Carbon nanotubes buckypapers of controlled porosity and their nanocomposites

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Abstract
In this work, multi-walled CNT buckypapers were prepared by vacuum filtration of carbon nanotubes, chemically modified by two different methods. This provided the desired degree of control over the textural properties of the CNT buckypapers, resulting in assemblies that exhibited a "foamy" or "dense" structure. Once the pressure-induced infiltration of the polymer matrix is completed, relatively high CNT volume fractions are obtained. The proposed fabrication procedure can be easily extended towards the preparation of CNT-based nanocomposites at an industrial scale.

1 Introduction
The excellent mechanical[1] and electronic[2] properties of carbon nanotubes (CNTs) have been well documented in recent years. CNTs are considered to be the most promising 1D candidate for the next generation of structural components/fillers in multifunctional materials. They have been shown to offer multiple options for the fabrication of supramolecular complexes through self-assembly principles[3] such as transparent sheets,[4] yarns,[5] buckypapers[6] and many other. In particular, buckypapers are thin sheets of entangled tubes with thickness in the micrometer scale. Their structural properties and porous character make them very useful in a broad range of applications, such as catalyst supports,[7] permeable membranes,[8] actuators, [9] capacitor electrodes[10] and electrical conductive components[11]. Recently, there has been a great deal of interest in CNT buckypapers as a platform for the production of nano impregnated sheets for laminate composite production.
A common notion in the design of these composites is the erroneous belief that the stronger and stiffer the as-prepared dry CNT sheets are, the better the mechanical properties of the resulting polymer nanocomposites. However, as the porosity of these "dense" dry films competes with the viscosity of prepolymer fluid and its wetting behavior, full impregnation of the films seems less favorable. Thus, "dense" dry CNT films may exhibit remarkable mechanical properties[12] and can be applied as such in a number of applications but they are, in fact, unsuitable as building blocks for polymer composite production. Therefore, a foamy preform is highly desirable in order to achieve homogeneous impregnation of individual nanotubes with resin.
This paper presents a first attempt to control the porosity of these sheets in such a way that a "foamy" structure is formed that can lend itself to efficient polymer wetting and impregnation. Such films may have poor properties in the dry state but they far exceed in

mechanical response the "dense" buckypapers, when both are impregnated with conventional engineering polymers.

2 Materials and testing methods

The processing method proposed here ensures an effective wetting of the carbon nanotubes by the polymer matrix. As mentioned above, unlike other conventional processing methods,[3] our procedure involves buckypaper soaking into epoxy prepolymer followed by impregnation of the latter within the free pores of a CNT network and subsequent curing the epoxy in a semi-industrial autoclave chamber. Through this two-step protocol, both flexural and tensile parameters (modulus and strength) of the resulting composites were enhanced appreciably, yet, the properties were found to strictly correlate with the textural characteristics of the used CNT preforms. By adjusting certain parameters in the processing steps, our method can also be employed for the fabrication of high CNT loading polymer composites.

An important issue which precedes the processing step described above is the modification of the inert CNT surface to make it compatible with the impregnating matrix. Here, we introduced oxygen-containing moieties, such as epoxide rings [13], or carboxylic groups, for the CNT preform production. Concerning the fabrication of multi-walled CNT buckypapers, stable CNT suspensions in H_2O at a concentration of 1 mg ml^{-1} were prepared by tip sonication for 16 min. The mass of the CNT material was 250 mg. These dispersions were then vacuum-filtered through polycarbonate filters of 0.2 μm pore size. After drying with hot air, CNT films were peeled off from the filtration membrane. The average thickness of the produced buckypapers was approximately 170 μm for the epoxidized and 100 μm for the oxidized and their diameter about 7 cm.

The aforementioned CNT buckypapers have been infiltrated with epoxy-based resin using a combination of soaking followed by infusion/curing process within an autoclave chamber. The resin system used in this study was an epoxy, the prepolymer of which contains a mixture of bifunctional epoxide derivative and a diamine, the latter acting as a curing agent. The prepolymer mixture showed diminished viscosity at 40 ^{0}C. The multi-walled CNT buckypapers were soaked in epoxy prepolymer solution in order to achieve a high CNT volume fraction in the resulting composite. These epoxy soaked buckypapers were deposited in a laminated structure (3 buckypapers on the top of each other) followed by epoxy impregnation through the application of high pressure (~6 bar) within a semi-industrial autoclave chamber. During the curing process, according to amine-epoxy coupling mechanism, amine groups of epoxy matrix can react with epoxide-modified CNT nanostructures, giving rise to ring opening and subsequent grafting reaction. In an analogous manner,[14] active epoxy rings of prepolymer can react with carboxylic groups onto the oxidized CNT surface towards the formation of ester moieties. Thus, an enhanced adhesion between filler and matrix is expected to occur, due to extended cross-linking reactions.

