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Engineering SWCNT bucky paper by heavy ion irradiation: An *in situ* –study

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Abstract: We present preliminary results from a combined ultrasound and resistance measurement to be conducted *in situ* during irradiation of single wall carbon nanotube (SWCNT) mats. We focused on whether it is possible to improve the mechanical properties of the SWCNT paper samples by means of C^{4+} - ion irradiation. Simulation work indicated that such engineering could be possible, and our earlier *ex post* results have shown that it is possible to modify the elastic moduli. We present results obtained with a setup for combined z-direction-ultrasound and conductivity probing which agree with those published earlier. In addition, we present stability test results obtained with the developed in-plane ultrasonic transducers combined with the electrical conductivity test. Our results show, that the measurement setup is ready for *in situ* experiments and that it produces reliable results.

Keywords: Single wall carbon nanotubes, bucky paper, materials engineering, ultrasound, conductivity

A. Introduction

Single walled carbon nanotubes (SWCNT) are a light-weight, strong material of the future. Both their tensile strength[1] and shear- and elastic modulus[2] are high, and thus propositions for their application have been made in e.g. the space industry.[3] SWCNTs have also been used to fabricate several different types of macroscopic structures[4, 5], of which we study fiber mats[6, 7], also known as bucky paper. Bucky paper can be considered to be a pile of randomly orientated hexagonal nanotube bundles interconnected by van der Waals forces. Up to date, however, these structures have yet to reach the mechanical properties possessed by single fibers[6, 8, 9].

There are several propositions for medical use of SWCNT bucky paper, e.g. artificial retinal transplants[10] and bio-compatible nets for cell- and organ transplantation.[11] Bucky paper is also applicable as a conducting coating due to its natural conductivity[12], and as an actuator[6]. Studies indicate that – due to its properties – bucky paper could also be used in Li-ion batteries to extend their lifetime[13], and even to replace LCD displays[14]. There is a need for light, strong materials arising from the industry. If its mechanical properties could be engineered, SWCNT bucky paper is a possible candidate to fulfil this need. In addition, SWCNTs combined with other materials could form strong composites

The strength of SWCNT bucky paper is traditionally engineered by adjusting the angle distribution of the fibre bundles and the amount of impurities.[15] Both of these methods are hard to implement, they require changes in the production process. This raises a need for a way to engineer the strength of the final product *post* production. Up to now, however, the final products lack the high shear modulus required for coating use.

There are several proposed methods to improve both the elastic- and shear modulus of bucky paper, e.g. one being carbon ion irradiation, which does not require high temperatures, and does not induce inpurities into the samples. In this method, the carbon ions striking the bucky paper induce covalent bonds between individual tubes[16, 17], which according to a recent simulation study[18] improves the shear- and elastic modulus up to 10-100 -fold. The results of this simulation, however, require experimental validation. Both of the moduli are important parameters for coatings, since they are often exposed to damage mechanisms incorporating both parameters.

B. Method

The aim of the study is to experimentally verify the effects of carbon ion irradiation on SWCNT bucky paper: 1) First, the feasibitily of the irradiation method needs to be verified *ex post* and then 2) the stiffness increase as a function of irradiation time needs to be studied *in situ*.

In the first phase, several samples cut from the same manufacturing sheet were irradiated with ^{4+}C ions at 23 MeV using different fluences, and the velocity of the ultrasonic signal transmitted through the sample *ex post* was studied[19]. The use of ultrasound allowed non-destructive evaluation, since the speed of sound is a function of density and both of the mechanic moduli.

To prepare for the second phase, we had to generate a novel in-plane ultrasonic transducer (Fig. 1) using four tungsten-carbide needles attached to PZ-27 disks (measurement span 18 mm). One of the needles acted as a TX transducer, while the other three acted as RX transducers. This allowed instantaneous determination of the speed of sound (SoS) at three different distances, and

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thus determination of the longitudinal ultrasound velocity and modulus of the sample.

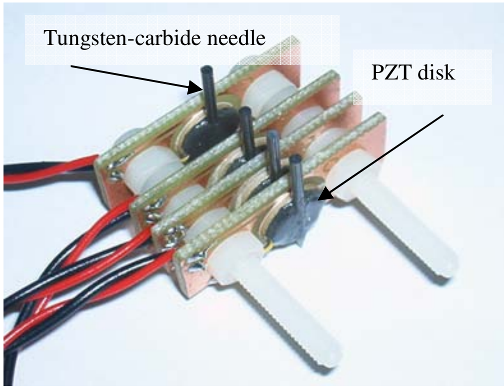

Fig. 1. In-plane ultrasonic device featuring three RX and one TX transducer

The in-plane ultrasonic setup was pressed through the sample to verify good contact. A pulser (Panametrics 5058PR, 10 Hz PRF, 100 V_{PP}, no filtering) was used to generate an ultrasonic pulse, that was transmitted via the TX transducer. The RX transducers picked up the signal, that was then received via a custom-made multiplexing device and digitized with an oscilloscope (HP 54540D, 200 MSa/s). The signal was transferred to a measurement computer running LabView 8.0 via an USB GPIB interface.

