Wear 350-351 (2016) 89–98

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Tribological behaviors of binary and ternary epoxy composites functionalized with different microcapsules and reinforced by short carbon fibers

N.W. Khun, H. Zhang, D.W. Sun, J.L. Yang *

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

ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form
12 January 2016
Accepted 12 January 2016
Available online 16 January 2016

Keywords:
Binary and ternary epoxy composites
Microcapsules
Hardness
Friction
Wear

ABSTRACT

The effects of compositional modifications on the sliding friction and wear against bearing steel were investigated for newly-developed binary and ternary epoxy composites. Some of the new materials included hexamethylene diisocyanate (HDI) filled microcapsules and wax filled microcapsules, and others used HDI filled microcapsules, wax filled microcapsules and short carbon fibers (SCFs) at different ratios. The hardness of the binary and ternary epoxy composites decreased with increased content of wax filled microcapsules. The wax filled microcapsules were larger than the HDI filled microcapsules. Due to the rigidity of the SCFs, the hardness of the epoxy composites with 8 wt% SCFs was higher than that of the composites without SCFs. Pin-on-disc, sliding friction and wear performance for the binary and ternary epoxy composites tested against a 100Cr6 steel ball, were improved as the content of wax filled microcapsules increased. This was due to their effective lubricating effects. It was proposed that the addition of 8 wt% SCFs, which lowered the friction and wear of the epoxy composites, promoted solid lubrication by free-rolling SCFs.

1. Introduction

Polymer composites have been successfully developed only with a small amount of fillers to obtain new materials with outstanding thermal, electrical, mechanical and tribological properties [1–7]. Epoxy is commonly used as an engineering thermoset for many engineering applications because of its several outstanding properties such as good mechanical and thermal properties and easy processing with various fillers as its various properties can be improved by incorporating different fillers, such as tubes, fibers, sheets, particles, capsules and so on [8,9].

Generally, the low load carrying capacity, poor wear resistance, and short running life of polymers limit their tribological applications [10]. Therefore, it is necessary to develop high wear resistant polymers to be suitable for tribological applications. Nowadays, the capability of polymer composites to improve their tribological properties with various fillers allows them to be widely employed in tribological applications [11–16]. Although polymer composites have much lower wear under lubrication condition than under dry condition, their absorption and osmosis of lubricants can result in their surface degradation so that the use of external lubrication may limit their applications [17]. It was reported [18] that polymer composites incorporated with lubricant oil filled microcapsules exhibited dramatic reductions in their friction and wear via their self-lubrication. Khun et al. [19] reported that silicone composite coatings filled with microencapsulated wax had much lower friction than pure silicone ones due to the effective lubricating effect of released wax lubricant. In addition, they [20] revealed that incorporation of microencapsulated mixture of multi-walled carbon nanotubes (MWCNTs) and wax resulted in dramatically lowered friction and wear of epoxy composites due to the combined lubricating effects of released wax and MWCNTs compared to those of pure epoxy. Furthermore, they [21] discovered that higher wax filled microcapsule content or incorporation of larger microcapsules gave rise to lower friction and wear of epoxy composite as a result of more release of wax lubricant during sliding.

Prolonged sliding or rolling contact in tribological service can lead to a significant failure risk of tribological components by inducing surface damages in materials [7,22]. Therefore, incorporation of healing agent filled microcapsules in polymer matrices would be a possible way to autonomously repair damages of polymer composites and subsequently restore their functions [23–26]. Liquid phase diisocyanates are very reactive with water or moisture in the environment to form new polyurea materials for self-healing of polymer composites so that one-part-self-healing

* Corresponding author. Tel.: +65 67906906; fax: +65 67924062.
E-mail address: MJLYang@ntu.edu.sg (J.L. Yang).

http://dx.doi.org/10.1016/j.wear.2016.01.007
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concept would be a possible solution to address wear issues for materials working in the open environment [27]. Recently, an excellent anti-corrosion performance of epoxy composite coatings was achieved by successfully developing and incorporating more reactive hexamethylene diisocyanate (HDI) filled polyurethane microcapsules [28]. Epoxy coatings with one-part-isocyanate-based healing chemistry exhibited successful self-healing performance to erosion damages [29]. Khun et al. [22] also successfully developed HDI filled microcapsules to effectively reduce abrasive wear of epoxy composites through instant self-healing of the composites with released HDI liquid [22].

It is clear that incorporation of HDI filled microcapsules gives rise to apparently lower wear of epoxy composites via their self-healing with released HDI liquid while incorporation of wax filled microcapsules significantly lowers wear of epoxy composites due to the lubricating effect of released wax lubricant. It is therefore expected that co-incorporation of HDI filled microcapsules and wax filled microcapsules would effectively improve wear resistance of binary polymer composites through their both self-healing and self-lubricating properties, which has not been reported yet. But, there is always a significant decrease in the hardness of polymer composites associated with an incorporation of microcapsules [7,19–22]. Khun et al. [9,30] reported that incorporation of short carbon fibers (SCFs) significantly improved the mechanical and tribological properties of polymer composites with an optimized content of about 8 wt%. Therefore, the further development of novel ternary polymer composites with an addition of 8 wt% SCFs would be a possible way to improve their mechanical properties while maintaining their relatively low friction and wear. However, it becomes challenged to understand collaborative effects of released two or three agents on tribological performance of polymer composites during wear test when they are co-incorporated in the composites. It is important to comparatively investigate the tribological properties of binary and ternary polymer composites for successful tribological applications.

In this study, the unitary epoxy composites with HDI or wax filled microcapsules, binary epoxy composites with mixtures of HDI filled microcapsules and wax filled microcapsules, HDI filled microcapsules and SCFs and wax filled microcapsules and SCFs, and ternary epoxy composites with a mixture of HDI filled microcapsules, wax filled microcapsules and SCFs were developed to comparatively investigate their mechanical and tribological properties using micro-indentation and ball-on-disc micro-tribological tests.

