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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. The 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.

Keyword: Polymeric composites; Nanocomposites; Carbon nanotubes; Deformation and fracture; Microstructure.

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 the 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 characterization 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 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 minutes at 100 rpm. After stirring it was ultrasonicated for 5 minutes at room temperature/full power (T490DH, Elm a, f = 40 kHz). After adding liquid ER (3.1102 g, D.E.R. 736 P, Dow Chemical), the suspensions were stirred for 30 minutes 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 minutes at 100 rpm and was then cast into a dog-bone shaped mould with gauge section of 10×6×1 mm. 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

Figure 1a shows typical stress-strain curves of the samples. Average values for fracture strain, fracture stress and Young’s modulus are shown in Figure 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.

Figure 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.

Figure 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 Figure 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 (Figure 2A-b). In Figure 2B-a, the fracture surface of SWNT/ER composite is relatively smooth and only a big agglomerate (zoom in Figure 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 (Figure 2A-c);
while in the SWNT/ER composites, long CNT strands were pulled out (Figure 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.

Figure 2. SEM micrographs of the fracture surface of A. SWNT/BCP/ER composites and B. SWNT/ER composites. White circles in A-a indicate some individual SWNTs.
Figure 3. Single-wall carbon nanotubes aligned in SWNT/BCP/ER.

Figure 3 shows single wall CNTs orientated in some parts of the SWNT/BCP/epoxy resin composites. These are probably regions of strain localization and local necking. The block copolymer might help the alignment of CNTs in these areas due to the enhanced interfacial bonding with the matrix.

We propose that the block copolymer works in two different ways: (i) it acts as a dispersing agent. The BCP consists of lyophobic (solvent-repelling) and lyophilic (solvent-attracting) blocks. The lyophobic parts adsorb onto the CNT surfaces, while the lyophilic parts are swollen by the solvent (ethanol in our experiment). The repulsion among the lyophilic blocks overcomes the attractive van der Waals forces between CNTs and keeps them separated; (ii) BCP acts as an interfacial bonding agent which improves stress transfer between CNTs and the epoxy resin.
4 Conclusions

We have shown that block copolymers can be used very effectively to disperse SWNTs homogenously in ER, and improve the load transfer between CNTs and the matrix. By adding small quantities of BCP (0.3 wt%) and SWNTs (0.03 wt%), the Young's modulus, fracture stress and strain increased by 141%, 127% and 43%, respectively, compared to the pure ER. SEM imaging revealed that CNTs were mostly broken in the fracture surface of SWNT/BCP/ER composites, while in the composites without copolymer, they were pulled out. All these improvements are attributed to the BCP acting as a dispersing and interfacial binding agent due to its amphiphilic character.

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