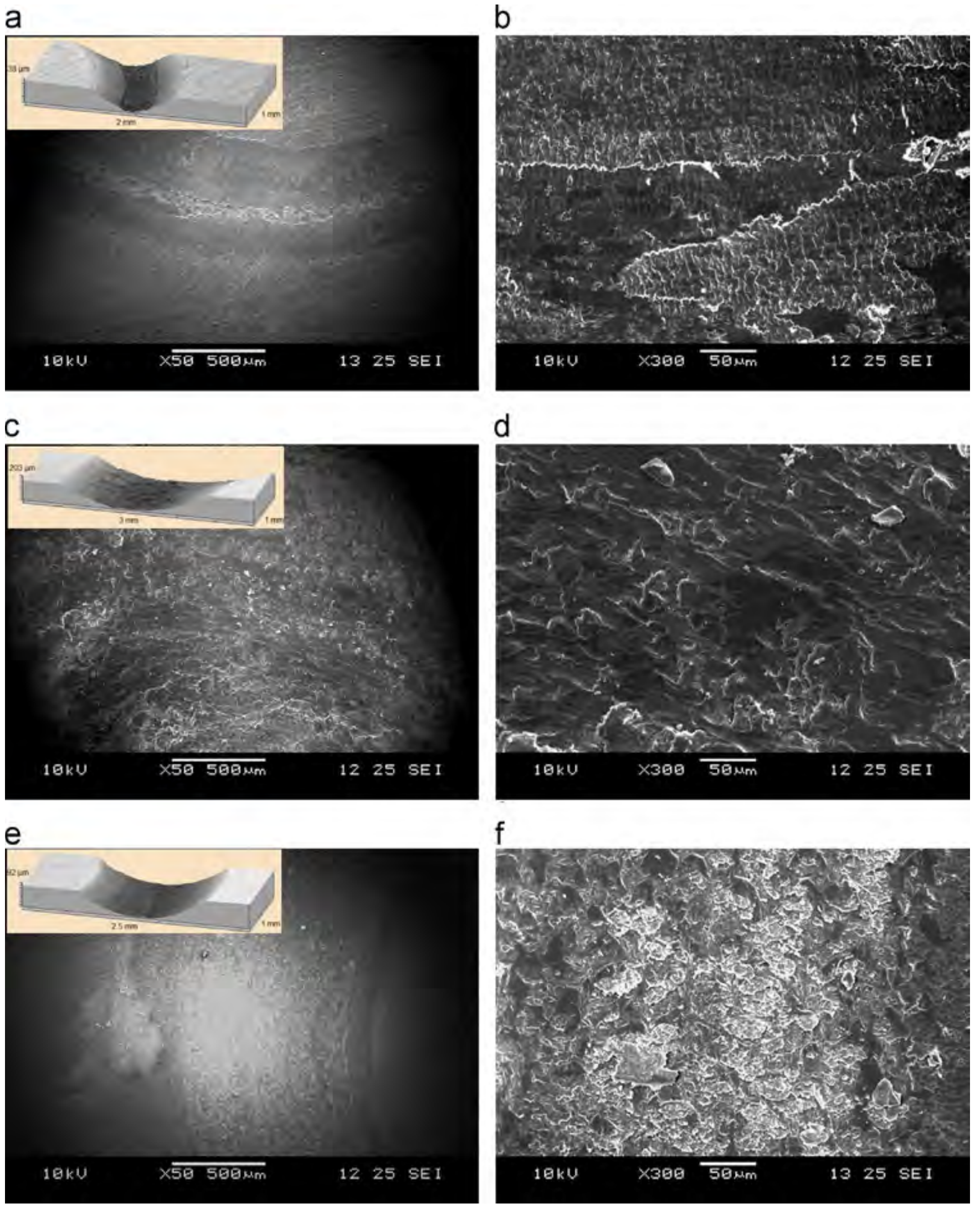


Fig. 9. SEM micrographs showing surface morphologies of worn epoxy, slid against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads: (a and b) 1 N, 3 cm/s, (c and d) 5 N, 3 cm/s and (e and f) 1 N, 12 cm/s, observed at different magnifications. The insets in (a), (c) and (e) show surface topographies of the same samples measured using surface profilometry.