2. Experimental details

2.1. Microencapsulation

The wax filled microcapsules were prepared by micro-encapsulating the wax lubricant, Episol B2538, with poly(urea-formaldehyde) (PUF) shell [19,21,30]. During the preparation, a 1000 ml beaker with liquid mixture consisting of 100 ml deionized (DI) water, and 25 ml of an aqueous solution containing 2.5 wt% ethylene maleic anhydride copolymer (EMA), 2.5 g urea, 0.25 g resorcinol ($C_6H_6O_2$) and 0.25 g ammonium chloride (NH_4Cl) (Sigma-Aldrich Singapore) was placed in a water bath with temperature controlled by a programmable hotplate (hotplate digital aluminum 230) and charged with 30 g wax at 400 rpm by a mechanical stirrer (Caframo, Model: BDC6015) [19,21,30]. The pH of the mixture was adjusted to 3.5 using 1 M sodium hydroxide (NaOH) solution. When the mixture was emulsified for 10 min at a stirring rate of 400 rpm, 6.3 g of an aqueous solution containing 37 wt% formaldehyde was dropped into the emulsion [19,21,30]. After the final mixture was heated to 55 °C at a heating rate of 35 °C/h and agitated for 4 h, the microencapsulation process was stopped and the achieved microcapsules were separated with a coarse-fritted filter under vacuum. The filtered microcapsules were then rinsed with DI water and air dried at room temperature (RT ~ 22–24 °C) for 24 h [19,21,30].

The HDI filled microcapsules were prepared by interfacial polymerization in an oil-in-water emulsion system using MDI prepolymer Suprasec 2644 and triethylenetetramine (TETA) (Sigma-Aldrich (Singapore)) [22]. Firstly, 2.25 g of gum Arabic surfactant was dissolved into 90 ml of DI water in a 1000 ml beaker that was suspended in a temperature-controlled water bath on a programmable hot plate and the solution was agitated with a mechanical stirrer at 550 rpm and heated to 50 °C [22]. After the aqueous solution was heated to the target temperature, the prepared oil solution containing 13.5 g of HDI and 3 g of Suprasec 2644 was slowly added to form a stable emulsion [22]. 10 g of diluted TETA aqueous solution was added slowly into the emulsion and the reaction was ended after additional 2 h. The achieved microcapsules were cooled down to RT and filtered followed by rinsing with DI water and air drying for 12 h [22].

2.2. Sample preparation

The epoxy specimens for tribological testing were fabricated according to the following procedure. Firstly, the epoxy resin, Epolam 5015 (Axson Technologies), and hardener, Hardener 5015 (Axson Technologies), were mixed by hand at the recommended ratio of 100:30 for about 10 min. After the mixing, the mixture was evacuated for about 15 min to remove air-bubbles. For the epoxy composite specimens with HDI filled microcapsules or/and wax filled microcapsules, the weighted amounts of HDI filled microcapsules or/and wax filled microcapsules were dispersed uniformly into the mixture [19–22]. For the epoxy composite specimens with mixtures of HDI filled microcapsules and SCFs, wax filled microcapsules and SCFs, and HDI filled microcapsules, wax filled microcapsules and SCFs, the mixture was mixed with 8 wt% SCFs (M-2007S, Kreca, average diameter of about 14.5 μm and average length of 90 μm [30]) in a glass beaker placed in a water bath at 60 °C and mechanically stirred at 1500 rpm for 30 min before hand-mixing with HDI filled microcapsules or/and wax filled microcapsules as mentioned above [9,30]. Then, the final mixtures were evacuated again for about 15 min to remove trapped air-bubbles. Eventually, the mixtures were poured into Teflon molds for molding. The molded samples were cured at RT for 24 h followed by post-curing in an oven (Binder, Model V53) at 60 °C for 3 h [19–22,30]. The lists of unitary, binary and ternary epoxy composites with their designated names were described in Table 1.

2.3. Characterizations

Scanning electron microscopy (SEM, JEOL-JSM-5600LV) was used to study the morphologies of the samples and microcapsules. A gold layer was applied on the samples to avoid charging prior to the SEM observation.

The surface morphology of the samples was also measured using surface profilometry (Talyscan 150, Taylor Hobson) with a diamond stylus of 4 μm in diameter and their average root-mean-squared surface roughnesses (R_q) were obtained from three measurements on each material [30].

The hardness of the samples was measured using a micro-indenter (micro-CSM) with a spherical shaped diamond tip of 20 μm in diameter under a total normal load of 3 N. The loading and unloading rates, and dwelling time at the peak load used were 6 N/min, 6 N/min and 5 s, respectively [30]. The hardness of the samples was derived using Oliver & Pharr's method [31] and the average hardness of the samples was taken from sixteen indentation measurements on each material.

A ball-on-disc micro-tribometer (CSM) (Testing conformed to DIN 50324 and ASTM G99) was used to evaluate the friction coefficients and specific wear rates of the samples. Each of the samples was rotated against a 100Cr6 steel ball of 6 mm in diameter in a circular path of 2 mm in radius for 60,000 laps at a sliding speed of 4 cm/s under a normal load of 6 N [30]. The relative humidity was 60–65% RH. The testing parameters were optimized based on the reports in Refs [21,22,30] where the wear resistance of the epoxy composites were systematically evaluated under different normal loads and sliding speeds. The steel ball was chosen as a counter ball in this study to understand the tribological behavior of the epoxy composites during rubbing contact with a metallic counter material and systematically compare with previously reported results in Refs.[21,22,30]. The samples were pre-polished using 1200 grit papers prior to tribological test. An average friction coefficient was taken from three measurements on each material. A specific wear rate was calculated by measuring width and depth of wear tracks using surface profilometry.

Table 1
Lists of unitary, binary and ternary epoxy composites.

Sample name	HDI filled microcapsules (wt%)	Wax filled microcapsules (wt%)	SCFs (wt%)
Neat epoxy			
EP	0	0	0
Unitary epoxy composites			
EP-10HDI	10	0	0
EP-10Wax	0	10	0
Binary epoxy composites			
EP-2.5HDI-7.5Wax	2.5	7.5	0
EP-5HDI-5Wax	5.0	5.0	0
EP-7.5HDI-2.5Wax	7.5	2.5	0
EP-10HDI-8SCF	10	0	8.0
EP-10Wax-8SCF	0	10	8.0
Ternary epoxy composites			
EP-2.5HDI-7.5Wax-8SCF	2.5	7.5	8.0
EP-5HDI-5Wax-8SCF	5.0	5.0	8.0
EP-7.5HDI-2.5Wax-8SCF	7.5	2.5	8.0

3. Results and discussion

3.1. Morphologies of microcapsules

Fig. 1 shows the SEM images of the wax filled microcapsules and HDI filled microcapsules. In Fig. 1a and b, the surfaces of the wax filled microcapsules have cotton-like features caused by the precipitation of PU nanoparticles [20,32]. As a result, the wax filled microcapsules have much rougher surface morphologies than the HDI filled microcapsules as shown by the comparison of Fig. 1a–d. The diameters of the wax filled microcapsules and HDI filled microcapsules are 209 ± 32 μm and 104 ± 19 μm, respectively, which indicates that the sizes of the wax filled microcapsules are significantly larger than those of the HDI filled microcapsules. As reported in Refs.[21–23,30], the core percentages of the wax filled microcapsules and HDI filled microcapsules are about 70 and 50 wt%, respectively.

