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## Benzoxazine as a reactive noncovalent dispersant for carbon nanotubes

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The dispersion of carbon nanotubes (CNTs) into individual particles or small bundles has remained a challenge and, thereby, has limited their applicability. Reactive noncovalent dispersion is an attractive option for changing the interfacial properties of nanotubes; the CNTs retain their graphene structure while the reactive functionalities of the dispersant moieties allow the dispersion of the CNTs within a thermosetting polymer matrix. Nevertheless, that approach typically requires multistep syntheses and expensive reactants. In this study, we used two commercially available benzoxazine monomers as reactive noncovalent dispersants of CNTs. We used transmission electronic microscopy and thermogravimetric analysis to study the morphologies and thermal properties, respectively, of the resulting benzoxazine-modified CNTs. The presence of benzoxazine coatings improved the compatibility of the CNTs with various organic solvents; in addition, the adsorbed benzoxazines retained their reactivity. Such benzoxazine-modified CNTs have potential application in the preparation of a variety of CNT/polymer composites.

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### Introduction

Carbon nanotubes (CNTs) are materials of interest for both academic research and industrial applications because of their unique chemical and physical properties. Exceptional mechanical properties and excellent thermal and electrical conductivities render CNTs as ideal reinforcing fillers in polymer nanocomposites. Nevertheless, the poor solubility and difficult manipulation of CNTs in organic solvents and aqueous solutions have greatly limited their utility.<sup>1–8</sup> Two general approaches have been developed to enhance the solubility of CNTs: covalent functionalization and noncovalent adsorption of organic molecules on CNT surfaces. The first method involves covalently bonding surface-modifying groups or molecules onto the CNTs to improve their solubility as well as their dispersion in solvents and polymeric matrices.<sup>4,5</sup> The covalent functionalization of a CNT can, however, change the hybridization of its carbon atoms from  $sp^2$  to  $sp^3$ , thereby disrupting its electrical properties. The second approach, which typically involves van der Waals interactions between organic molecules/polymers and CNTs, generally preserves nearly all of the intrinsic features of the CNTs. Although much progress has been made in noncovalent strategies involving nonreactive

organic molecules or polymers,<sup>7,9–15</sup> only a few studies have addressed reactive dispersants. When a reactive noncovalent dispersant binds tightly to a CNT surface through van der Waals interactions, its reactive functional groups remain available for reactions with other molecules or through the formation of a thermosetting polymer matrix. In the latter case, the reactive functional groups of the reactive noncovalent dispersant enable seamless connection of the CNTs to the thermosetting polymer network, thereby allowing them to become an integral part of the resultant composite.<sup>16–19</sup> Nevertheless, multistep syntheses processes, stringent preparation specifications, and expensive reactants have heretofore limited their practical applications.

Benzoxazine resins, which have been developed recently as new types of phenolic resins, are attracting academia and industrial interest because of their low cost, ease of processing, and high performance. In addition to these features, which they share with traditional phenolic resins, polybenzoxazines also possess several unique properties: low degrees of water absorption (despite a large number of hydroxyl groups in their backbone structure), high moduli, excellent resistance to chemicals and UV light, near-zero volumetric shrinkage/expansion upon polymerization, low surface free energies, and high glass transition temperatures.<sup>20–26</sup> Recent studies of CNTs and benzoxazine resins have focused mainly on incorporating CNTs into polybenzoxazines to enhance the properties of the resultant nanocomposites.<sup>27–32</sup> In this paper, we report the use of a commercially available benzoxazine as a reactive noncovalent dispersant for CNTs, leading to functionalized CNTs exhibiting high dispersibility in organic solvents as well as

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thermal reactivity. Furthermore, the commercial availability of the raw materials and the simple fabrication and operation processes described herein suggest that such dispersants have great potential for further use in academic research and industrial applications.

## Experimental section

Bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)propane (BA-a benzoxazine) was supplied by Shikoku Chemicals. Bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)methane (BF-a benzoxazine) was obtained from Huntsman. Multiwalled CNTs (average diameter: 10–20 nm; length: 5–15  $\mu\text{m}$ ) were purchased from Centron Biochemistry Technology. These materials were used as received.

