

Cross-Linked Single-Walled Carbon Nanotube Buckypapers and their Composites

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ABSTRACT

Non-woven sheets of carbon nanotubes (CNTs), often called buckypapers, in which the CNTs are covalently crosslinked within and between bundles, provide a practical approach to strengthen CNT-CNT interactions in CNT assemblies and improve their mechanical properties. We recently reported several variations on a crosslinking approach based on single-walled CNTs (SWCNTs) modified either with -OH functional groups by covalent functionalization or by encapsulating with a functionalized polymer wrapping (Jakubinek *et al.*, *RSC Advances* 4, 57564, 2014). These SWCNTs were subsequently assembled into buckypapers and crosslinked by reaction with bifunctional linkers. The cross-linked buckypapers displayed improved mechanical properties while retaining their porous character. The strongest and stiffest papers ($\sigma = 32$ MPa, $E = 3.1$ GPa), which approached 10 \times that of the pristine non-crosslinked buckypaper, were obtained at the expense of a loss of electrical conductivity. In other cases, such as cross-linking using an epoxy resin monomer, increases in strength and stiffness of $\sim 5\times$ were obtained while retaining electrical and thermal conductivity. Epoxy-crosslinking also was found to be favorable for production of epoxy composites, where cross-linking using an epoxy resin prior to impregnation with the same resin results in substantially better mechanical properties in comparison to epoxy-impregnation alone. This suggests potential for improved multifunctional composites based on buckypaper.

Keywords: carbon nanotubes, buckypaper, nanocomposites

1 INTRODUCTION

Macroscopic assemblies of carbon nanotubes (CNTs), such as papers, arrays and yarns, are promising material forms to harness the outstanding properties of CNTs for development of engineering materials. Non-woven sheets of CNT paper called buckypaper (Fig. 1) are most commonly formed by vacuum filtration of a suspension of randomly distributed and oriented CNTs and have garnered

interest for mechanical reinforcement in composites as well as a wide range of multifunctional applications.

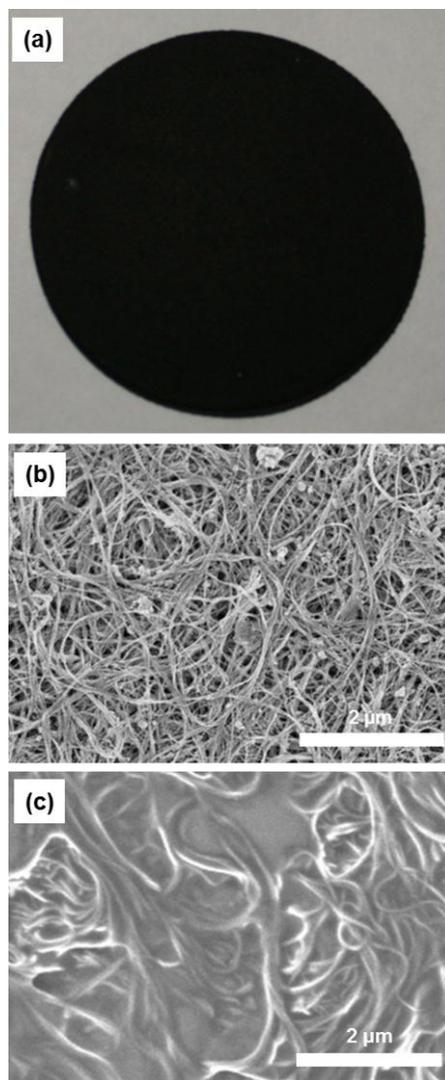


Figure 1: (a) SWCNT Buckypaper (~35 mm diameter) and SEM images of (b) buckypaper and (c) a buckypaper-epoxy composite formed by epoxy-impregnation. Adapted from reference [1].