After completion of the curing process, we obtained about 2 mm thick CNT/epoxy composite sheets that could be cut in the form of narrow strips. The material was stiff and slightly flexible. In the case where "foamy" epoxide-modified CNT buckypaper was used as filler material, the CNT volume fraction was about 9 %. In addition, "dense" buckypapers gave nanocomposites of 16% volume fraction. To further understand and quantify the effects of chemical modification on the textural characteristics of the buckypapers, the porosity was measured by means of mercury porosimetry.

3 Results and discussion

The profiles of pore distribution for all types of CNT buckypapers are shown in **Figure 1**. In general, the epoxide-modified buckypapers show a broad pore size distribution. The profile in the mesopore region (0.002-0.05 μm) has a maximum at 12 nm, whereas the majority of

porous structure consists of small macropores, which mainly lie in the range between 0.050 and 2 μm (maximum at 200 nm). The mesopores and small macropores are formed between entangled adjacent tubes criss-crossing each other. On the contrary, in the case of $KMnO_4$-mediated oxidized sample, the major distribution is observed at the mesopore range, which is centered at 20 nm. The absence of small macropores in the $KMnO_4$-mediated oxidized material clearly indicates that the distribution of inter-tube channel sizes is well defined and an enhanced packing order has taken place during the filtration process.

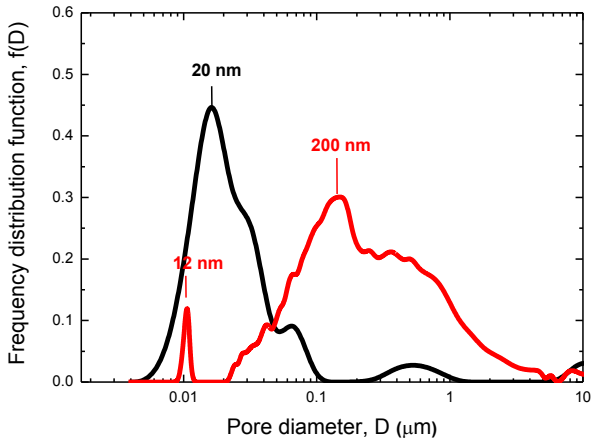

Figure 1. Pore size distribution from Hg intrusion curves of oxidized (black) and epoxidized (red) buckypaper.

The room temperature stress-strain curves in tension of the buckypapers are presented in **Figure 2** and the important parameters derived from these tests are given in **Table 1**.

Sample	Young's modulus (GPa)	Ultimate Strength, UTS (MPa)	Strain at failure (%)
Oxidized buckypaper	2.83±0.20	14.03±1.80	0.68±0.10
Epoxidized buckypaper	0.22±0.04	2.09±0.22	2.29±0.35

Table 1. Tensile properties of the tested buckypapers.

The ultimate fracture tensile strength (UTS) and Young's modulus of the epoxidized samples were measured as 2.29±0.35 MPa and 0.22±0.04 GPa, respectively. The poor tensile properties of these samples are attributed to their "foamy" character, which implies that the amount of interconnection (bridging) between CNTs has now been decreased and that reflects adversely to the mechanical properties (mainly UTS). On the contrary, the dense $KMnO_4$-treated buckypapers comprising of randomly entangled tubes, exhibited at the dry state improved mechanical properties. The UTS and Young's modulus were approximately 14 MPa and 2.8 GPa, respectively. In conclusion, the major factor enhancing the structural integrity of the dense buckypaper is the increased number of interconnects, which lead to more efficient interactions between adjacent tubes, through van der Waals forces and/or hydrogen bonding between polar surface groups.

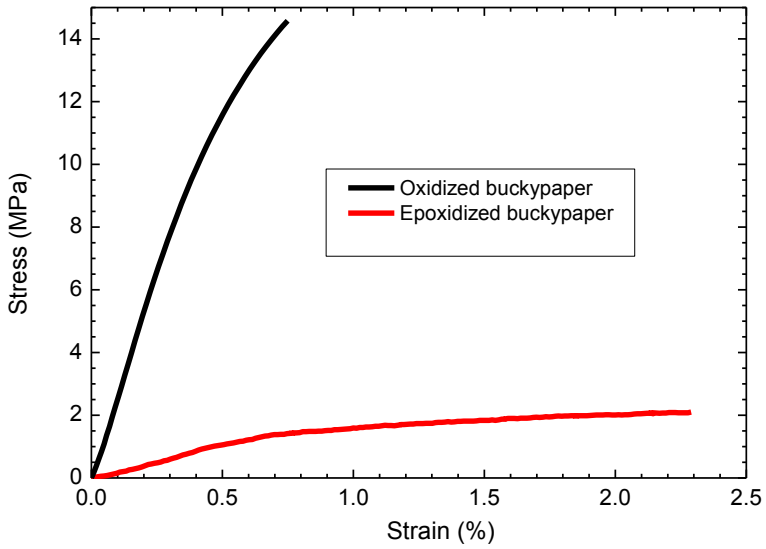

Figure 2. Stress-strain curves from tensile experiments of buckypapers.