In conjunction with the ultrasonic modulus measurements a four-wire electrical conductivity measurement was done. Custom-made copper electrodes were attached to the sample using a constant load, and the resistance of the samples was measured using a LCR meter (HP34401A) in a 4-wire mode. Figure 2 depicts the combined conductivity and ultrasonic measurement setup.

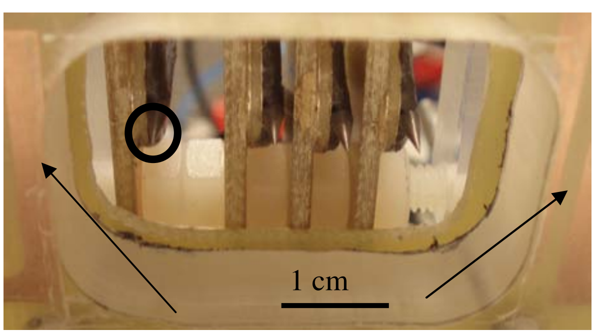

Fig. 2. Combined ultrasonic and conductivity measurement setup. The four transducers are visible, TX transducer marked with a circle. The electrodes used in the conductivity measurement are marked with arrows.

The in-plane ultrasonic setup was first verified using a standard sheet of copy paper (80 g/cm^2) to ensure that the signal propagates through the sample and that the results are comparable to the ones in literature. In addition, a sheet of mixture (single + double walled) bucky paper was studied *ex ante* to verify the applicability of the setup for this research.

The combination of the earlier out-of-plane ultrasonic setup[19] and the conductivity measurement was validated using MWCNT bucky paper, for which there are earlier published results.

The effect of vacuum in the beam pipe was studied by placing the ultrasonic setup inside a vacuum chamber and committing three consecutive measurements: one with air inside, one with a pre-vacuum (10^{-2} mbar) and the last one with high vacuum (10^{-6} mbar, the same conditions as during irradiation). A CAD-image of the setup inside the accelerator beam pipe is shown in Figure 3.

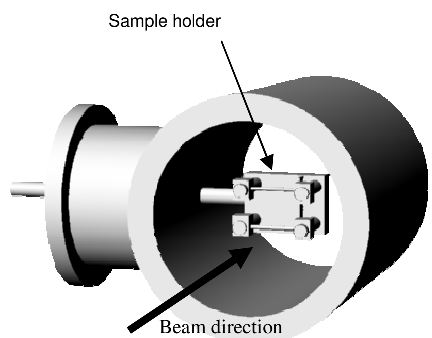

Fig. 3. Implementation of the setup into the accelerator beam pipe.

A baseline measurement to ensure reliable results was conducted. The combined ultrasonic and conductivity setup was placed inside a vacuum for 20 hours and measurements were conducted every five minutes.

C. Results

As a first test the in-plane needle device transmitted an ultrasonic burst into a copy paper and a Mylar sample, and the received signals arrived in expected order. The measured longitudinal ultrasound velocity, 3800±100 m/s for copy paper and 2350 ± 5 m/s for Mylar agreed with earlier published in-plane results with 23 kHz transducers[20], thus verifying the applicability of the developed device.

In addition, a transmission test through bucky paper was done. The signals arrived in expected order (Fig. 4.) and the velocity reading was plausible (Fig. 5.)

The in-plane vacuum test showed no change in ultrasonic velocity while going from ambient air pressure to UHV (ultra high vacuum). The measured sound velocities were 1930 ± 20 m/s for ambient air pressure, 1950 ± 20 m/s for low vacuum and 1950 ± 50 m/s for UHV. The stability test showed good stability for both the ultrasonic and the conductivity measurement (Fig. 6 and 7).