Mechanical performance is critical even in many non-structural applications as the robustness and flexibility of the buckypaper is crucial during processing, integration, manufacturing and use; however, the mechanical properties of pristine buckypaper sheets are often poor. The buckypapers are highly porous (often 60–75 vol% void) and the interaction between adjacent CNTs and CNT bundles is through van der Waals forces. For example, even in a bundle where the CNTs are perfectly aligned, the strength of the assembly is limited by CNT–CNT sliding over a wide range of CNT aspect ratios [2]. As a consequence, the elastic modulus (E) and ultimate tensile strength (UTS) of randomly oriented CNT buckypapers are often very low compared to individual CNTs and in the range of 0.1–1 GPa and 1–10 MPa, respectively [3–6]. A theoretical model for the moduli of buckypapers containing nanotube ropes indicates that strong joints (no sliding) at CNT interconnects can increase the elastic modulus to 1% to 10% of the bundle elastic modulus [4], which suggests that significant improvements are possible if the volume fraction and connections between CNTs are improved. A buckypaper in which the nanotubes are covalently cross-linked within and between bundles provides a practical embodiment of this structure, where covalent bonds would provide stronger CNT–CNT interaction. Experimentally, tensile strengths up to twice that of pristine buckypaper were achieved by functionalization with a chain containing multiple amide groups that hydrogen bond to increase the strength of CNT–CNT interaction [7]. Covalent cross-linking of NH_2 -functionalized MWCNT buckypapers with a benzoquinone solution has been reported to increase tensile strength and simultaneously improve electrical conductivity [8]. Thiol-functionalized MWCNTs also have been cross-linked with benzoquinone [9].

As adapted herein, we recently reported several variations of CNT–CNT cross-linking based primarily on infiltration of OH-functionalized SWCNT buckypapers with bi- (or tri)-functional reagents to create 3D covalently cross-linked buckypapers [1]. The approach can be applied with a wide range of crosslinking reagents. Selected cross-linkers were found to substantially improve mechanical properties and it was possible to produce stronger papers that retained their multifunctional character. Furthermore a combination of epoxy-mediated cross-linking followed by epoxy-impregnation is shown to provide substantially better mechanical properties than impregnation alone.

2 METHODS

Pristine SWCNT (P-SWCNT) buckypapers were produced by dispersion and vacuum filtration of unmodified SWCNTs. The steps for production of cross-linked buckypapers are shown in Fig. 2 and described in more detail in our recent publication [1]. Briefly, functionalized SWCNTs (f-SWCNTs) with CH_2OH (abbreviated to SWCNT-OH) were prepared based on literature procedures [10] and the SWCNT core-shell

structures were prepared through a diazonium reaction between SWCNTs and 1,4-vinylaniline followed by *in situ* polymerization [11]. The f-SWCNT buckypapers were prepared following the same dispersion/filtration protocol employed with pristine SWCNTs and the buckypapers were crosslinked by post-production steps consisting of wetting with one of several bifunctional reagents (interconnecting reagents Int. A – Int. F listed in Fig. 2) followed by hot compression. The cross-linking reactions for several of the selected reagents, which cover the various reaction types, are illustrated in Fig. 3.

The resulting buckypapers were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), uniaxial tensile tests, and electrical and thermal conductivity measurements, with additional detail reported in reference [1].

3 RESULTS & DISCUSSION

The SWCNT-OH and cross-linked buckypapers (Fig. 4) display similar morphology and porous character to the P-SWCNT case (Fig. 1b), with small changes in topology including more porosity (SWCNT-OH) or less porosity (cross-linked BPs). This shows that the buckypapers have not been substantially impregnated by the cross-linking reagents in contrast to a polymer-impregnated case (Fig. 1c). Buckypaper derived from the core-shell SWCNTs has a similar, non-woven fiber, appearance (not shown) but with large-diameter fibers due to the larger diameter SWCNT-polymer core shell structure.