Typical experimental procedure for solubilization of CNTs: benzoxazine monomer (2.0 mg) was added to suspension of CNTs (2.0 mg) in a solvent (10.0 mL) and then the resulting mixture was sonicated for 30 min in a water bath maintained at a temperature of approximately 20  $^{\circ}\text{C}$ . The tested solvents included ethyl acetate (EA), ethyl-3-ethoxypropionate (EEP), methyl ethyl ketone (MEK), propylene glycol monomethyl ether acetate (PGMEA), and tetrahydrofuran (THF). After sonication, the insoluble CNTs were removed through centrifugation. Scanning electron microscopy (SEM) images were recorded using a Hitachi-S-4700 microscope operated at 15 kV. Sample of CNT/polybenzoxazine composites for SEM imaging were prepared by depositing a drop of the CNT/benzoxazine suspension (in THF) onto a silicon wafer (10 mm  $\times$  10 mm) and then curing in an oven at 240  $^{\circ}\text{C}$  for 1 h. Transmission electron microscopy (TEM) images were recorded using a Philips Tecnai 20 microscope operated at 200 kV. The polybenzoxazine-modified CNT samples for TEM imaging were prepared through a three-step process: (i) a CNT/benzoxazine suspension (in THF) was filtered through a 0.2  $\mu\text{m}$  PTFE membrane to remove the free benzoxazine; (ii) the collected benzoxazine-modified CNTs

were dispersed in THF followed by ultrasonication in a water bath for 30 min; (iii) a drop of the benzoxazine-modified CNT suspension was deposited on a holey carbon-coated copper grid (Ted Pella, USA) and then cured in an oven at 240  $^{\circ}\text{C}$  for 1 h. Thermogravimetric analysis (TGA) was performed under  $\text{N}_2$  using a TA Instruments Q50 apparatus (heating rate: 20  $^{\circ}\text{C min}^{-1}$ ; temperature range: from room temperature to 800  $^{\circ}\text{C}$ .  $\text{N}_2$  flow rate: 60 mL  $\text{min}^{-1}$ ).

## Results and discussion

We used two typical bifunctional benzoxazine monomers—BA-a and BF-a—as target dispersants for this study (Fig. 1a). To compare the dispersion abilities of the benzoxazines BA-a and BF-a for CNT in various organic solvents, we dispersed CNTs separately in solution of BA-a and BF-a through ultrasonication for 30 min and then centrifugation. Both the BA-a- and BF-a-treated CNTs exhibited excellent stabilities for up to three months (Fig. 1b and c). The pristine CNT in EA, MEK, and THF (*i.e.*, in the absence of a benzoxazine) underwent rapid aggregation and precipitated completely from these organic solvents after centrifugation; furthermore, the supernatant was transparent and colorless. The CNT/benzoxazine solutions were highly stable and did not precipitate after three months under ambient conditions. Thus benzoxazines significantly improved the solubility of CNTs in various organic solvents and provided stable dispersions for long periods of time.

In previous paragraph, it was shown that benzoxazine monomers may have been adsorbed onto the surfaces of CNT, thereby separating larger CNT agglomerates into highly stable dispersion. To further explore the interactions between CNTs and benzoxazines BA-a and BF-a, we used SEM to observe the structures of the CNT/polybenzoxazine composites (Fig. 2a–d). First, we deposited the CNT/benzoxazine suspension onto a silicon wafers and then them cured to form corresponding CNT/polybenzoxazine composites. Fig. 2a and b present top-view

