

Spinning CNT based Composite Yarns using a dry spinning process

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Abstract— A process for manufacturing polymer carbon nanotube (CNT) based composite yarns is reported. The aligned CNT structure was combined with a polymer resin and, after being stressed through the spinning process, the resin was cured and polymerized, with the CNT structure acting as reinforcement in the composite yarn. The present method obviates the need of special and complex treatments to align and disperse CNTs in a polymer matrix. The process allows development of polymer/CNT based composite yarns with different mechanical properties suitable for a range of applications by using various resins.

Keywords—CNT web; sliver; CNT polymer composite yarns; modified dry spinning process; resin.

I. INTRODUCTION

The unique properties of carbon nanotubes (CNTs) of high tensile strength and Young's modulus, high aspect ratio, and good electrical and thermal conductivities [1] have opened up various novel application areas, for example, in nano-mechanics [2], advanced electronics [3] and biotechnology [4]. The superior mechanical properties of the individual CNTs alone do not ensure mechanically superior pure CNT-based products [5,6]. There has been significant effort into the fabrication of macroscopic CNT structures, including the study of blended polymer fibre-CNT composites with improved physical and mechanical properties [7]. In the most recent CNT polymer composite studies, CNTs have been used as discontinuous reinforcement of polymer matrices where CNTs are dispersed into polymers systems and subsequently fabricated into films and yarns, using a variety of techniques. Several different mixing techniques have been used to facilitate incorporation of CNTs into polymer films via solution processing [8-9]. However, the most difficult and complex problem for these approaches are the alignment and dispersion capability of CNTs because of their easy agglomeration in polymer liquids [10-11].

Recently, CSIRO has developed a modified dry spinning process for converting CNT forests into yarn in which the CNT structure is more aligned and the mechanical properties of yarns are improved [5]. The partitioning of the spinning system into separate zones has enabled further development

of other types of CNT based products. Using this modified system, a CNT polymer composite yarn manufacturing process was set up with simple control of the alignment and tension of the CNT-based reinforcing structure. In contrast to previous methods where the CNTs are dispersed in polymer solution, in this work, the polymer filled the pores between the stretched and aligned CNT web/sliver and formed a unique CNT-polymer composite. The aim of this work was to demonstrate a different approach for producing the CNT-based polymer composite yarns with properties that may satisfy many different engineering specifications, including biomedical device applications.

II. POLYMER/CNT COMPOSITE MANUFACTURING PROCESS

The process for manufacturing polymer/CNT composite yarn extends the modified dry CNT spinning process, shown in Figure 4 of [5], by inserting the extra relevant processing stages. This process consists of (i) web formation from CNT forests together with the arrangement and alignment of CNT fibers, (ii) application of polymer onto CNT web or sliver, (iii) compressing, squeezing polymer in the CNT reinforcing layer and (iv) curing the composite (Figure 1).

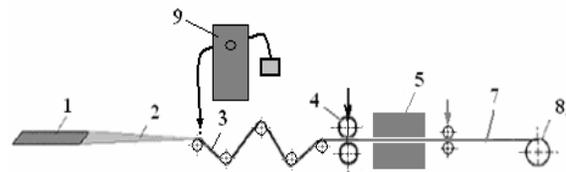


Figure 1. Schematic of the CNT polymer composite yarn spinning: Wafer (1), web (2), sliver (3), squeeze rollers (4), furnace (5), guide rods (6), yarn (7), bobbin (8), polymer applicator (9) process.

A. Preparing CNT aligned and drawn web

The CNT web (network of CNT bundles) formed from a CNT forest is aligned and stretched or drafted when drawn through an arrangement of capstans. The micrograph image (Figure 2) indicates that the bundles in the web and sliver

structures obtained by the modified process are parallel and highly aligned in the direction of spinning.