3.2. Surface roughnesses of unitary, binary and ternary epoxy composites

Fig. 2 presents the R_q values of the polished neat epoxy, and unitary, binary and ternary epoxy composites. The formulation of each point in the figure is a combination of the lower *x*-axis for

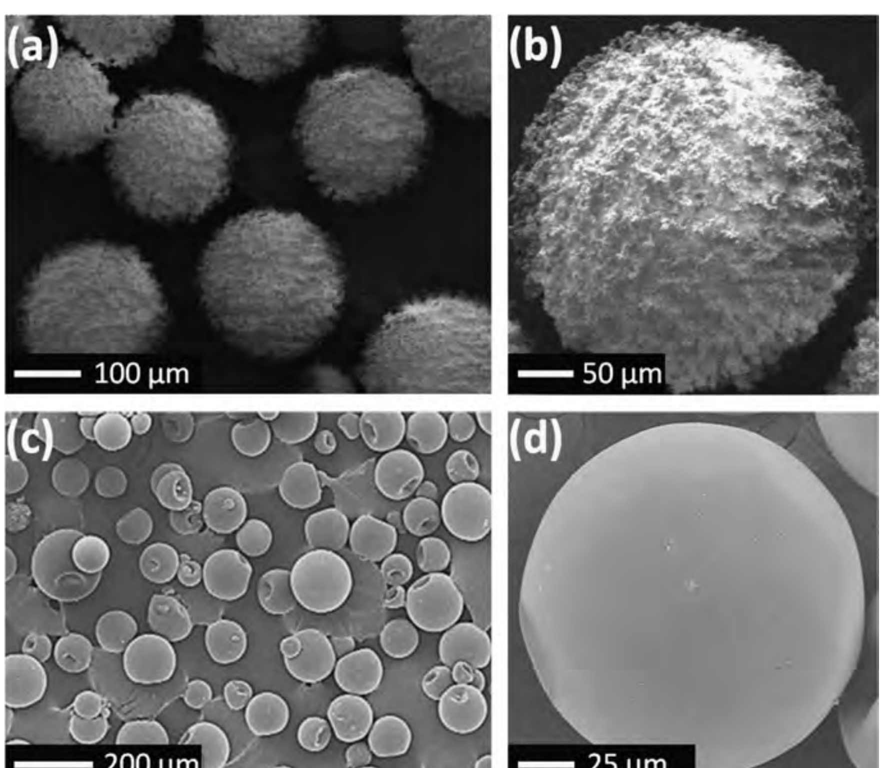

Fig. 1. SEM micrographs of (a) wax filled microcapsules, (b) single wax filled microcapsule, (c) HDI filled microcapsules, and (d) single HDI filled microcapsule.

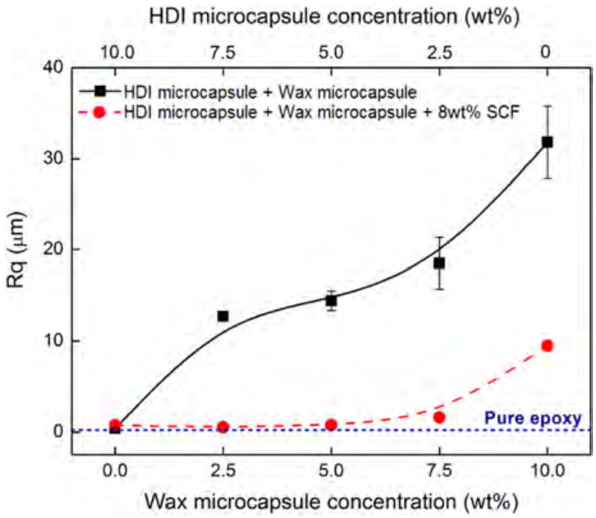

Fig. 2. Root-mean-squared surface roughnesses (R_q) of polished neat epoxy, and unitary, binary and ternary epoxy composites.

wax filled microcapsules and the upper *x*-axis for the HDI filled microcapsules. As the neat epoxy has a R_q value of about 0.3 μm, the R_q value of the binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules significantly increases from about 12.7 to 18.5 μm with increased content of wax filled microcapsules from 2.5 to 7.5 wt%. Since the rupture of larger wax filled microcapsules during the mechanical polishing results in larger single holes on the surface compared to that of smaller HDI filled microcapsules, the increased content of larger wax filled microcapsules in the binary epoxy composites increases their R_q values by increasing the number of larger single holes on their surfaces [19–22,30]. As shown in Fig. 2, the R_q values of the binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules are apparently larger than that (about 0.4 μm) of the unitary epoxy composite with 10 wt% HDI filled microcapsules, but significantly smaller than that (about 31.8 μm) of the unitary epoxy composite with 10 wt% wax filled microcapsules. It confirms that the content of larger wax filled microcapsules has a more significant influence on the R_q values of the binary epoxy composites than that of smaller HDI filled microcapsules.

The R_q value of the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs consistently increases from about 0.5 to 1.6 μm with increased content of wax filled microcapsules from 2.5 to 7.5 wt%, as shown in Fig. 2, as a result of the increased number of larger single holes on their polished surfaces. The R_q value of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs is about 0.7 μm while the R_q value of the binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs is about 9.5 μm. The significantly larger R_q values of the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs than that of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs further confirm that the higher content of larger wax filled microcapsules in the epoxy composites gives rise to their larger R_q value. It is clear that the epoxy composites with an addition of 8 wt% SCFs have much smaller R_q values than the ones without SCFs because the improved wear resistance of the epoxy composites associated with the addition of 8 wt% SCFs significantly lessens the surface wear and consequently the rupture of microcapsules during the mechanical polishing [30].

Fig. 3 shows the surface morphologies of the polished neat epoxy, and unitary, binary and ternary epoxy composites. As shown in Fig. 3a–c, single holes formed by the rupture of microcapsules are found on the surface of the unitary epoxy composite with 10 wt% wax filled microcapsules although the single holes are not apparently found on the surface of the unitary epoxy composite with 10 wt% HDI filled microcapsules [19–22,30]. It indicates that the released HDI core liquid via the rupture of microcapsules during the mechanical polishing effectively heals the ruptures [22,27–29]. Therefore, the R_q value of the unitary epoxy composite with 10 wt% HDI filled microcapsules is not very much different from that of the neat epoxy, but much smaller than that of the unitary epoxy composite with 10 wt% wax filled microcapsules (Fig. 2).

The binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules have more circular shaped single holes on their surfaces for the higher content of wax filled microcapsules, as shown in Fig. 3d and e, because the lowered content of HDI filled microcapsules lessens the self-healing of the ruptures (Fig. 3d) via less release of HDI core liquid. It is consistent with the increased R_q value of the binary epoxy composites with increased content of wax filled microcapsules (Fig. 2).

Comparison of Fig. 3b and f shows that the ruptures on the surface of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs are more apparent compared to those on the surface of the unitary epoxy composite with 10 wt% HDI filled microcapsules because the decreased surface wear of the binary epoxy composite associated with the addition of 8 wt% SCFs lessens the release of HDI core liquid for the effective self-healing of the ruptures [30]. As a result, the R_q value of the binary epoxy composite is slightly larger than that of the unitary epoxy composite (Fig. 2).

The binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs has the smaller number of single holes on the surface than the unitary epoxy composite with 10 wt% wax filled microcapsules as shown by the comparison of Fig. 3c and g, indicating that the addition of 8 wt% SCFs lessens the rupture of microcapsules via the decreased surface wear.

It is consistently found that the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs (Fig. 3h and i) have the much smaller number of single holes on their surfaces compared to the binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules (Fig. 3d and e). The reason is that the improved surface wear resistance of the ternary epoxy composites with the addition of 8 wt% SCFs dramatically lessens the rupture of microcapsules and the released HDI core liquid effectively heals and eliminates the ruptures as found in Fig. 3h and i. However, the decreased content of HDI filled microcapsules in the ternary epoxy composites increases the number of the apparent ruptures (Fig. 3h and i).

3.3. Hardnesses of unitary, binary and ternary epoxy composites

The hardnesses of the neat epoxy, and unitary, binary and ternary epoxy composites are presented in Fig. 4. The neat epoxy has hardness of about 286 MPa. The hardnesses of the unitary epoxy composites with 10 wt% HDI filled microcapsules and 10 wt% wax filled microcapsules are about 189 and 91 MPa, respectively, which indicates that the incorporation of larger wax filled microcapsules gives rise to the lower hardness of the unitary epoxy composites than that of smaller HDI filled microcapsules [21,30]. Therefore, the hardness of the binary epoxy composite with a mixture of wax filled microcapsules and HDI filled microcapsules decreases from about 167 to 113 MPa with increased content of wax filled microcapsules from 2.5 to 7.5 wt%. It is consistently found in Fig. 4 that the hardness of the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs decreases from about 286 to 224 MPa

