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
0043-1648/

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.