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Optimization of tribological and mechanical properties of epoxy through hybrid filling

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ABSTRACT

In the present work, epoxy based quaternary composites were produced by filling lubricant oil-loaded microcapsules, surface grafted nano-SiO_2 and discontinuous carbon fibers. Through orthographic tests, the optimal contents of the fillers were determined for achieving significantly improved tribological properties. The lowest specific wear rate and friction coefficient of the composite can be 9.8×10^{-7} $mm^3/N\,m$ and 0.12, respectively, much lower than those of unfilled epoxy, i.e. 1.3×10^{-4} $mm^3/N\,m$ and 0.56. In addition, mechanical properties, especially the maximal loading ability, of the quaternary composite were evidently higher than those of the binary composite with oil-loaded microcapsules. The oil released from the broken microcapsules during sliding wear mainly accounted for the lubrication, while nano-SiO_2 and carbon fibers serve as both solid lubricant and reinforcement. As a result, positive synergetic effect appeared and the proposed quaternary composites might be applicable in practice.

1. Introduction

Epoxy possesses on-the-spot processing characteristics, good affinity to heterogeneous materials, considerable creep and solvent resistance, and higher operating temperature. As a result, it finds increasing use in a wide range of engineering applications. In the case of tribological environments, however, it mostly could not be utilized alone due to its three-dimensional network structure as compared with thermoplastics. To satisfy demands of consumers for various working conditions, fillers have to be incorporated to formulate wear resistant composite materials [1].

Recently, an approach was developed in our lab by adding lubricant oil-loaded microcapsules into epoxy composites [2], which integrates the merit of fluid lubrication but excludes the drawbacks of external lubrication. During sliding wear, the capsules were damaged by the asperities of the counterface, releasing the oil to the contact area. Owing to the lubrication effect of the librated oil, and the entrapment of wear particles in the cavities left by the ruptured capsules, significant reduction in frictional coefficient and specific wear rate was observed. It is worth noting that, however, the embedded soft capsules resulted in significantly deteriorated mechanical performance of epoxy. Load bearing capability of the composites, an important feature of tribological components, has to be lowered as a result.

To solve the problem, we plan to employ hybrid fillers including the oil-loaded microcapsules, short carbon fiber and silica nanoparticles. In fact, combination of fibrous and particulates fillers has proved to be an effective way to improve overall performance of polymeric composites even when friction and wear are concerned [3–7]. We also found positive synergetic effect in the epoxy based composites containing nano-SiO_2 and short carbon fibers [8], that is, both wear rate and friction coefficient of the hybrid composites were significantly lower than those of the composites containing individual nano-SiO_2 or short carbon fiber. In addition, the same trends were observed in the case of mechanical properties measurements. Therefore, it can be reasonably expected that the above recipe would impart ultra low friction and wear rate as well as higher load bearing capacity to epoxy.

Hereinafter, feasibility of our consideration is verified. More importantly, the composites compositions are optimized in terms of orthographic factorial design [9] to achieve the target at relatively lower filler content. For enhancing interfacial interaction between epoxy matrix and nano-SiO_2, graft treatment of the particles with polystyrene-maleic anhydride (SMA) is conducted, so that the nanoparticles can be covalently connected to epoxy through the reaction between anhydride and epoxide groups during curing.

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2. Experimental

2.1. Materials

Bisphenol-A epoxy resin (type E-51), used as the matrix polymer of the composites, was supplied by Guangzhou Dongfeng Chemical Co., China. The curing agent, 4,4-diamino-diphenylsulfone (DDS), was purchased from the National Medicine Co. of Shanghai, China. Lubricant oil (trade name: 70SN, density = 0.8175 g/cm^3) was provided by Guangzhou Mechanical Engineering Research Institute, China. The lubricant oil-loaded microcapsules (diameter: 110 μm; core content: 82.9 wt.%) were prepared by in situ polymerization with poly(melamine-formaldehyde) (PMF) as the shell material [2]. Pitch-based short carbon fibers (SCF) with an average diameter of 7 μm and length of 1 mm were provided by Shanghai Special Fiber Co., China. Nano-SiO_2 (Aerosil 200) was supplied by Degussa Co., Germany, with an average size of 12 nm and a specific surface area of 200 m^2/g. Polystyrene-maleic anhydride was grafted onto the nanoparticles (denoted as SiO_2-g-SMA) according to the method described elsewhere [8]. The grafted nanoparticles with a percent grafting of 17.2% were selected to fill the epoxy composites.

2.2. Composites preparation

Epoxy composites were prepared by firstly mixing the pre-weighted quantities of epoxy and SiO_2-g-SMA at 80 °C with mechanical stirring for 3 h and ultrasonication for 1 h. Afterwards, the lubricant oil-loaded microcapsules were incorporated under stirring for 1 h. Then the mixture was compounded with SCF. After stirring for 30 min at a speed of 400 rpm, the compounds were heated to 130 °C and the curing agent DDS (32 phr, phr = parts per hundreds of epoxy resin by weight) was added with stirring for 10 min. For curing the composites, the procedures shown below were followed step by step: 3 h at 100 °C, 2 h at 140 °C, 2 h at 180 °C and 2 h at 200 °C.