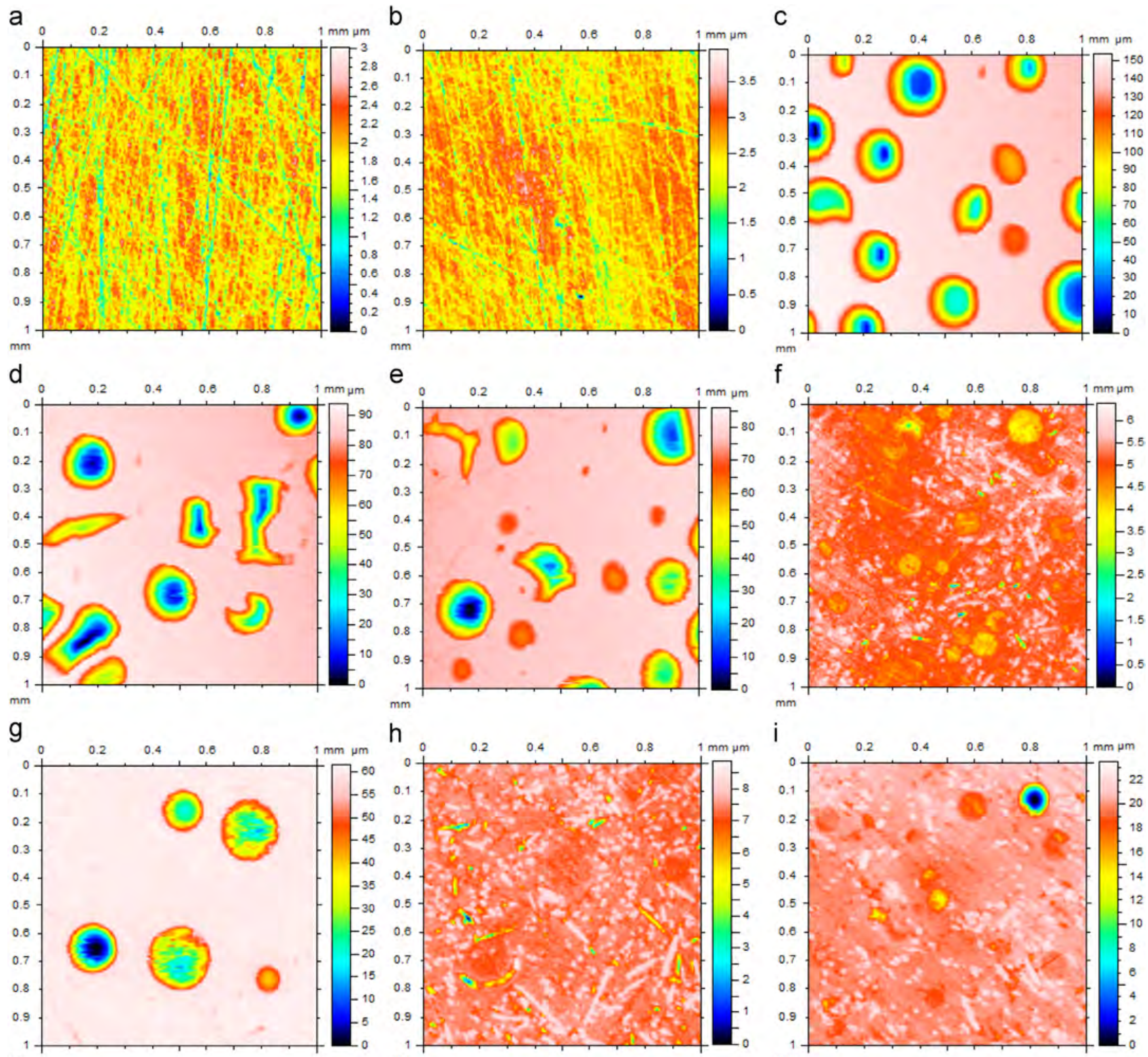

Fig. 3. Surface morphologies of polished (a) neat epoxy, unitary epoxy composites with (b) 10 wt% HDI filled microcapsules, and (c) 10 wt% wax filled microcapsules, binary epoxy composites with mixtures of (d) 7.5 wt% HDI filled microcapsules and 2.5 wt% wax filled microcapsules, (e) 2.5 wt% HDI filled microcapsules and 7.5 wt% wax filled microcapsules, (f) 10 wt% HDI filled microcapsules and 8 wt% SCFs, and (g) 10 wt% wax filled microcapsules and 8 wt% SCFs, and ternary epoxy composites with mixtures of (h) 7.5 wt% HDI filled microcapsules, 2.5 wt% wax filled microcapsules and 8 wt% SCFs, and (i) 2.5 wt% HDI filled microcapsules, 7.5 wt% wax filled microcapsules and 8 wt% SCFs.

with increased content of wax filled microcapsules from 2.5 to 7.5 wt%. The hardness of the binary epoxy composites with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs is about 241 MPa that is consistently lower than that (about 261 MPa) of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs.

The ternary epoxy composites exhibit higher hardness for their higher HDI filled microcapsule content than the SCF containing binary epoxy composite with 10 wt% HDI filled microcapsules, but lower hardness for their higher wax filled microcapsule content than the SCF containing binary epoxy composite with 10 wt% wax filled microcapsules, which are opposite from those of the epoxy composites without SCFs. The possible reason is that different sizes and types of microcapsules would cause different dispersions of SCFs in the epoxy matrices for different mechanical behaviors of the epoxy composites although specific explanations cannot be clearly provided. Nevertheless, the hardnesses of the epoxy composites with 8 wt% SCFs are significantly higher than those of the ones without SCFs due to the incorporation of rigid SCFs [9,30].

3.4. Tribological properties of unitary, binary and ternary epoxy composites

Fig. 5 presents the friction coefficients of the neat epoxy and unitary, binary and ternary epoxy composites tested against a 100Cr6 steel ball for 60,000 laps under a normal load of 6 N. The epoxy has a friction coefficient of about 0.67. The friction coefficients of the unitary epoxy composites with 10 wt% wax filled

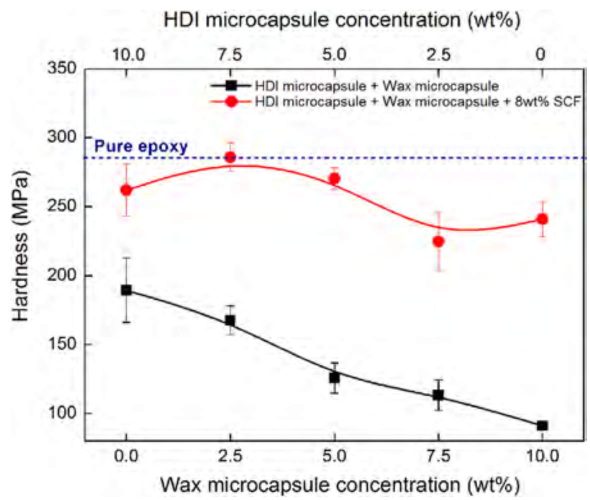

Fig. 4. Hardnesses of neat epoxy and unitary, binary and ternary epoxy composites.

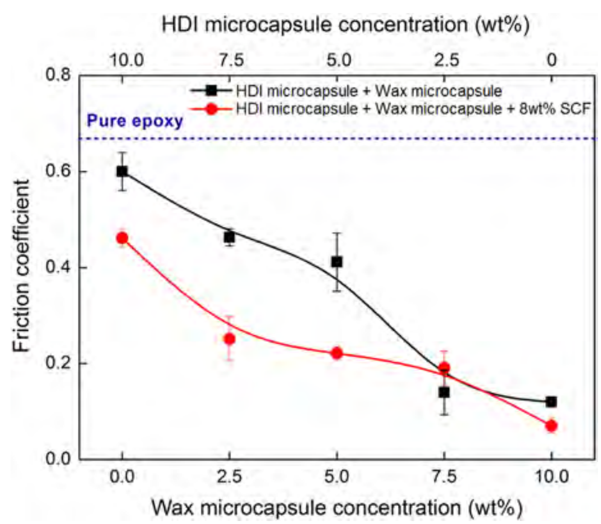

Fig. 5. Friction coefficients of neat epoxy and unitary, binary and ternary epoxy composites tested against a 100Cr6 steel ball of 6 mm in diameter in a circular path of 2 mm in radius for 60,000 laps at a sliding speed of 4 cm/s under a normal load of 6 N.

microcapsules and 10 wt% HDI filled microcapsules are about 0.12 and 0.6, respectively, indicating that the released wax lubricant more significantly reduces the friction of the epoxy composites than the released HDI liquid due to the more effective lubricating effect of the wax lubricant [21,30]. Therefore, the friction coefficient of the binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules decreases from about 0.46 to 0.14 with increased content of wax filled microcapsules from 2.5 to 7.5 wt% due to the increased amount of released wax lubricant.

The friction coefficient (about 0.07) of the binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs is consistently lower than that (about 0.46) of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs. It is also consistently found that the friction coefficient of the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs decreases from about 0.25 to 0.19 with increased content of wax filled microcapsules from 2.5 to 7.5 wt%. As found in Fig. 5, the epoxy composites with an addition of 8 wt% SCFs have relatively lower friction coefficients than the ones without SCFs due to the combined lubricating effects of released core liquids and incorporated SCFs. In addition, released SCFs into an interface between the counter ball and composite help to reduce the friction by preventing a direct contact between them and freely rolling or sliding under a lateral force [5,6,9,16,20,30].

The opposite trends between the surface roughness (Fig. 2) and friction (Fig. 5) of the epoxy composites with respect to microcapsule content clearly show that the surface roughness of the epoxy composites does not have a significant influence on their friction since a higher surface roughness can give a higher friction via an effective mechanical interlocking between two mating surface asperities [33–36]. Normally, a higher wear of polymers associated with their poor mechanical strength can result in a higher friction via their larger contact with a counter ball [33–36]. However, the similar trends between the hardness (Fig. 4) and friction (Fig. 5) of the epoxy composites with respect to microcapsule content clearly imply that the effect of mechanical strength of the epoxy composites on their friction is not significant in this study. It can be deduced that the release of wax lubricant is mainly responsible for reducing the friction of the both epoxy composites without and with SCFs while the addition of SCFs gives rise to the further lower friction of the epoxy composites via the solid lubricating and free-rolling effects of the SCFs [5,6,9,16,20,30].