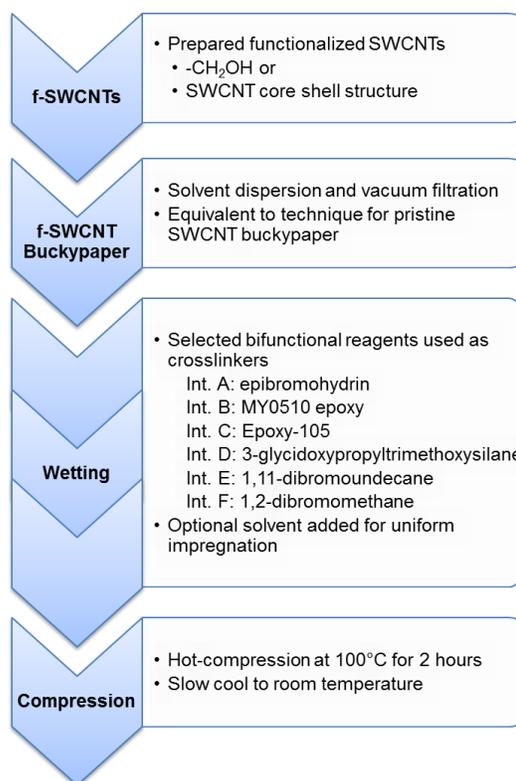


Figure 2: Preparation of cross-linked SWCNT buckypapers.

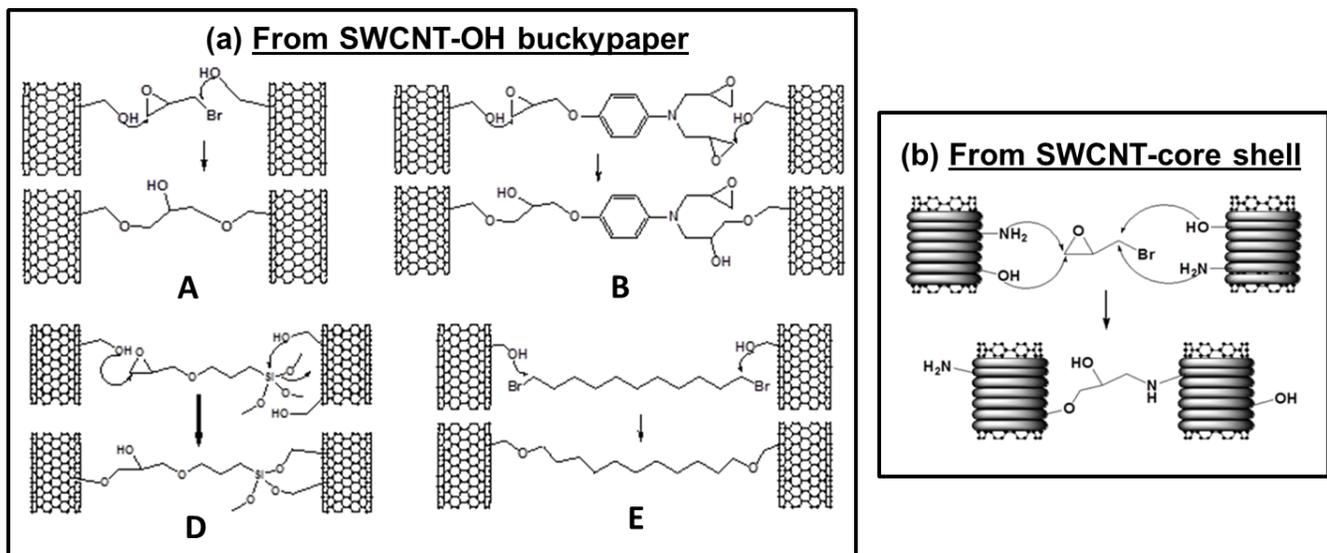


Figure 3: Schematic illustrations of chemical crosslinking of (a) SWCNT-OH and (b) SWCNT core-shell structures. Selected interlinkers are shown (refer to Fig. 2 for identification of the cross-linking reagents by the letter label). Adapted from Ref. [1].