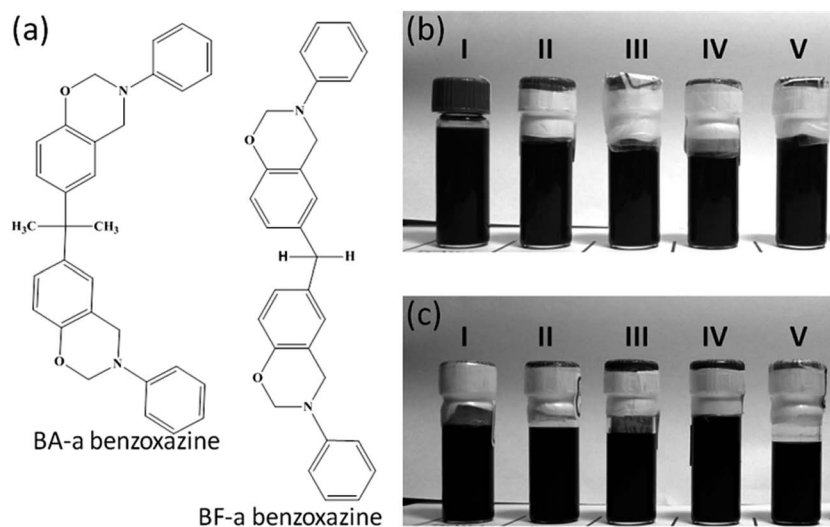


Fig. 1 (a) Structures of the benzoxazines BA-a and BF-a (b and c) photographs of CNTs dispersed with (b) BA-a benzoxazine and (c) BF-a benzoxazine in (I) EA, (II) EEP, (III) MEK, (IV) PGMEA, and (V) THF, after standing for three months.

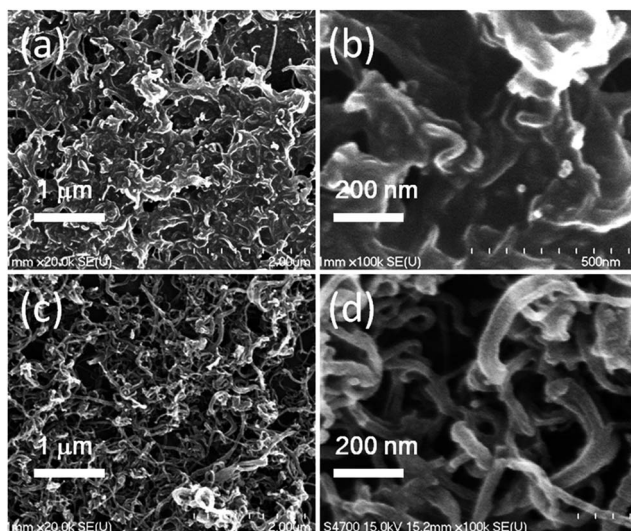
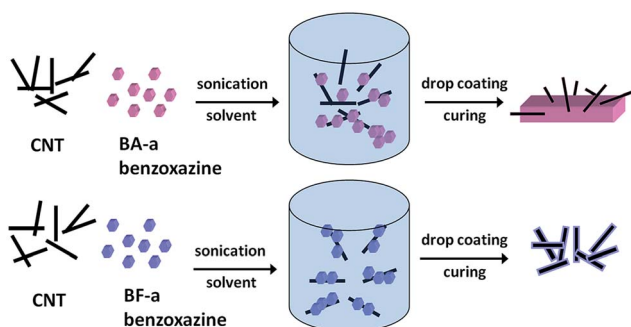


Fig. 2 (a and c) SEM images of the (a) CNT/BA-a polybenzoxazine composite and (c) CNT/BF-a polybenzoxazine composite. (b and d) Enlarged views of the microstructures in (a) and (c).

SEM images of the CNT/BA-a polybenzoxazine composites at different magnifications. The BA-a polybenzoxazine coating was present over the entire surface (Fig. 2a), with the branch-like CNT nanostructures connected together by the polybenzoxazine film (Fig. 2b). Fig. 2c and d display SEM images of the CNT/BF-a polybenzoxazine composites at different magnifications. The morphology of the CNT/BF-a polybenzoxazine composite was very different from that of the CNT/BA-a polybenzoxazine composite. The CNT/BF-a polybenzoxazine composites were deposited on the silicon wafer individually (Fig. 2c), with no evidence for the presence of any polybenzoxazine film between each pair of CNT/BF-a polybenzoxazine nanostructures (Fig. 2d). Moreover, the diameters of the CNT nanostructures in the CNT/BF-a polybenzoxazine composites were greater than those of the CNT nanostructures in the CNT/BA-a polybenzoxazine composites. According to these SEM images, it appears that the two benzoxazine monomers possess different absorption capacities toward the CNTs. Scheme 1 provides an illustration of a suggested mechanism of formation of the CNT/BA-a polybenzoxazine and CNT/BF-a



Scheme 1 Cartoon representation of the formation of CNT/BA-a polybenzoxazine and CNT/BF-a polybenzoxazine composites.