Fig. 6 illustrates the friction coefficients of the neat epoxy and unitary, binary and ternary epoxy composites as a function of the number of laps. The friction of the neat epoxy dramatically increases for the first 15,000 laps and becomes stable for the rest. The unitary epoxy composite with 10 wt% HDI filled microcapsule shows a slightly lower trend of friction coefficient versus laps than the neat epoxy, which indicates that the released HDI core liquid reduces the friction by serving as a lubricant to lubricate rubbing surfaces and as a spacer to prevent a direct solid–solid contact between two rubbing surfaces before reacting with moisture to form new polyurea materials, and changing a sliding mode from steel-on-polymer to polymer-on-polymer as a result of forming new polyurea layers on the both rubbing surfaces [19–22,30,37–41].

The binary epoxy composite with a mixture of 7.5 wt% HDI filled microcapsules and 2.5 wt% wax filled microcapsules exhibits relatively low friction for a certain number of laps before reaching much higher friction for the rest, as shown in Fig. 6, as a result of the insufficient release of wax lubricant during the prolonged sliding. The higher content of wax filled microcapsules in the binary epoxy composites lowers the friction of the composite due to the more release of wax lubricant so that the content of 7.5 wt% wax filled microcapsules in the binary epoxy composite gives rise to a closer trend of friction coefficient versus laps to that of the unitary epoxy composite with 10 wt% wax filled microcapsules (Fig. 6).

The binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs exhibits a more significant decrease in the friction during the prolonged sliding than the unitary epoxy composite with 10 wt% HDI filled microcapsules due to the solid lubricating and free-rolling effects of incorporated SCFs. Therefore, the incorporation of 8 wt% SCFs effectively depresses the trends of friction coefficient versus laps of the ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs. In addition, the ternary epoxy composite with the higher content of wax filled microcapsules has the lower trend of friction coefficient versus laps as found in Fig. 6. The co-incorporation of 10 wt% wax filled microcapsules and 8 wt% SCFs results in the lowest friction of the unitary epoxy composite throughout the wear test among the epoxy composites used in this study probably due to the most effective lubricating effect coming from the released SCFs and wax lubricant.

Fig. 7 presents the specific wear rates of the neat epoxy and unitary, binary and ternary epoxy composites. The specific wear rate of the neat epoxy is about 19.57×10^{-14} m^3/Nm [30]. The

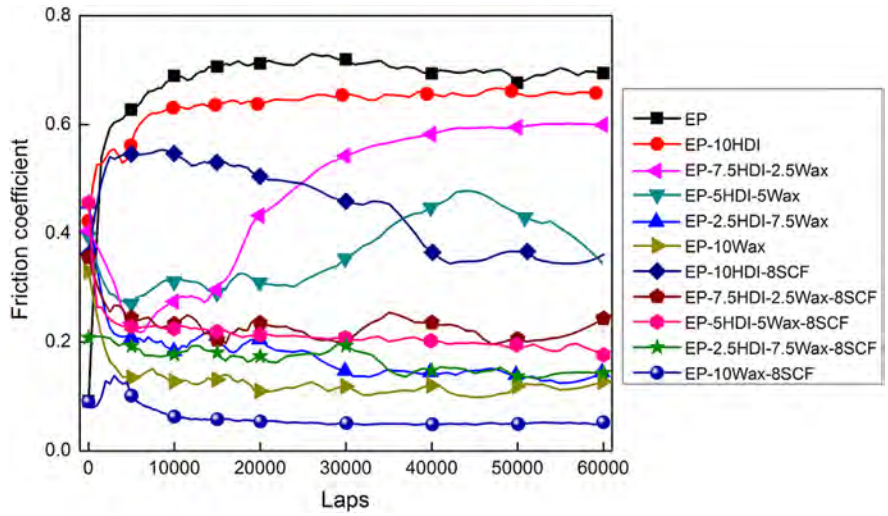

Fig. 6. Friction coefficients of neat epoxy and unitary, binary and ternary epoxy composites, tested under the same conditions as described in Fig. 5, as a function of the number of laps.

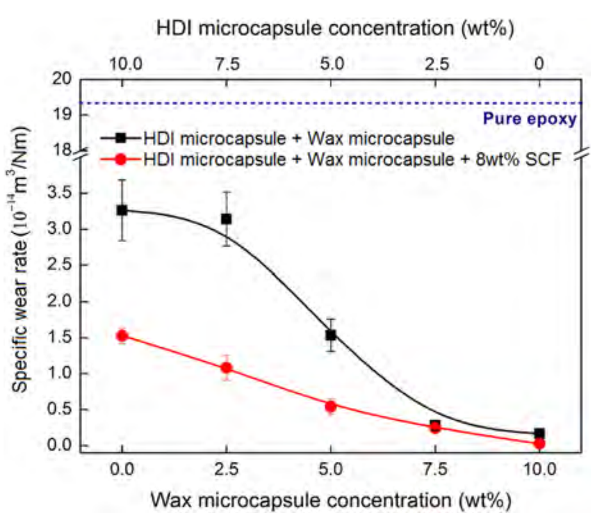

Fig. 7. Specific wear rates of neat epoxy and unitary, binary and ternary epoxy composites tested under the same conditions as described in Fig. 5.

specific wear rates of the unitary epoxy composites with 10 wt% HDI filled microcapsules, and 10 wt% wax filled microcapsules are about 3.26 and 0.17×10^{-14} m^3/Nm, respectively, which indicates that the incorporation of 10 wt% wax filled microcapsules gives rise to the much lower wear of the unitary epoxy composite than that of the neat epoxy compared to that of 10 wt% HDI filled microcapsules. As a result, the specific wear rate of the binary epoxy composites with a mixture of wax filled microcapsules and HDI filled microcapsules decreases from about 3.14×10^{-14} m^3/Nm to about 0.28×10^{-14} m^3/Nm with increased content of wax filled microcapsules from 2.5 to 7.5 wt%.

In Fig. 7, the specific wear rate of the binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs is about 0.03×10^{-14} m^3/Nm that is lower than that (about 1.53×10^{-14} m^3/Nm) of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs due to the more effective lubricating effect of released wax lubricant. In addition, their specific wear rates are lower compared to those of the unitary epoxy composites with respective microcapsules, indicating that the wear of the unitary epoxy composites further decreases with the addition of 8 wt% SCFs.