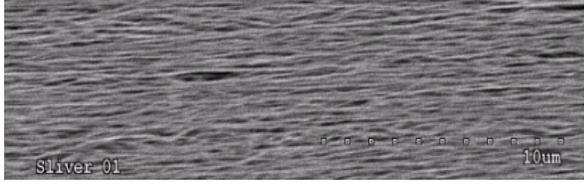


Figure 2. Micrograph of a CNT sliver (web) using the modified process depicting CNT bundle alignment

B. Applying polymer to the CNT web/sliver

To distribute the polymer evenly and throughout the yarns, polymer was applied directly to the CNT web/sliver instead of coating only on the yarn's surface. Several approaches for adding polymeric species to CNT web/sliver have been evaluated: (i) combination of the CNT spinning process and a polymer electro-spinning, (ii) absorbing PU solution using the capillary effect and (iii) combination between the above methods. The selected method depends on the specification of resin (melting temperature, characteristics of the components of polymerization (resin and hardener)) used for curing composites. In this paper, method (ii) is described with the use of polyurethane (PU) resin. While passing through a capstan effect rod system (CERS), the web/sliver (2) & (3) contacts with a membrane of solution of polymer. This solution was applied on the first rod of CERS using a peristaltic pump (9). After contact with the CNT web/sliver, the polymer solution was absorbed into the web/sliver spaces by the capillary effect.

The polymer solution penetrates and is distributed more evenly in the CNT macro-structure when the sliver passes through the CERS. The adjustable radial pressure is imposed on the sliver and given by Equation (1) (see [5] for more details)

$$N_i = \frac{T_i}{\mu} (e^{\mu\theta_i} - 1) \quad (1)$$

where μ , T_i , θ_i and N_i are the friction coefficient of yarn on the rods, outgoing tension, contact angle and radial pressure of sliver on the rod i of a CERS, respectively.

C. Squeezing CNT sliver and curing composite yarn

Following the radial pressure on the yarn at the CERS, further compression of the very low twist yarn is achieved when the yarn passes through the squeeze rollers (4) before curing in the furnace (5). The speed of these rollers was synchronized with the take-up speed of the bobbin (using computer control) to maintain yarn tension. The squeeze rollers and guide rods allow control of some twist flowing back into the sliver through the CERS, which assists controlling the drafting.

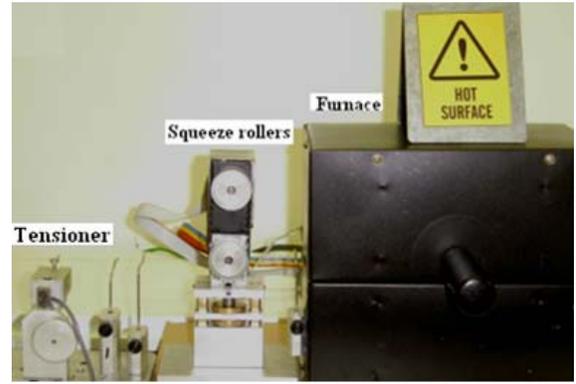


Figure 3. An actual installation of the compressing, squeezing and curing zones

III. RESULTS AND DISCUSSION

In this work, the experimental plan involved using MWCNT forests grown on silicon wafers using chemical vapor deposition (CVD) whose CNT's length and outer diameter are approximately 300-400 μm and 7.5-8.5 nm, respectively. Although many different resins were considered for this research, urethane polymer was employed throughout this paper as an example for applying the present method in manufacturing the polymer/CNT yarns. Polyurethane (PU) is one of the most popular polymers used in a variety of products, such as coatings, adhesives, flexible and rigid foams, tough solids. Several articles have reported the preparation of PU/CNT composites using the dispersion method with significantly improved mechanical properties [12-14]. Polyurethane elastomer (supplied by Urethane Compounds PTY. LTD.) dissolved in dimethylformamide (6% – 10%wt) before being applied into the CNT web/sliver.

A. Morphology of the polymer/CNT composite and yarns

To qualitatively investigate the distribution of polymer in the yarn core, a morphological observation of web, sliver and yarn was carried out using the scanning electron microscope (SEM). Figure 4 shows a micrograph of matrix comprising CNT bundles and interspersed PU. After going through the CERS, the PU was dispersed evenly into the networks of aligned CNT bundles (see Figure 4). The image depicted in Figure 4b was obtained by rupturing the PU/CNT composite sliver to illustrate the internal composite. The SEM images show the progress from the initial stage of polymer application on the web/sliver to the influence of CERS in the formation of the PU/CNT matrix. After squeezing, the sliver was twisted into a yarn and then dried at 40°C. Figures 5a and b show the surface of PU/CNT composite and pure CNT yarns, respectively, showing some differences in surface character.

