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Friction and wear of high electrical conductive carbon nanotube buckypaper/epoxy composites

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ABSTRACT

Carbon nanotube (CNT) buckypaper (BP) is a kind of non-woven nano-fiber film with excellent mechanical and electrical properties. Herein, we applied it to enhance the tribological performance of epoxy resin. A relatively big BP film with a diameter up to 285 mm was obtained through a solution filtration method. The CNTs were surface-modified by ozone in order to improve their interfacial adhesion with the matrix. It was found that the CNTs were well impregnated by the epoxy resin and the interfacial adhesion was fairly good, especially for the modified ones. The wear tests were performed using a ball-on-disc ("steel-on-polymer") configuration under dry sliding condition. Depending on the conditions of the wear tests, the frictional coefficient can be reduced from 0.71 of the neat resin down to 0.32 of ozone-modified BP/epoxy composite and the wear resistance can be improved by more than 4 times. The SEM morphologies and Raman spectra of worn surfaces for the samples were given to explain the possible wear micromechanisms. The BP/epoxy composites, even after subjected to harsh wear, still retained high electrical conductivity due to the robust CNTs network.

1. Introduction

Polymers, e.g. epoxy, polyamide, polyacrylate and polyetheretherketone, are increasingly used for developing anti-wear composites and coatings [1–3], owing to their lightweight, flexibility, excellent corrosion resistance, good processability and low cost, compared to metals and ceramics.

Adding appropriate fillers to polymers can further tailor their wear and friction behaviors [3–5]. Among the various fillers, carbon-based fillers, such as carbon fibers, graphite, graphene and carbon nanotubes (CNTs), are frequently used to enhance the wear resistance of the polymer matrix. Carbon fibers can be utilized in continuous or discontinuous forms. With the addition of 15–25% volume percent of short carbon fibers, the wear resistance of polymers is dramatically increased [6] and the coefficient of friction (COF) decreases in most cases [7,8]. Previous studies indicate that at the beginning of the wear process the carbon fibers could support the major applied load and protect the polymer matrix from being ploughed and torn [9]. With the increase of the applied load, sliding velocity or sliding time, the carbon fibers gradually thin. When they fail to support the applied load, they are broken and pulled out of the matrix under shearing load [1,6].

Graphite, as a traditional solid lubricant, is composed of parallel graphene layers which connected with each other via van der Waals interaction. Under wear process, the graphene layers are dissociated by shear stress and transferred onto the counterface, thereby forming a lubricating transfer film. It is reported that graphite reinforced polymer composites show an obvious anti-wear and self-lubricating effect in comparison with the neat polymers under normal test conditions [7]. In some studies, combining the graphite flakes with other fillers, such as short carbon fibers and nanoparticles, is found to have synergetic anti-wear effect [10–12].

Graphene, as an emerging member of the carbon family, has received remarkable attention due to its excellent mechanical and electrical properties. It is also considered to be a promising candidate in the anti-wear field. For example, it can serve as a protecting film for various substrates (Si, PMMA, PS, etc) in microelectromechanical systems [13,14] and as the additive for lubricating liquids [15] or polymers [16]. Some works indicate that graphene, similar to graphite, shows self-lubricating effects in polymer matrix, leading to the reduction of the COF values [17,18] and wear rate [19–21].

CNTs are also reported to exhibit wear-reducing effect in polymers owing to their excellent mechanical and thermal performance [5,22–25]. It is demonstrated that CNTs can improve the mechanical properties of the composites such as elastic modulus, failure strength and fracture toughness [26]. At the same time they can decrease the wear volume and COF of the matrix due to the

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self-lubricating effect of the CNTs [27]. It should be noted that the large aspect ratio and huge specific surface area of CNTs will bring about significant thickening effect to polymers (especially for epoxy resin), and thus result in processing difficulty and poor dispersion of the CNTs. The weight fractions of CNTs in epoxy composites are often less than 5% [28] in most cases. So it is usually not feasible to fabricate epoxy composites with high-loading of CNTs by traditional mechanical dispersing techniques.

Buckypaper (BP), as a non-woven film of CNTs, inherits the superior properties of CNTs and is believed to be a good candidate for rendering multifunctional properties to polymers [29–32]. BP-based polymer composites with high loading of CNTs (as high as 20–70 wt% [29,33]) exhibit ultrahigh tensile strength and Young's modulus, which are comparable to those of the unidirectional carbon-fiber reinforced composites [31]. Moreover, owing to the network structure of CNTs, BP-based polymer composites show much higher electrical conductivity (10^2–10^3 S/m [34,35]) than that of polymer composites filled with graphite, graphene or CNTs, the conductivity of which only reaches the anti-static level (10^{-6}–10^{-1} S/m) [20,36,37]. To the best of our knowledge, so far, studies on tribological behaviors of BP-based composites have not been found in the open literature.