The ternary epoxy composites with a mixture of wax filled microcapsules, HDI filled microcapsules and SCFs have a decrease in their specific wear rate from about 1.08×10^{-14} m^3/Nm to about 0.24×10^{-14} m^3/Nm with increased content of wax filled microcapsules from 2.5 to 7.5 wt% as shown in Fig. 7. It can be seen that the specific wear rates of the ternary epoxy composites are significantly lower than those of the binary composites with a mixture of wax filled microcapsules and HDI filled microcapsules as a result of the incorporation of 8 wt% SCFs. The binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs has the lowest specific wear rate among the epoxy composites used (Fig. 7), which is in agreement with its lowest friction coefficient (Fig. 5).

3.5. *Wear morphologies of unitary, binary and ternary epoxy composites*

Fig. 8a shows the wear morphology of the neat epoxy on which micro-wave features caused by surface fatigue are apparently found [19–22,42,43]. As shown in Fig. 8b, no observation of ruptured microcapsules on the wear track of the unitary epoxy composites with 10 wt% HDI filled microcapsules is indicative of the effective self-healing of the ruptures because the released HDI liquid heals the ruptures with newly formed polyurea materials via its rapid reaction with mositure [22,27–29]. Although single holes are apparently found on the surface of the unitary epoxy composite with 10 wt% wax filled microcapsules as shown in Fig. 8c, the incorporation of 10 wt% wax filled microcapsules gives rise to a much smoother wear morphology of the composite because the released wax lubricant significantly lowers the wear and suppresses the surface fatigue [20,21,30].

Comparison of Fig. 8d and e clearly shows that the increased amount of released HDI core liquid and the decreased number of larger wax filled microcapsules result in the suppression of ruptured microcapsules on the wear track of the binary epoxy composite with a mixture of 7.5 wt% HDI filled microcapsules and 2.5 wt% wax filled microcapsules. However, the binary epoxy composite with a mixture of 7.5 wt% HDI filled microcapsules and 2.5 wt% wax filled microcapsules (Fig. 8d) has a larger wear track than the binary epoxy composite with a mixture of 2.5 wt% HDI filled microcapsules and 7.5 wt% wax filled microcapsules (Fig. 8e) due to the less amount of released wax lubricant during the sliding. It confirms that the released wax lubricant has a more

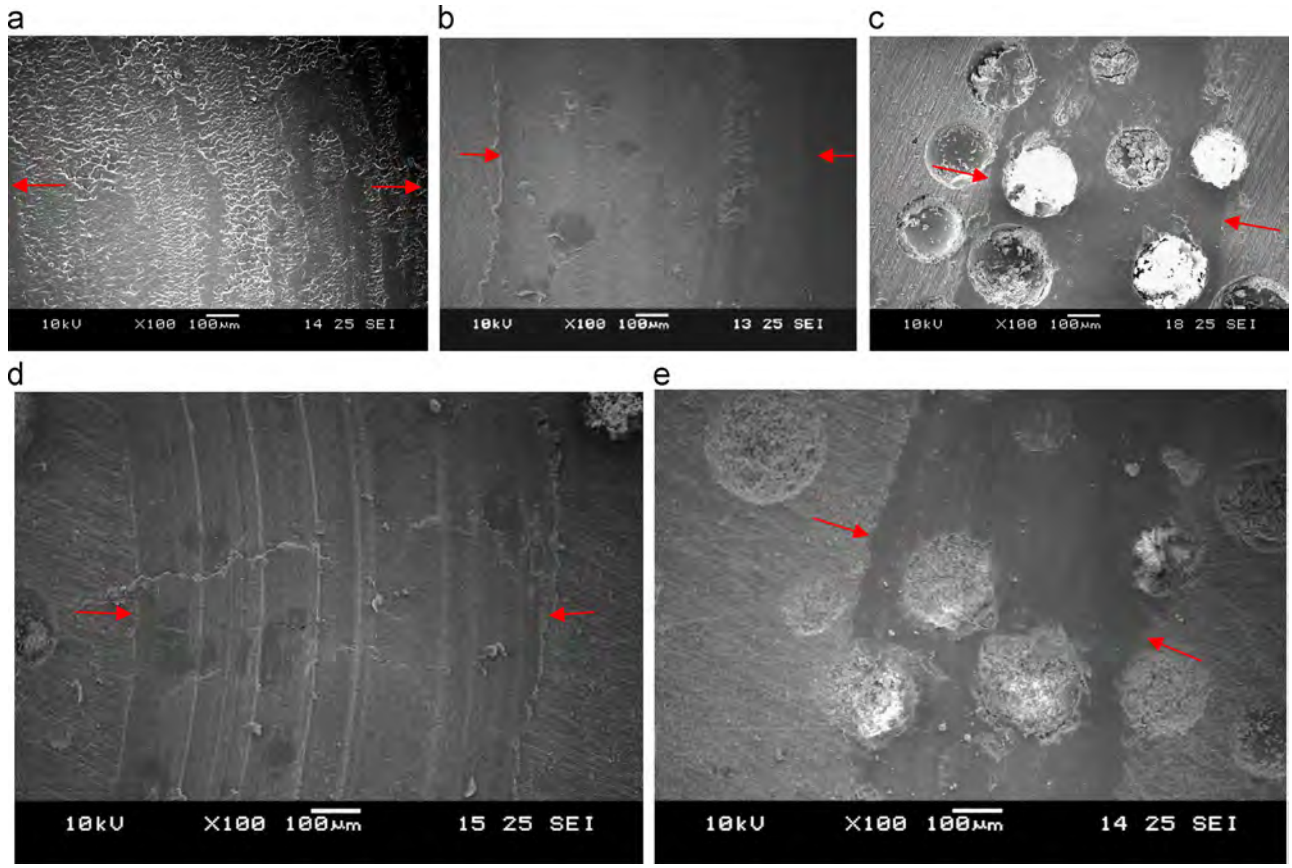

Fig. 8. SEM micrographs showing wear morphologies of (a) neat epoxy, unitary epoxy composites with (b) 10 wt% HDI filled microcapsules, and (c) 10 wt% filled wax filled microcapsules, and binary epoxy composites with mixtures of (d) 7.5 wt% HDI filled microcapsules and 2.5 wt% wax filled microcapsules, and (e) 2.5 wt% HDI filled microcapsules and 7.5 wt% wax filled microcapsules observed after tribological tests.

