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Mechanical properties and microstructure of single-wall carbon nanotube/elastomeric epoxy composites with block copolymers

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ABSTRACT

Single-wall carbon-nanotube (SWNT) reinforced elastomeric epoxy composites were fabricated by adding 0.03 wt% SWNTs and using 0.3 wt% block copolymer to obtain a good dispersion of carbon nanotubes in the epoxy matrix. Young's modulus, fracture stress and strain of the SWNT/epoxy composites with block copolymer were increased by 141%, 127% and 43%, respectively, compared to the pure epoxy resin. Scanning electron microscopy observation revealed that using the block copolymer as a dispersing agent significantly improved both SWNT dispersion in the epoxy matrix and interfacial bonding/load transfer.

1. Introduction

Carbon nanotubes (CNTs) are ideal candidates for composite reinforcement owing to their extremely high Young's modulus, strength and aspect ratio in combination with low density [1–4]. These properties cannot be fully exploited unless CNTs are homogenously dispersed and robustly integrated in matrix materials. However, CNTs are difficult to disaggregate due to their strong van der Waals attractions, large surface area and high aspect ratio. Different dispersion methods have been investigated such as combining CNT dispersion in a solvent with ultrasonication [5,6], and chemical CNT functionalization [7,8]. However, ultrasonication alone may be unable to efficiently disperse network fragments consisting of tube bundles even on macroscopic scales [5], and unsuitable ultrasonication settings can damage CNTs [9–11]. Chemical functionalization introduces defects into the structure of CNTs and may degrade their properties [12–14].

We were the first to report the use of a block copolymer (BCP) to improve the dispersion of multi-walled CNTs (MWNTs) in rubbery epoxy composites [15]. Mechanical properties such as Young's modulus and fracture stress of such composites were about 50% higher than for pure epoxy. BCPs have since been adopted to improve CNT dispersion in various matrices: polymers [16–19] and metals [20,21].

In the present study, the same BCP was used with SWNT/epoxy composites and we discuss the resulting enhancement of mechanical properties. Mechanical characterisation is complemented by scanning electron microscopy (SEM) of the fracture surfaces. As in our previous study, an elastomeric epoxy was chosen because the low viscosity facilitates processing and a compliant matrix maximizes the strength enhancement by reinforcements [17,22] allowing the study of stress–strain behaviour up to high strain levels [23]. By using SWNTs instead of MWNTs we hope to exploit the larger specific surface area and aspect ratio which arise from the smaller diameter of single-walled structures and render them potentially superior for mechanical reinforcement. However, SWNTs aggregate more easily, which may compromise their intrinsic advantages [24]. Comparative studies of the reinforcing effect of different CNT types in polymer matrices [25,26] show partly contradictory results. This indicates that differences in dispersion between matrix and CNTs can outweigh the expected advantage of SWNTs.

2. Material and methods

The block copolymer – Disperbyk-2150 (BYK Chemie) – was chosen because it has already been shown to improve CNT

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dispersion in ethanol and epoxy resin (ER) [15,27]. The copolymer (0.01 g) was first dissolved in ethanol (0.5 g). Then SWNTs (0.001 g, diameter 1-2 nm, Chengdu Organic Chemicals) were added to the copolymer solution. This mixture was stirred for 10 min at 100 rpm. After stirring it was ultrasonicated for 5 min at room temperature/full power (T490DH, Elma, $f=40$ kHz). After adding liquid ER (3.1102 g, D.E.R. 736P, Dow Chemical), the suspensions were stirred for 30 min at 100 rpm to remove ethanol and homogenize the mixture. After stirring, hardener (1.0368 g, D.E.H. 24, Dow Chemical) was added. The solution was stirred again for 15 min at 100 rpm and was then cast into a dog-bone shaped mould with gauge section of $10\times6\times1$ mm^3. The resin was hardened in a vacuum oven at 25 °C for 18 h at a pressure of less than 1 mbar. The hardened resin (SWNT/BCP/ER) was put in the preheated oven at 100 °C for 3 h for post curing and then removed from the mould and cooled to room temperature under ambient conditions. 30 samples were produced for each case in five batches. Reference samples were made using exactly the same procedure but without BCP (SWNT/ER), with copolymer but not SWNTs (BCP/ER), and also pure epoxy resin (ER). To determine mechanical properties, all samples were tested in tension using standard testing equipment (Instron Model 3369, 1-kN force transducer). Tests were conducted at ambient temperature and at a constant cross-head speed of 3 mm/min until fracture. All strain values refer to engineering strain. Scanning electron microscopy (SEM) was used to observe the fracture surfaces. For SEM, samples were coated with a 6–8 nm layer of 60%/40% gold palladium alloy to achieve good conductivity and examined in a HITACHI S-4700 field emission scanning electron microscope at an accelerating voltage of 5 kV.