Based on such a background, in this work we systematically investigated the mechanical properties, wear and friction properties as well as the electrical conductivities of the BP/epoxy composites. The CNTs were functionalized by a convenient ozone treatment [38] to tailor their interface with the epoxy matrix. The BP/epoxy composites not only showed excellent wear and friction resistance, but also possessed high electrical conductivity before and after the wear tests. These features may make them applicable in the fields where both excellent wear resistance and high electrical conductivity are required simultaneously. The possible wear mechanisms were further discussed based on the Raman analysis and the SEM morphology.

2. Experimental

2.1. Materials

The pristine CNTs synthesized by floating catalysis process (6–8 nm in diameter, up to 50 μm in length, and purity >93 wt%, FloTube™ 7000) were supplied by CNano Technology Ltd., Beijing, China. The O_3 was produced by an O_3 generator (CF-G-3–10 g, Qindao Guolin Industry Co. Ltd., China) using oxygen (O_2) as the gas supplier. The neat epoxy resin was a bisphenol-A type of epoxy with an epoxy equivalent weight of 185 g/eq (Wuxi Resin Factory of Bluestar New Chemical Materials Co., Ltd., China). The curing agent (Albidur HE600) was composed of 4-methylhexahydrophtahlic anhydride (MHHPA, Puyang Huicheng Chemicals Co., Ltd., China) and *N*, *N*-benzyldimethylamide (BDA, Sino-pharm Chemical Reagent Co., Ltd., China) with a weight ratio of 100:1.

2.2. Ozone modification of CNTs

2 g pristine CNTs were placed into a home-made vertical reactor, which the O_3/O_2 mixture passed through (O_3 concentration ≈3 wt%) at a flow rate of 200 L/h. The oxidation process lasted for 2 h at room temperature [38].

2.3. Preparation of BP and BP/EP composites

BP films were fabricated through a solution filtration method as described in our previous work [32]. The BPs used in this work were ~42 mm in diameter and ~150 μm in thickness. Bigger BP films (with a diameter up to ~285 mm, Fig. 1a), if needed, can be obtained by the same method only using more CNTs dispersion and larger filter equipment.

The BP/epoxy composite samples for the wear tests were prepared as illustrated in Fig. 1b. The BP was soaked in a mixture of epoxy resin, curing agent and acetone (weight ratio = 37:34:35) at 45 °C for 4 h and thereafter at 65 °C for 4 h under vacuum to be fully infiltrated by the resin (Step 1). The wet BP film was laid on the mould part A (Step 2). Then a certain amount of epoxy-curing agent mixture was further poured onto the top of the wet film (Step 3). The additional epoxy resin served as the sample supporter during wear tests. The composite samples were cured in oven according to the recommended procedure [26] (Step 4). The neat epoxy samples were prepared by the same way. The thickness of the samples is about 4 mm.

For clarity, in the following sections the prefix '*p*-' is used to denote the pristine CNTs and their related BP, BP/epoxy composite samples, and prefix '*f*-' is used to denote the ozone-modified matters. For example, *p*-BP denotes the buckypaper sample made up of pristine CNTs.

2.4. Weight fraction of CNTs in the composites

To analyze the weight fraction of CNTs in the composites, thermal gravity analysis (TGA, TA Instrument SDT Q600) experiments were carried out on the cured composite films. The samples were held at 100 °C for 10 min to eliminate the residual water, and then heated to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere with the nitrogen flow rate of 100 mL/min. Three tests were performed on each sample to obtain an average value of the residue percentage of the samples. According to previous works [32,39], the weight fraction of CNTs (w_{CNTs}) can be calculated from the TGA thermograms (Fig. 2) using the following equation:

$$w_{\mathrm{CNTs}} = \frac{R_{compos} - R_{EP}}{R_{BP} - R_{EP}} \times R_{BP} \tag{1}$$

where, R_{BP}, R_{EP} and R_{compos} are the residue percentage of the BP, the epoxy matrix and the composite sample obtained from TGA thermograms, respectively. The weight fractions of CNTs were calculated to be 27 wt% and 30 wt% for *p*-BP/EP and *f*-BP/EP samples, respectively. The slightly increased weight fraction for the latter could be ascribed to the enhanced stacking density of the *f*-CNTs, which has also been reported in Ref. [40].

2.5. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of the CNTs were recorded using Perkin Elmer Spectrum One spectrometer. The CNTs were pressed into a pellet with potassium bromide (KBr) and scanned from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using ESCALAB 250Xi electron spectrometer with Mg Kα (1253.6 eV) radiation. The energy step was 0.05 eV and the pressure in the XPS analyzing vacuum chamber was less than 3×10^{-9} mbar. Peak fitting of the C 1s spectra for both samples was carried out using a Gaussian–Lorentzian function after performing a Shirley background correction. Raman spectra of the *p*-CNTs, *f*-CNTs and the composite samples before/after the wear tests were obtained via Renishaw 2000 at an excitation wavelength of 514 nm.

The tensile properties of the epoxy, BP and their composite films were measured by a dynamic mechanical analyzer (TA Instruments, DMA Q800). Samples were cut manually by a razor blade into strips (30 mm × 2 mm × ~50 μm) and then dried at 60 °C for 12 h under vacuum before tests. The static tensile tests were conducted in a ramp displacement mode with a pre-strain