Fig. 9a and b. The repeated sliding of the steel ball under a high normal load causes surface fatigue, which initiates and propagates minute cracks perpendicular to the sliding direction into the subsurface [44,45]. The formaiton of a network of micro-cracks creates micro-wave features as found in Fig. 9b [44,45]. The smoother layers on the wear track (Fig. 9b) are evident of the formation of tribolayers.

Fig. 9c and d shows the worn surfaces of the epoxy tested at a sliding speed of 3 cm/s under a normal load of 5 N. The whole wear track of the epoxy is not included in the SEM image (Fig. 9c) due to the much higher wear of the epoxy tested under the higher normal load of 5 N. The micro-wave features are not apparently found on the wear track of the epoxy (Fig. 9d) because the higher wear of the epoxy suppresses the initiaiton and propagation of cracks. Micro-plastic flow on the wear track of the epoxy implies that the sliding of the steel ball under the higher normal load removes surface materials through micro-plastic deformaiton and micro-cutting caused by the surface asperities of the steel ball [33–35,46,47]. In addition, the removal of surface materials as platelets is found on the wear track of the epoxy (Fig. 9d) because the repeated sliding of the steel ball initiates minute cracks in the subsurface and propagates the cracks parallel to a free surface for some extent before removing materials as a platelet [44–47].

The wear track of the epoxy slid at the higher sliding speed of 12 cm/s under the normal load of 1 N (Fig. 9e) is apparently larger than that of the one tested at the lower sliding speed of 3 cm/s under the same load (Fig. 9a), which confirms that the repeated sliding of the steel ball at the higher sliding speed results in the higher wear of the epoxy. Comparision of Fig. 9b and f clearly shows that the removal of surface materials as platelets is more apparently found on the wear track of the epoxy tested at the higher slidng speed of 12 cm/s because the higher sliding speed gives rise to the faster surface fatigue via the higher frequency of cyclic loading.

Fig. 10a and b shows the worn surfaces of the epoxy composite with 15 wt% microcapsules slid against a Cr6 steel ball at a sliding