TGA traces provide support for CNT functionalization, with shifts to lower oxidation temperature and increased mass loss for both air-oxidation and desorption under argon. TGA for the pristine and SWCNT-OH buckypapers were similar but with a clear shift to lower oxidation temperature for SWCNT-OH, attributed to interruption in the sp^2 structure associated with functionalization [1].

To facilitate comparisons, Fig. 5 shows the mechanical, thermal and electrical properties for cross-linked buckypapers relative to pristine buckypaper (e.g., $E_{\text{cross-linked}}/E_{\text{pristine}}$). The inferior properties for SWCNT-OH buckypaper can be explained primarily by its lower density. With the exception of Int.-E, which involves a long alkane chain, the cross-linked buckypapers have lower ultimate strain, attributed to an inhibiting effect of the cross-links on CNT-CNT sliding. Conversely, Int.-F uses the shortest dibromoalkane chain and results in higher stiffness but provides the lowest ultimate strain.

While the cross-linking with dibromoalkanes was ineffective to improve properties, crosslinking via epoxide groups for one or both links (Int. A-D) provided improved strength, stiffness and toughness. The epibromohydrin or epoxy resin crosslinked cases, where a significant portion of the electrical conductivity is retained, provide multifunctional buckypapers due to maintained conductivity and improvements ($2\times$ to $5\times$) in stiffness, strength, and toughness relative to P-SWCNT buckypaper.

While crosslink stiffness could also relate to higher thermal conductivity, the increased density (*i.e.*, reduced porosity) caused by crosslinking can account for most of the observed thermal conductivity differences. Conversely, electrical conductivity was reduced in most crosslinked buckypapers. The electrical conductivity of the Int.-A case was equal to that with P-SWCNTs. In this case, epibromohydrin forms a good mechanical interconnection,

keeping the nanotubes in close contact and significantly increasing density relative to the SWCNT-OH buckypaper. Density is increased in most crosslinked buckypapers but the longer interconnections could have a more significant influence on CNT-CNT resistance.

The stiffest, strongest and toughest buckypaper was obtained by crosslinking between SWCNT-polymer core shell structures (Fig. 3b). This is in some sense intermediate between a buckypaper and a SWCNT-polymer composite,

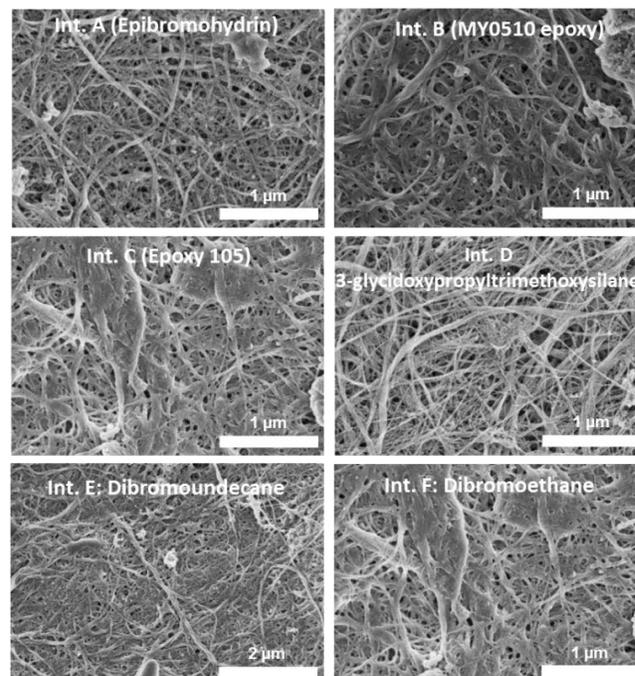


Figure 4: SEM images of cross-linked buckypapers derived from SWCNT-OH buckypaper. Reproduced from Ref. [1] with permission.