In order to assess the mechanical properties of the produced CNT/epoxy composites, 3-point bending experiments according to ASTMD790 were conducted. The flexural stress-strain curves of the nanocomposites recorded at room temperature (25^{o}C) are presented in **Figure 3** and the important parameters derived from these tests are summarized in **Table 2**.

Sample	**Modulus of elasticity (GPa)**	**Flexural Strength, (MPa)**	**Strain at failure (%)**
Oxidized CNT/ Resin	8.40±0.32	173±3	3.50±0.3
Epoxidized CNT/ Resin	6.54±0.15	207±6	4.60±0.5

Table 2. Flexural properties of the tested composites.

It is evident that epoxidized CNT/epoxy composite films demonstrated a relatively large, 4.6%, flexural strain-to-failure. The large flexural strains could be attributed to the high deformation ability of the CNT preforms that reinforce the composite films. The flexural strength of the epoxide-modified CNT/epoxy film was approximately 207 MPa and the modulus was 6.5 GPa. This corresponds to a 51 % and 88 % enhancement, respectively, compared to those of the neat matrix. Regarding the composite film reinforced by the $KMnO_4$-oxidized CNTs, the brittleness is appreciably increased whereas modulus is enhanced by 140%, most probably due to the higher CNT loading. These results clearly reveal that unlike conventional composites, the flexural strength of the studied nanocomposites, does not depend on the amount of filler but on the level of CNT/ epoxy interaction which, in turn, is governed by the amount (or not) of agglomeration between the CNTs.

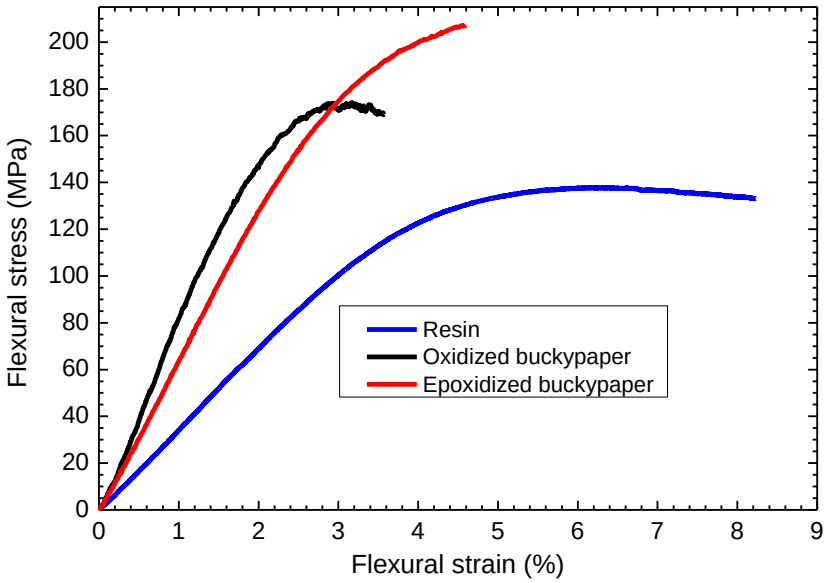

Figure 3. Stress-strain curves of resin and corresponding MWCNT nanocomposites from 3-point bending experiments.

4 Conclusions

Based on the buckypaper approach, enhanced mechanical properties of MWCNT/epoxy composites were prepared and characterized. Depending on the modification treatment of CNTs, buckypapers with different textural properties ("foamy" or "dense") were produced. These buckypaper formations give new impetus to the fabrication of nanocomposites with controlled porosity and, subsequently, volume fraction. The experimental results showed that the proposed fabrication scheme is an efficient way to improve substantially the mechanical response of MWCNT/resin composites. This fabrication procedure can be easily extended towards the preparation of laminated nanocomposites. The balancing of the various parameters such as the grafting ratio of functionalities onto the CNT surface, buckypaper porosity and prepregging at high pressures will lead to lightweight composite membranes for various applications.

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