A focused ion beam (FIB) combined with SEM was used to compare the morphology of cross-sections of pure CNT yarns and PU/CNT composite yarns with diameters between 15-20 μm . The figure 6a is the cross-section of a PU/CNT yarn and shows defects near the circumference where the PU has not completely filled the areas between the bundles. An

extraction of the Figure 6a near the defect (I) was enlarged to the Figure 6b.

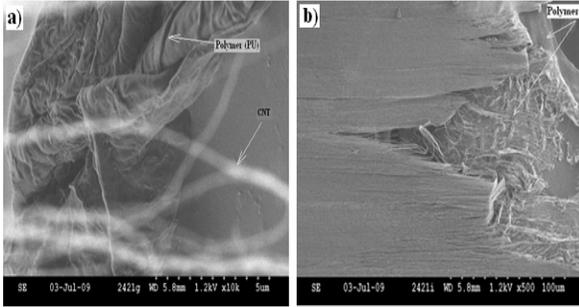


Figure 4. SEM images of PU/CNT structures using the current approach: a) The initial formation of PU matrix and CNTs; b) A sliver structure of PU/CNT composite

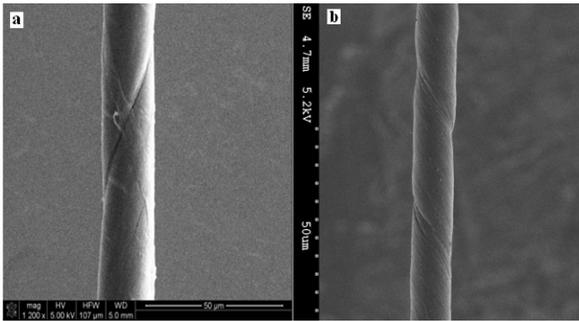


Figure 5. Micrograph (SEM images) of the surface layer for MWCNT yarn using the modified process: a) CNT-PU composite yarns (Left); b) Pure CNT yarn (Right).

A large difference in appearance of the cross-section of the pure and polymer CNT composite yarns was very obvious. In fact, Figures 6b and c compare SEM images of PU/CNT composite with pure CNT yarn sections. The pure CNT yarn (Figure 6c) shows individual CNT bundles whereas the PU/CNT section shows the PU has filled the spaces between the bundles. The penetration and distribution of polymer in the yarn core are the important factors to evaluate the effectiveness of the method.

B. The mechanical properties of PU/MWCNT composite yarn

The mechanical properties of a polymer/CNT composite yarn depend on many different factors, for example density of PU, CNT geometry, the interaction between PU and CNT and polymerization. For the mechanical property testing, all samples were spun using the same spinning parameters (Twist number of 5000 TPM and take-up speed of 4m/hour), polymer add-on of 20-30wt% and test gauge length of 10mm. The tensile strength and strain data measured on a tensile tester (0.2 mm/min, room temperature) cover a range from 1.6GPa to 2GPa and 1.8%-2.5%, respectively (Figure 7). Although there is some variability in the mechanical properties of the PU/CNT composite yarns, the results show the tensile strength was higher at low twist than highly twisted pure CNT yarn (see Figure 11, ref [5]).

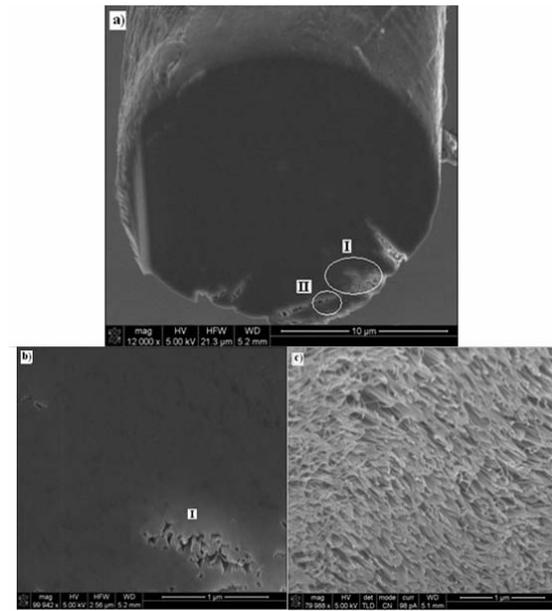


Figure 6. Morphology of the cross-sections of pure CNT and PU/CNT composite yarns using SEM-FIB: a) Cross-section of a PU/CNT composite yarn with some defects (I, II) near the circumference; b) An enlargement of the cross-sections extracted from (a) at the position near the defect (I) and c) Cross-sections of a pure CNT yarn.