polybenzoxazine composites. In the CNT/BA-a system, only a few of BA-a monomers absorbed onto the CNTs. During the drop-coating process, the unabsorbed benzoxazine monomers combined together to form benzoxazine films. Finally, the CNT nanostructures became embedded in the polybenzoxazine films during the curing process. In contrast, in the CNT/BF-a system, a great amount of BF-a monomers absorbed onto the CNTs, thereby increasing the diameter of the CNT nanostructures. To further investigate the dispersion ability of benzoxazine-modified CNTs, we filtered the CNT/benzoxazine suspension in THF through a PTFE membrane to remove the free benzoxazine and obtain benzoxazine modified-CNT. We then evaluated the dispersion stability of these benzoxazine-modified CNTs in organic solvents through visual observation at different periods of times after sonication (Fig. 3). Immediately after sonication, the solutions of both BA-a- and BF-a-modified CNTs were black (Fig. 3a); we could not tell whether any nanotube aggregates were present in these solutions because of their darkness. After two days, the BA-a-modified CNTs had precipitated (Fig. 3b, vials I–III). In contrast, the suspensions of the BF-a-modified CNTs were stable and did not precipitate after two days (Fig. 3b, vials IV–VI); indeed, they remained suspended after two months of standing at room temperature. Thus, the benzoxazine BF-a significantly enhanced the solubility of CNTs in organic solvents and extended their long-term dispersion stability.

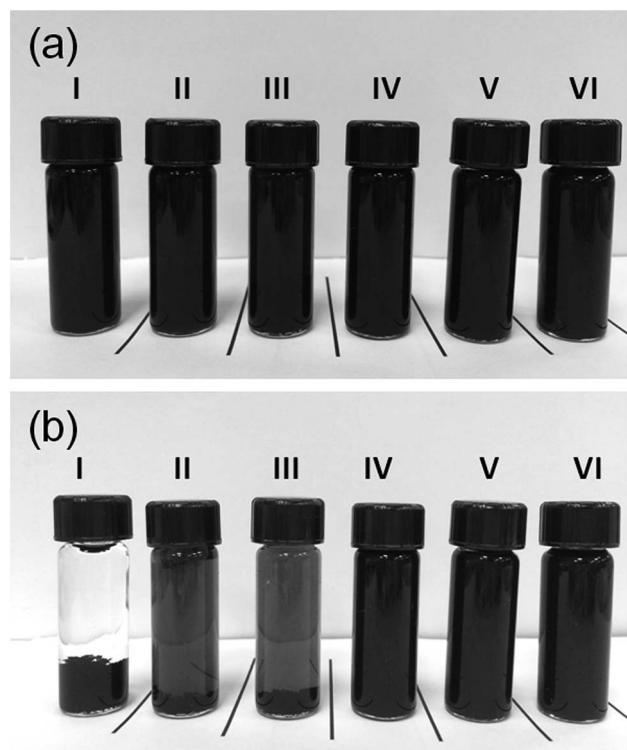


Fig. 3 Photographs of the (I–III) BA-a benzoxazine-modified CNTs and (IV–VI) BF-a benzoxazine-modified CNTs in (I and IV) MEK, (II and V) EA, and (III and VI) THF at different periods of time after sonication: (a) immediately; (b) two days.

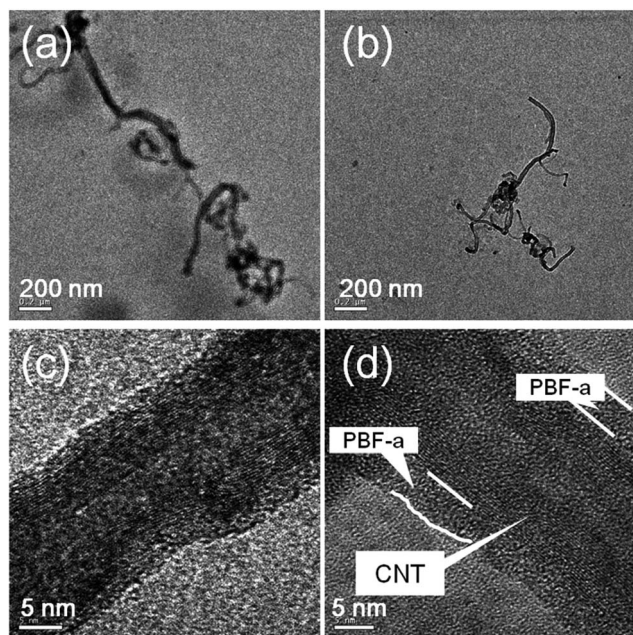


Fig. 4 TEM images of the (a and c) pristine CNTs and (b and d) BF-a polybenzoxazine-modified CNTs.