3. Results and discussion

Fig. 1a shows typical stress–strain curves of the samples. Average values for fracture strain, fracture stress and Young's modulus are shown in Fig. 1b, c and d respectively. Using the block copolymer as the dispersing agent resulted in considerable enhancement of Young's modulus, fracture stress and strain. The Young's modulus, fracture stress and strain of SWNT/BCP/ER composite specimens were increased by 141%, 127% and 43% respectively compared to pure ER; and by 41%, 44% and 27% respectively compared to SWNT/ER composites.

Fig. 2 shows SEM micrographs of the fracture surfaces of (A) SWNT/BCP/ER and (B) SWNT/ER composites. In the micrograph of the fracture surface of SWNT/BCP/ER shown in Fig. 2A-a, many small white dots can be observed (some are highlighted by white circles). Higher magnification reveals the white dots to be individual SWNTs (Fig. 2A-b). In Fig. 2B-a, the fracture surface of SWNT/ER composite is relatively smooth and only a big agglomerate (zoom in Fig. 2B-b) but no individual CNTs can be observed. Furthermore, CNTs with short broken ends can be clearly observed on the fracture surface of the SWNT/BCP/ER composites (Fig. 2A-c); while in the SWNT/ER composites, long CNT strands were pulled out (Fig. 2B-c). These observations suggest that the BCP not only enhances dispersion but also improves the interfacial bonding and therefore the load transfer between CNTs and the epoxy matrix.

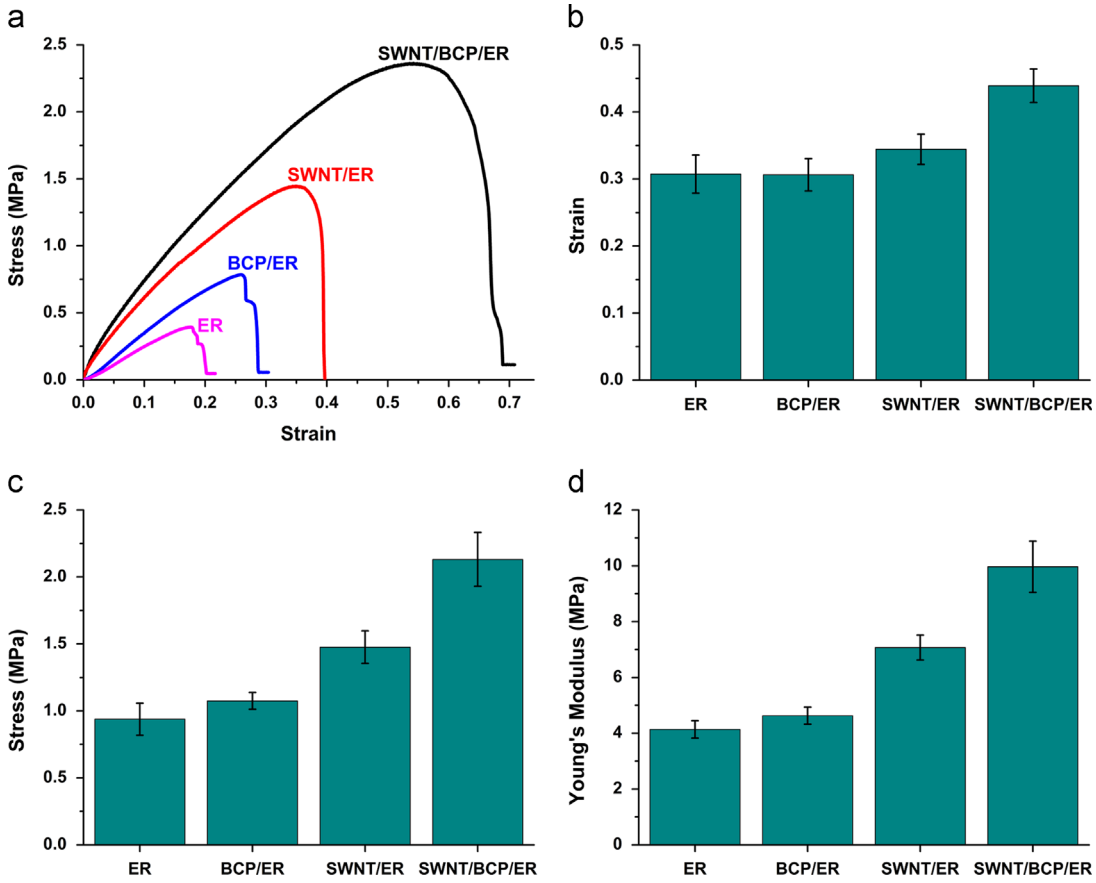

Fig. 1. (a) Typical tensile stress – (engineering) strain curves of pure epoxy resin (ER), copolymer/epoxy resin (BCP/ER), single-wall CNT/epoxy resin (SWNT/ER), single-wall CNT/copolymer/epoxy resin (SWNT/BCP/ER); comparison of (b) fracture strain, (c) fracture stress, and (d) Young's modulus as obtained from 5 sets of 6 samples for each case.