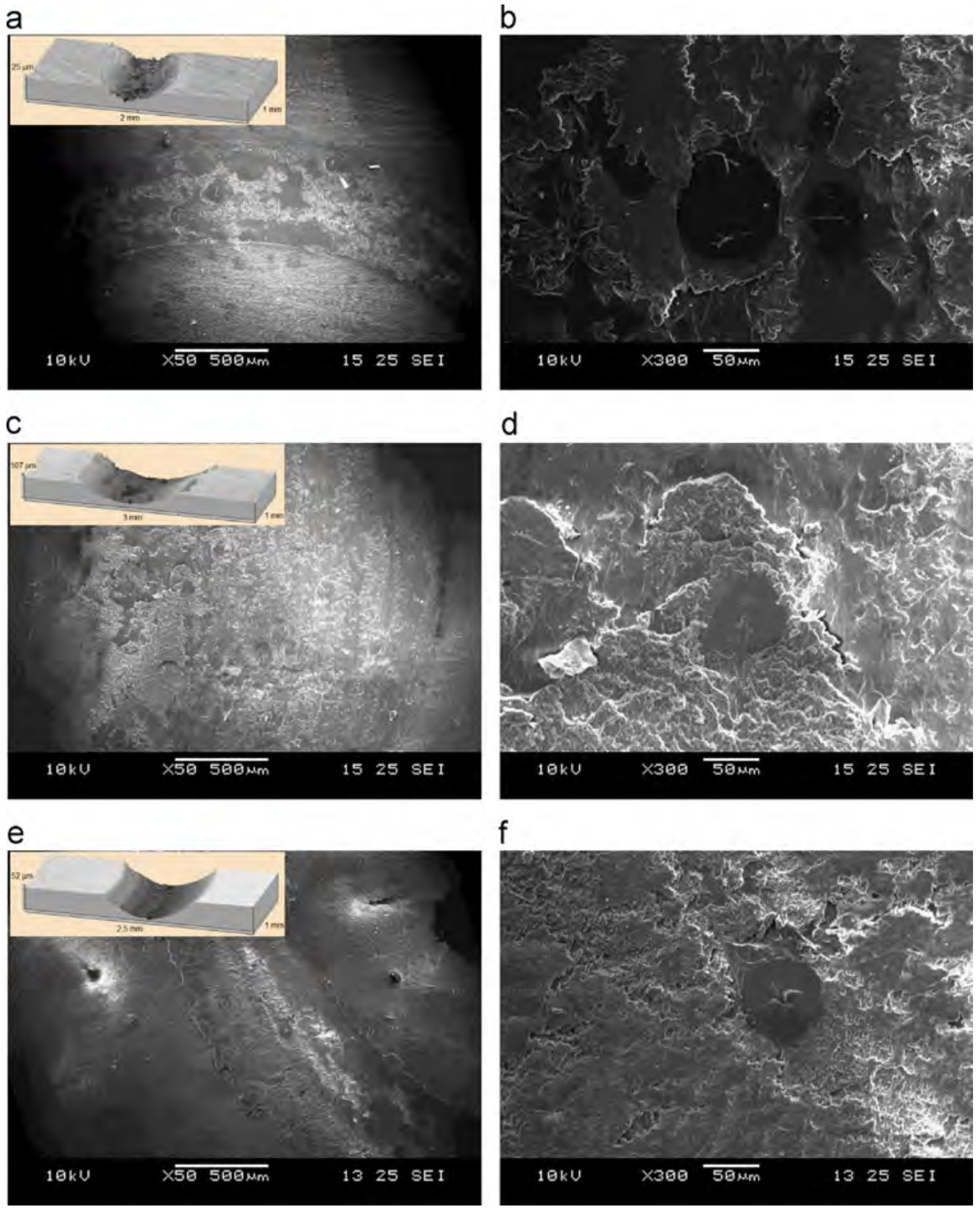


Fig. 10. SEM micrographs showing surface morphologies of worn epoxy composite with 15 wt% microcapsules, slid against a Cr6 steel ball of 6 mm in diameter in a circular path of 4 mm in diameter for about 170,000 laps at different sliding speeds under different normal loads: (a and b) 1 N, 3 cm/s, (c and d) 5 N, 3 cm/s and (e and f) 1 N, 12 cm/s, observed at different magnifications. The insets in (a), (c) and (e) show surface topographies of the same samples measured using surface profilometry.

speed of 3 cm/s under a normal load of 1 N. The formation of a new polyurea layer is found on the wear track of the epoxy composite, especially around the ruptured microcapsules, which indicates the self-healing of the worn surface of the epoxy composite. Comparison of Figs. 9c and 10c clearly shows that the incorporation of 15 wt% microcapsules significantly lowers the wear of the epoxy composite tested under the normal load of 5 N than that of the epoxy due to the self-healing of the composite during the sliding. The larger wear track of the epoxy composite slid under the higher normal load of 5 N (Fig. 10c and d) than that of the one tested under the lower normal load of 1 N (Fig. 10a and b) clearly indicates that the higher normal load still can generate the higher surface wear of the epoxy composite. Although comparison of Fig. 10a and e shows that the wear of the epoxy composite with 15 wt% microcapsules is still higher for the higher sliding speed of 12 cm/s, the incorporation of 15 wt% microcapsules apparently lowers the wear of the epoxy composite slid at 12 cm/s (Fig. 10e and f) than that of the epoxy (Fig. 9e and f). It indicates that the incorporation of microencapsulated HDI liquid can effectively reduce the wear of the epoxy composite slid at the high sliding speed via the self-healing of the composite. The formation of micro-wave features and the removal of surface materials as platelets are not apparently found on the wear tracks of the epoxy composite with 15 wt% microcapsules tested at different sliding speeds under different normal loads (Fig. 10) because the self-healing of the epoxy composite with the released HDI liquid eliminates the surface fatigue of the composite. It can be deduced that the incorporation of microencapsulated HDI liquid results in the effective self-healing of the epoxy composites during the sliding via the formation of new polyurea layers as the surface fatigue wear of the composites is apparently suppressed.