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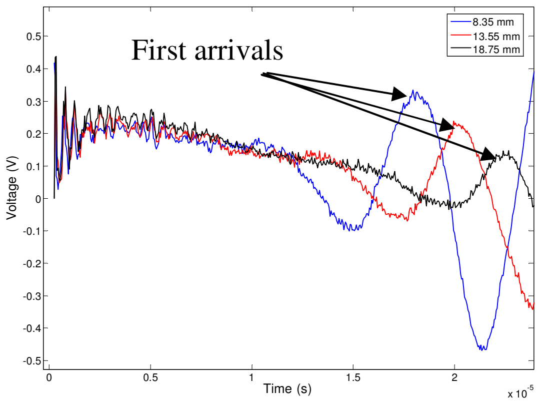

Fig. 4. A measurement conducted through a bucky paper sample. The signals arrive in the expected order.

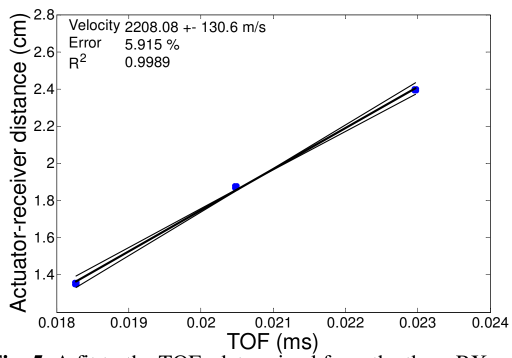

Fig. 5. A fit to the TOFs determined from the three RX transducers in a bucky paper measurement (Fig. 4).

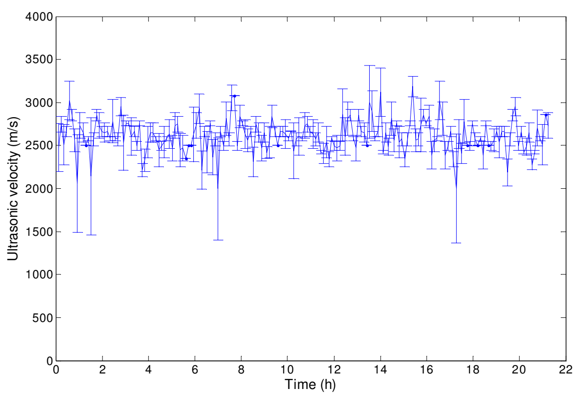

Fig. 6. Stability test for the in-plane ultrasonic device. Mean relative error during 20h was 4.5%.

The combined ultrasonic out-of-plane and conductivity measurement on irradiated MWCNT bucky paper samples indicated a drop in both elastic moduli and conductivity, as expected from earlier results[21] (Fig. 8).

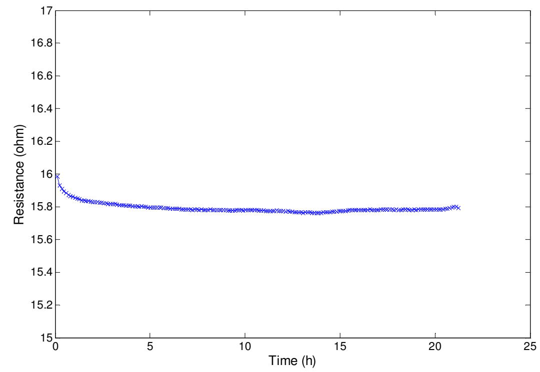

Fig. 7. Conductivity stability test. The initial drop is most probably due to outgassing.

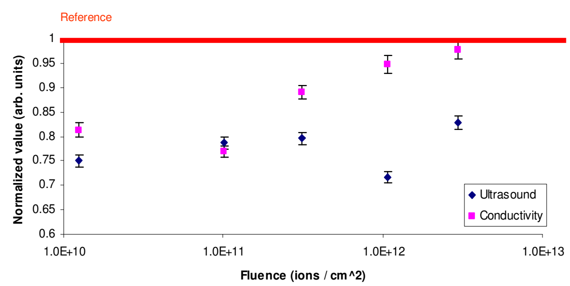

Fig. 8. Combined ultrasound and conductivity measurement on MWCNT bucky paper samples. Results are normalized to the nonirradiated reference sample, which is "1".

D. Conclusions

The developed in-plane needles work well, and are capable of characterization of changes in the velocity on the order of 5%. The results from the copy paper and mylar test verified the applicability of the setup. The conductivity measurements show that the 4-wire method allows detection of very small changes in sheet resistivity: on the order of 1%. The conducted stability and vacuum tests show the applicability of the combined ultrasonic and conductivity setup for *in situ* characterization during irradiation.

In the future, an *in situ* measurement of irradiation effects on combined single and double walled carbon nanotube bucky paper using the setup described in this paper will be conducted. The results shown here indicate that the changes we will see are due to the irradiation, and that the changes we can detect are well below the expected 1-2 orders of magnitude.

E. References

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