The specimens for sliding wear tests were machined with a geometry of 16 mm × 10 mm × 6 mm, resulting in an apparent contact area of about 60 mm^2. Rectangular bars with sizes of 80 mm × 10 mm × 4 mm were used for three-point bending tests.

2.3. Characterization

Three-point bending tests were carried out using a SANS universal tester (type: CMT6103) in accordance with GB/T 2570-1995 standard at a crosshead speed of 5 mm/min. All the specimens were stored at 30 °C and a relative humidity of 50% for 48 h prior to measurements at the same temperature and relative humidity.

Unlubricated sliding wear tests were carried out on a block-on-ring apparatus (M-200) under a constant velocity of 0.42 m/s and a constant pressure of 3MPa. The carbon steel ring (0.42–0.45 wt.% C, 0.17–0.37 wt.% Si and 0.5–0.8 wt.% Mn, HRC 50) had a diameter of 40 mm, and an average initial surface roughness was about 0.2 μm. Prior to wear testing, all the samples were pre-worn (by SiC abrasive paper) to average surface conditions and to reduce the running-in period. The actual steady-state test was conducted for 3 h using the same steel ring as that used for the pre-worn procedure. Friction coefficient was obtained from the frictional torque measured by a load cell sensor. After each wear test, the specimen's weight loss, Δm, was weighed, so that the specific wear rate, $\dot{w}_s$, can be calculated from:

$$\dot{w}_s = \frac{\Delta m}{\rho \cdot F \cdot \Delta L} \quad (1)$$

where ρ is the specimen density, F is the normal load applied to the specimen during sliding, and ΔL is the total sliding distance. At least three specimens of each composition were measured. Worn surfaces of the specimens and the counterparts were examined by a Quanta 400F scanning electronic microscope (SEM).

Static contact angles of water on steel rings (i.e. counterparts) were measured with a drop shape analysis system DSA100 by gently placing a water droplet (10 μl) onto a counterpart surface over the time span of 1 min for each test. The presented values were averaged over at least five different locations. X-ray photoelectron spectra (XPS) of the composites' surfaces were recorded by means of a Thermo VG Scientific ESCALab250 X-ray photoelectron spectrometer with an energy step size of 1.0 eV. A monochromatic Al Kα source was used with a spot size of 500 μm in diameter. The pass energy was set at 70 eV for the survey spectra and at 20 eV for the high-resolution spectra of all elements of interest. Peak fitting was performed using the supplier's software (XPSPEAK). Prior to the XPS measurements, the specimens were immersed in acetone with ultrasonication for cleaning.

Table 1
Creation of an orthographic factorial design of three factors and four levels.

Factor	Level			
	1	2	3	4
Content of oil-loaded microcapsules, C_m (phr)	3	6	8	10
Content of SiO_2, C_p (phr)	1	3	5	10
Content of SCF, C_f (phr)	0.5	1	2	5

2.4. Optimization of filler contents

An orthogonal $L_{16}(4)^5$ test design was used to find out the optimal filler contents of the composites (Tables 1 and 2). The term $L_{16}(4)^5$ represents an orthogonal array that handles up to 5 factors (i.e. 5 columns in the array) at 4 levels each, and requires 16 trial runs. When the number of factors is less than 5, the remaining

Table 2
Results analysis of the orthographic factorial design.

Test no.	Factor					μ	$\dot{w}_s$ ($\times 10^{-6}$ mm^3/N m)
	C_m	C_p	C_f	–[a]	–[a]		
1	1	1	1	1	1	0.51	18.92
2	1	2	2	2	2	0.42	10.74
3	1	3	3	3	3	0.41	9.65
4	1	4	4	4	4	0.48	8.23
5	2	1	2	3	4	0.23	4.78
6	2	2	1	4	3	0.20	5.66
7	2	3	4	1	2	0.18	3.22
8	2	4	3	2	1	0.25	4.13
9	3	1	3	4	2	0.14	1.01
10	3	2	4	3	1	0.13	0.96
11	3	3	1	2	4	0.12	1.46
12	3	4	2	1	3	0.16	1.25
13	4	1	4	2	3	0.13	0.87
14	4	2	3	1	4	0.12	0.98
15	4	3	2	4	1	0.11	0.75
16	4	4	1	3	2	0.15	1.08
μ							
$K1$[b]	0.455	0.253	0.245	0.242	0.250		
$K2$	0.215	0.217	0.230	0.230	0.223		
$K3$	0.138	0.205	0.230	0.230	0.225		
$K4$	0.128	0.260	0.230	0.232	0.237		
R[c]	0.327	0.055	0.015	0.012	0.027		
$\dot{w}_s$ ($\times 10^{-6}$ mm^3/N m)							
$K1$	11.885	6.395	6.780	6.093	6.190		
$K2$	4.448	4.585	4.380	4.300	4.013		
$K3$	1.170	3.770	3.943	4.117	4.358		
$K4$	0.920	3.672	3.320	3.913	3.863		
R	10.965	2.723	3.460	2.180	2.327		

[a] Dummy factors.
[b] Ki denotes the average of friction coefficient or specific wear rate with level i.
[c] R denotes the result of extreme analysis.