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The influence of nano/micro hybrid structure on the mechanical and self-sensing properties of carbon nanotube-microparticle reinforced epoxy matrix composite

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ABSTRACT

Nano/micrometer hybrids are prepared by chemical vapor deposition growth of carbon nanotubes (CNTs) on SiC, Al_2O_3 and graphene nanoplatelet (GNP). The mechanical and self-sensing behaviors of the hybrids reinforced epoxy composites are found to be highly dependent on CNT aspect ratio (*AR*), organization and substrates. The CNT–GNP hybrids exhibit the most significant reinforcing effectiveness, among the three hybrids with *AR*1200. During tensile loading, the *in situ* electrical resistance of the CNT–GNP/epoxy and the CNT–SiC/epoxy composites gradually increases to a maximum value and then decreases, which is remarkably different from the monotonic increase in the CNT–Al_2O_3/epoxy composites. However, the CNT–Al_2O_3 with increased $AR \geqslant 2000$ endows the similar resistance change as the other two hybrids. Besides, when $AR < 3200$, the tensile modulus and strength of the CNT–Al_2O_3/epoxy composites gradually increase with *AR*. The interrelationship between the hybrid structure and the mechanical and self-sensing behaviors of the composites are analyzed.

1. Introduction

Carbon nanotubes (CNTs) with exceptional mechanical [1] and electrical properties [2] have emerged as superior multifunctional fillers for polymer composites. A significant improvement of composite properties would be achieved by incorporating only a small amount of CNTs [3–6]. Such CNT-based polymer composites are ideal candidate materials in numerous engineering applications including automotive, aerospace and electronics. With regard to the structural composites, their reliability and long-term safety is a critical issue. For some electrically conductive CNT/polymer composites, it is worth noting that their *in situ* electrical resistance change makes them capable to *in situ* monitor deformation or damage evolution under loading [7–10]. Nowadays, the development of CNT/polymer composites with excellent structural and self-sensing properties has been focused on.

The efficient stress transfer from CNTs to the matrix is prerequisite to attain required mechanical properties of the composites, which is dependent on the CNT dispersion [11], orientation [12] and aspect ratio [13], and the CNT/matrix interfacial properties [14,15]. It has been generally accepted that the uniform dispersion and large aspect ratios of CNTs could enable enhanced mechanical properties in the composites [13,16]. Besides, for the composites with self-sensing capabilities, the formation of continuous conductive networks is needed. In this case, the percolation threshold is also related to CNT dispersion, aspect ratio and orientation [12,17–20]. However, most of the available studies on the self-sensing composites are limited to randomly distributed CNTs as *in situ* sensors [21–23]. In general, their *in situ* electrical resistance monotonically increases under tensile loading till the catastrophic failure. More recently, the effect of CNT alignment on the self-sensing properties of the composites has also been addressed [24,25]. The anisotropy of the aligned networks results in improved sensing capabilities. It is reasonable to conclude that the *in situ* sensing behaviors are structure-dependent, which can be controlled by tailoring the morphology of CNT conductive networks. Thus, in order to exploit multifunctional CNT/polymer composites with outstanding mechanical and self-sensing properties, the challenging tasks consist in attaining uniform CNT dispersion, optimal CNT aspect ratio and arrangement as well as a strong interface interaction between the CNTs and polymer matrix.

The hybrid fillers composed of CNTs and microparticles have been reported to possess certain advantages in achieving more controllable CNT dispersion and improved interfacial properties in the polymer matrix, compared to the randomly distributed CNTs. These hybrid architectures were obtained by self-organizing CNTs grown on microsubstrate surface, rather than simply mechanically mixed them. And the CNT aspect ratio can be controlled by varying the growth parameters [26,27]. These

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multi-scale hybrids with CNTs grown on SiC microplates or graphene nanoplatelets showed the enhanced mechanical, electrical properties [28–30] and novel self-sensing behaviors [31,32] at low CNT contents. However, the related research on these multifunctional hybrids is still at an early stage and their underlying reinforcement mechanisms in the composites are not clear to date. Understanding the effect of the hybrid structure on the mechanical and self-sensing properties of the composites is extremely desired in order to fully take advantage of these nano/micro hybrids.

In this paper, three kinds of hybrid fillers with CNTs grown on SiC microplates (CNT–SiC), Al_2O_3 microparticles (CNT–Al_2O_3) and graphene nanoplatelets (CNT–GNP) were synthesized by chemical vapor deposition (CVD) process. The CNT aspect ratios and organizations in the hybrids can be adjusted by optimizing the CVD conditions. Then electrically percolative epoxy composites reinforced with the various hybrids were fabricated using mechanical shearing methods. Mechanical and self-sensing properties of the composites were simultaneously investigated. The underlying mechanisms associated to the composite properties with relation to the hybrid structure (CNT aspect ratio, orientation and substrate morphology) were analyzed.