Fig. 11a and b shows the worn surfaces of the Cr6 steel balls slid on the epoxy and epoxy composite with 15 wt% microcapsules, respectively, for about 170,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N. As found in Fig. 11a, the steel ball slid on the epoxy exhibits a significant surface wear. However, no

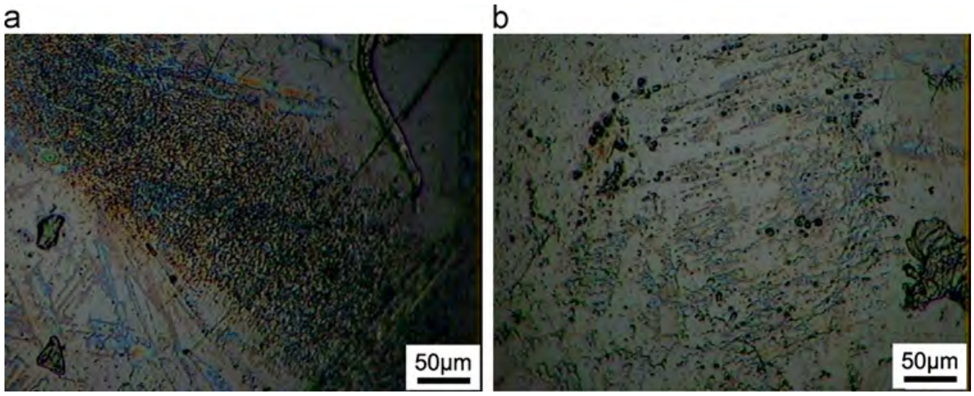


Fig. 11. Optical images showing surface morphologies of worn Cr6 steel balls slid on (a) epoxy and (b) epoxy composite with 15 wt% microcapsules in a circular path of 4 mm in diameter for about 170,000 laps at a sliding speed of 3 cm/s under a normal load of 1 N.

significant observation of the surface wear of the steel ball slid on the epoxy composite with 15 wt% microcapsules (Fig. 11b) clearly implies that the released HDI liquid can effectively prevent the wear of the counter steel ball by lubricating the ball surface and forming a polyurea layer on the ball surface.

4. Conclusions

In this study, a new type of wear resistant epoxy composites with HDI-based self-healing functionality was developed. The tribological properties of the epoxy composites with different microcapsule contents were systematically investigated. The main conclusions were drawn as follows:

1. The tribological results clearly showed that the friction of the epoxy composites slightly decreased with increased microcapsule content because the released HDI liquid via the surface wear of the composites severed as a lubricant to lubricate the rubbing surfaces and as a spacer to prevent a direct contact between the steel ball and composite. In addition, the rapid reaction of the released HDI liquid with moisture formed new polyurea layers on the rubbing surfaces to decrease the friction of the epoxy composites by preventing a direct contact between the steel ball and composite.
2. The wear of the epoxy composites significantly decreased with increased microcapsule content due to the self-lubricating effect and the promoted self-healing performance to generate new polyurea layers on the wear tracks, which dominated the whole process and compensated the possible poor wear resistance caused by the decreased mechanical properties.

Therefore, it can be concluded that the incorporation of microencapsulated HDI liquid results in the significantly improved wear resistance of the epoxy composites via the effective self-lubricating and self-healing processes during the sliding.

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