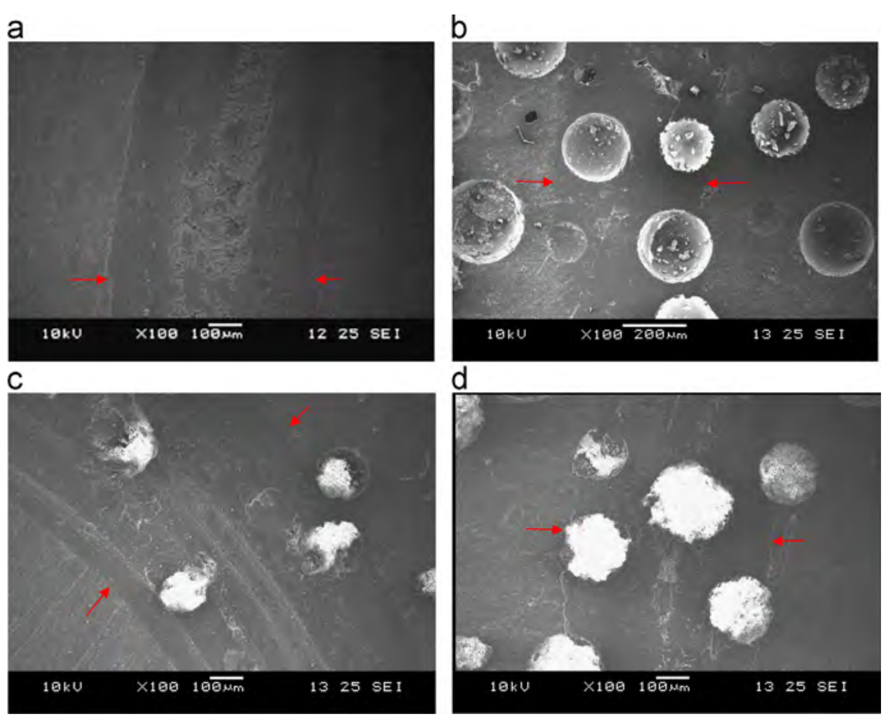

Fig. 9. SEM micrographs showing wear morphologies of binary epoxy composites with mixtures of (a) 10 wt% HDI filled microcapsules and 8 wt% SCFs, and (b) 10 wt% wax filled microcapsules and 8 wt% SCFs, and ternary epoxy composites with mixtures of (c) 7.5 wt% HDI filled microcapsules, 2.5 wt% wax filled microcapsules and 8 wt% SCFs, and (d) 2.5 wt% HDI filled microcapsules, 7.5 wt% wax filled microcapsules and 8 wt% SCFs observed after tribological tests.

significant influence on the wear of the binary epoxy composites than the released HDI liquid.

The binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs (Fig. 9a) has a smaller wear track than the unitary epoxy composite with 10 wt% HDI filled microcapsules (Fig. 8b) due to the solid lubricating and free-rolling effects of incorporated SCFs [5,6,9,16,20,30]. However, the significant removal of materials from deeper regions is apparently found in the center of the wear track of the binary epoxy composite with a mixture of 10 wt% HDI filled microcapsules and 8 wt% SCFs where the contact pressure is highest, which is indicative of the promoted surface fatigue associated with the additon of 8 wt% SCFs together with HDI filled microcapsules. The possible reason is that the released HDI core liquid lessens the solid lubricating effect of SCFs during the prolonged sliding by covering them with newly formed polyurea layers so that the repeated sliding of the steel ball initiates minute cracks at polymer/SCF interfaces, propagates them along the interfaces via debonding of the SCFs, and eventually removes surface materials from the deeper regions. The binary epoxy composite with a mixture of 10 wt% wax filled microcapsules and 8 wt% SCFs (Fig. 9b) exhibits a less apparent wear track than the unitary epoxy composite with 10 wt% wax filled microcapsules (Fig. 8c) due to the combined lubricating effects of released SCFs and wax lubricant.

The wear track of the ternary epoxy composite with a mixture of 7.5 wt% HDI filled microcapsules, 2.5 wt% wax filled microcapsules and 8 wt% SCFs (Fig. 9c) is apparently larger than that of the ternary epoxy composite with a mixture of 2.5 wt% HDI filled microcapsules, 7.5 wt% wax filled microcapsules and 8 wt% SCFs (Fig. 9d) as a result of the less amount of released wax lubricant while the ternary epoxy composite with higher content of HDI filled microcapsules has the smaller number of ruptured microcapsules on the wear track due to the higher amount of released HDI core liquid and the lower content of wax filled microcapsules. However, it is clear that the ternary epoxy composites (Fig. 9c and d) have less wear than the binary epoxy composites (Fig. 8d and e), confirming that the addition of 8 wt% SCFs improves the wear resistance of the epoxy composites.

4. Conclusions

In this study, the mechanical and tribological properties of the unitary, binary and tenary epoxy composites developed with microcapsules or/and SCFs were systematically investigated. The following conclusions were drawn.

- The incorporation of wax filled microcapsules gave rise to the lower hardness of the unitary epoxy composites than that of HDI filled microcapsules due to the larger sizes of wax filled microcapsules. As a result, the binary and ternary epoxy composites had a decrease in their hardnesses with increased content of wax filled microcapsules. It indicated that the wax filled microcapsules had a more significant influence on the hardness of the epoxy composites compared to the HDI filled microcapsules. The addition of 8 wt% SCFs resulted in the significantly increased hardness of the epoxy composites. It was clear that the decreased hardness of the epoxy composites associated with the incorporation of microcapsules could be improved by the addition of rigid SCFs.
- The tribological results clearly showed that the unitary epoxy composites with wax filled microcapsules tested against the steel ball had lower friction and wear than the ones with HDI filled microcapsules, indicating that the released wax lubricant had a more significant influence on the tribological performance of the epoxy composites than the released HDI core liquid. It was confirmed by the decreased friction and wear of the binary and ternary epoxy composites with increased content of wax filled microcapsules as a result of the increased amount of released wax lubricant. In addition, the friction and wear of the binary and ternary epoxy composites were further decreased by the addition of 8 wt% SCFs through the solid lubricating and free rolling effects of incorporated SCFs.

Acknowledgment

The authors would like to acknowledge the financial support from the Materials Innovation for Marine and Offshore (MIMO) program with the Grant numbers of SERC1123004028 and SERC1123004032 under the Agency for Science, Technology and Research (A*Star) of Singapore.

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