Fig. 4a–d display TEM images of the pristine CNTs and the BF-a polybenzoxazine-modified CNTs. At low magnification, the pristine CNTs appeared highly entangled, with a non-uniform bundle size (Fig. 4a). After modification with the BF-a polybenzoxazine, the bundle size decreased significantly (Fig. 4b), with most of the CNTs appearing to have dispersed as individual tubes or in small bundles. A higher-resolution TEM image of the pristine CNTs (Fig. 4c) reveals that the surfaces of CNTs were clean. In contrast, Fig. 4d reveals that a coating of polybenzoxazine covered the CNTs of the BF-a polybenzoxazine-modified CNTs, such that the individual nanotubes were separated from one another. We used TGA under a  $N_2$  atmosphere to determine the thermal properties of BF-a benzoxazine, the BF-a polybenzoxazine, the pristine CNTs, the BF-a benzoxazine-modified CNTs and the BF-a polybenzoxazine-modified CNTs. Fig. 5a reveals that the thermal stability of the BF-a polybenzoxazine was higher than that of the BF-a monomer, consistent with its cross-linked network structure. The pristine CNTs did not undergo any obvious weight loss during their TGA analysis (Fig. 5b). Hence, we can attribute the weight losses observed for the BF-a benzoxazine-modified CNTs and BF-a polybenzoxazine-modified CNTs to the decomposition of their dispersants. The thermal properties of the BF-a benzoxazine-modified CNTs and the BF-a polybenzoxazine-modified CNTs follow were similar to those of the BF-a monomer and the BF-a polybenzoxazine, respectively; that is, the thermal stability and char yield of the BF-a polybenzoxazine-modified CNTs were higher than those of the BF-a benzoxazine-modified CNTs because of the cross-linked network structure in the former. Thus, the BF-a monomer units that had adsorbed on the CNTs retained their reactivity, allowing homo-crosslinking and, potentially, reactions with other functional groups (*e.g.*, epoxy,

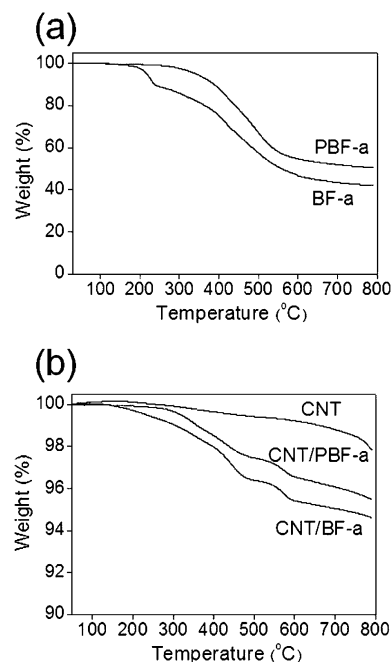


Fig. 5 (a) TGA traces of the BF-a benzoxazine (BF-a) and the BF-a polybenzoxazine (PBF-a). (b) TGA traces of the pristine CNTs, the BF-a benzoxazine-modified CNTs (CNT/BF-a), and the BF-a polybenzoxazine-modified CNTs (CNT/PBF-a).

isocyanate, oxazoline, maleimide, cyanate ester)<sup>26</sup> under suitable conditions.

## Conclusions

Benzoxazine monomers have intrinsic affinity for pristine CNTs. When using such monomers as reactive noncovalent dispersants, we found that CNTs could be dispersed well in several organic solvents. The strength of the interactions between the CNTs and the benzoxazines was dependent on the chemical structure of each monomer. A coating of the benzoxazine BF-a on a CNT surface greatly enhanced its dispersibility in organic solvents; the monomer units remained reactive for crosslinking and, presumably, for reactions with other functional groups in other polymeric systems (*e.g.*, polybenzoxazine, polyimide, polyurethane, epoxy resin, phenolic resin). Accordingly, BF-a benzoxazine-modified CNTs appear to be promising candidates for use in the preparation of various CNT/polymer composites.

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