2. Experimental

2.1. Materials and preparation

The pristine CNTs (randomly distributed) with 10–15 μm in length (synthesized using CVD) were provided by Shenzhen Nanotech Port Company. And their morphology has been stated in our recent research [32]. The hybrid structures were synthesized by growing multi-walled CNTs on three different substrates (Al_2O_3, SiC and GNPs), respectively, using a CVD procedure [26,28,29]. In brief, ferrocene (concentrated at 0.05 g ml^{-1}) was dissolved in xylene solution to serve as catalyst precursor. Then, the mixture was fed by a syringe system and carried into the preheated stable reaction zone in the form of spray by carrier gas argon mixed with 10–40% hydrogen. The total gas flow rate was fixed at 1 L min^{-1}. Acetylene (10 ml min^{-1}) was injected as another carbon source. The CNT synthesis temperatures used were between 550 and 600 °C. The CNT growth time varied from 2 to 30 min in order to obtain CNTs of different lengths. After, the reactor was cooled down to room temperature under argon atmosphere (1 L min^{-1}). Here, Al_2O_3 particles with 3–10 μm in size were purchased from Performance Ceramic Company (Peninsula, OH, USA). SiC microplates with the size of ~2 μm (see Fig. 1a) were provided by Marion Technologies, France. GNPs with high aspect ratio, i.e., 3–4 μm in length and ~30 nm in thickness (Fig. 1b) were obtained from Xiamen Kano Graphene Technology Co., Ltd. The basic information of the different fillers used is listed in Table 1. Epoxy resin (1080S, Resoltech Ltd., France) was used as the matrix material.

Table 1
Basic information of the randomly distributed CNTs (*rand*-CNTs), the CNTs grown on the particles and the particle substrates.

Materials	CNT length (μm)/diameter (nm)	Average CNT aspect ratio	CNT density (g/cm^3)	Substrate density (g/cm^3)
rand-CNTs	(10 ~ 15[a])/(~10[a])	1200		
[1]CNT–Al_2O_3	(4 ~ 6)/(~10)	500		
[2]CNT–Al_2O_3	(10 ~ 15)/(~10)	1200	1.78	3.1
[3]CNT–Al_2O_3	(18 ~ 22)/(~10)	2000		
[4]CNT–Al_2O_3	(30 ~ 35)/(~10)	3200		
CNT–SiC	(10 ~ 15)/(~10)	1200	1.78	3.9
CNT–GNP	(10 ~ 15)/(~10)	1200	1.78	2.25[a]

[a] According to the values provided by the companies.

Table 2
The parameters of three-roll mill for preparing the composites.

Epoxy composites	Rotation speed of rollers (r/min)	Rotation time (min)	Roll gap (μm)
CNT + SiC(AR1200)	120	30	25
CNT + GNP(AR1200)	120	30	25
CNT + Al_2O_3(AR1200)	120	30	25
CNT–SiC(AR1200)	80	10	35
CNT–GNP(AR1200)	80	10	35
CNT–Al_2O_3(AR500)	80	10	15
CNT–Al_2O_3(AR1200)	80	10	35
CNT–Al_2O_3(AR2000)	80	10	50
CNT–Al_2O_3(AR3200)	80	10	70

The as-synthesized hybrids (CNT–Al_2O_3, CNT–SiC and CNT–GNP), the mechanical mixtures of the pristine CNTs and microparticles (CNTs + Al_2O_3, CNT + SiC and CNT + GNP) were respectively dispersed into epoxy using a three-roll mill (EXAKT 80, Germany), following well-established protocols. The parameters of the three-roll mill used for preparing the different composites are listed in Table 2. The curing agent (1084, Resoltech Ltd.) was added to the obtained suspension at mass ratio of 1/3 to the epoxy resin. The resulting mixture was degassed for 30 min, and then cured at 60 °C under 10 MPa. Dumbbell-shape samples with 1 mm in thickness, 50 mm in length and 4 mm in gage width were obtained and edge-polished for tensile testing. After being polished, the samples with dimensions about 10 × 10 × 1 mm were achieved for ac conductivity measurements. The schematic in Fig. 2 shows the detailed procedure used for the composite preparation.

2.2. Characterization

Scanning Electron Microscope (SEM) observation of the samples was carried out on Germany ZEISS, LEO 1530 Gemini. Quasi-static and incremental cyclic tensile tests were carried out on a micro-tensile machine (Instron 5544) at a fixed displacement rate of

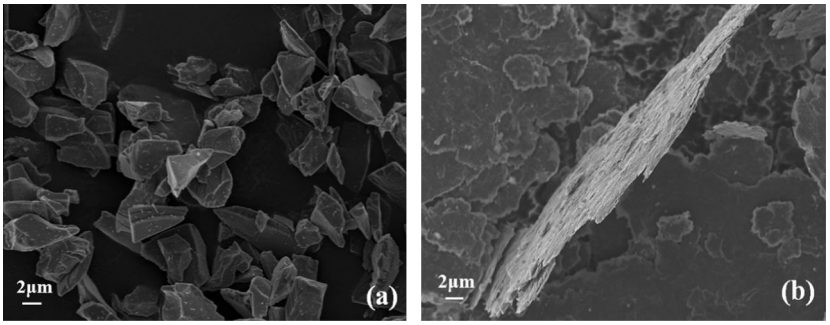

Fig. 1. SEM micrographs of the substrates used for CNT growth (a) SiC microplates; and (b) graphene nanoplatelets.