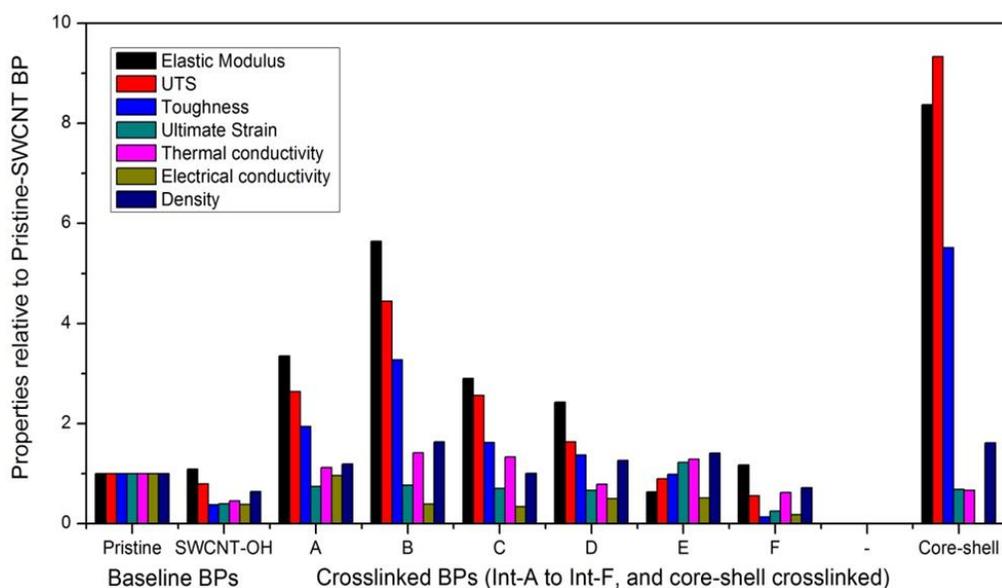


Figure 5: Properties of crosslinked buckypapers in comparison to P-SWCNT buckypapers. Reproduced from Ref. [1] with permission. NB: The properties of the baseline, P-SWCNT buckypaper were: $E = 370 \pm 90$ MPa, UTS = 3.4 ± 0.9 MPa, Toughness = 2.4 ± 0.3 J mm, Ultimate strain = 0.016 ± 0.010 , $\kappa = 2.4 \pm 0.3$ W m⁻¹ K⁻¹, $\sigma = 117 \pm 6$ S/m, $\rho = 0.42 \pm 0.06$ g/cm³.

as the SWCNTs are polymer-coated and the density is higher than that of buckypaper but the less than that of a polymer or typical polymer composite, and the structure remains porous. This approach results in better tensile properties but greatly reduces electrical conductivity.

Finally, crosslinked buckypapers were found to be an promising starting point for integration into composite structures (*e.g.*, impregnation, lamination). Crosslinking *via* epoxy resin is of particular interest as an example of a buckypaper-epoxy composite. In this case both P-SWCNT and cross-linked SWCNT buckypapers based on MY0510 (*i.e.*, Int. B) were impregnated with MY0510 resin. The epoxy for impregnation was first mixed with a chemical hardener, 4,4'-diaminophenyl sulfone (49 parts per 100 parts epoxy) and, after impregnation, was cured following the manufacturer's recommended protocol. As shown in Table 1, using cross-linked buckypaper as a starting point for impregnation resulted in substantially improved mechanical properties compared to direct impregnation of P-SWCNT buckypaper alone. This conclusion can also be drawn from other recent work with epoxidized CNTs [12] and suggests that crosslinking prior to epoxy-impregnation is a promising route for composite fabrication.

Table 1: Strength and stiffness of epoxy-impregnated buckypapers, with and without epoxy-cross-linking.

| Buckypaper | E (GPa) | UTS (MPa) |
|---|-----------------|---------------|
| P-SWCNT | 0.37 ± 0.09 | 3.4 ± 0.9 |
| P-SWCNT, epoxy-impregnated | 4.3 ± 1.2 | 23 ± 10 |
| Epoxy-cross-linked (Int. B) | 2.1 ± 0.2 | 15 ± 2 |
| Epoxy-cross-linked (Int. B) + epoxy-impregnated | 7.5 ± 1.9 | 41 ± 8 |

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