The PU/CNT composite yarns were also characterized using a dynamic mechanical analyzer (DMA) (TA Instruments Q800). Twenty samples comprising of the different diameters were tested, using the controlled force mode, to obtain static stress-strain curves (0.02N/min, 25°C). The results show a good agreement with the results from the tensile tester.

Figure 8 shows a typical result of the constant frequency temperature scan mode (1Hz, 5°C/min) on the elastic and damping behavior of the PU/CNT composite yarns. The curves show that the storage modulus varies with respect to temperature (decreasing until 60°C and nearly constant between 60°C and 100°C before increasing). Irrespective of the variations in storage modulus between 0°C and 120°C, all values obtained are regarded as high (from 120GPa to 150GPa).

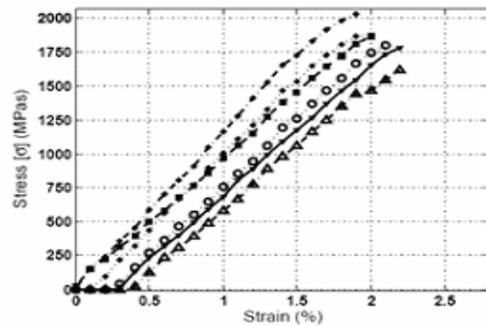


Figure 7. The tensile strength of PU/CNT composite yarns: a) Stress-strain curves of samples on the tensile tester (0.2mm/min, room temperature, 25°C);

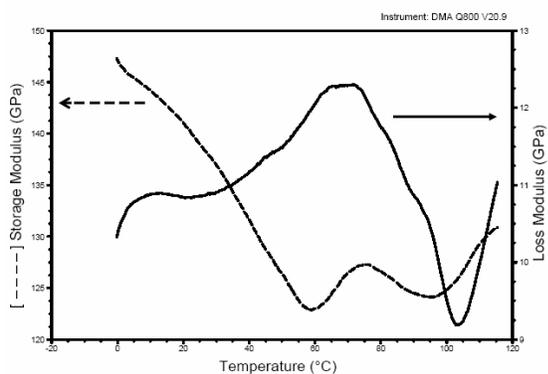


Figure 8. DMA results for a PU-CNT composite yarn: Storage and Loss Modulus plotted against temperature using the constant frequency mode.

C. Extension of this approach for improved composite CNT yarns

The separation of the web and yarn stages of the modified spinning process allows for new concepts to be introduced into the manufacture of polymer/CNT composite yarns to improve the interaction between CNTs and the polymer matrix. Functionalization can be an efficient method to improve the interfacial interaction and to enhance the covalent bonding between a polymer and CNTs [15-17]. A plasma torch using helium and operating at atmospheric pressure has been installed to functionalize the CNT web (Figure 9) prior to the polymer application. The presence of polymeric bonding to CNTs can be detected using analytical techniques (for example Fourier transform infrared spectroscopy) and will be mentioned in our future work.

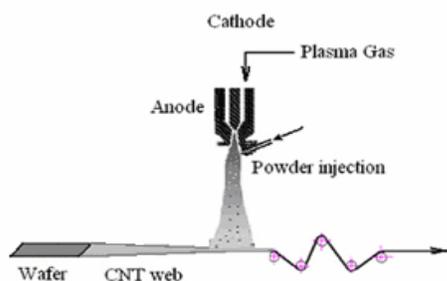


Figure 9. Web treatments before being applied polymer: Schematic of plasma torch configuration applied to the CNT web/sliver

IV. CONCLUSION

A process for manufacturing polymer/CNT composite yarns has been developed and evaluated. The process is based on the modified dry spinning method and provides a continuous process to manufacture CNT based composite

yarns. The alignment of CNT bundles during the process is simply and easily carried out. The capillary methods for applying resin on web/sliver before CERS assures an even distribution of polymer on the CNT web and subsequently in the yarn cross-section. Composite PU/CNT yarns with high tensile strength of approximately 2 GPa have been produced. This preliminary study shows the potential to extend the dry spinning approach to obtain new CNT yarn properties. Those may provide favorable interactions between the polymer matrix and the CNTs to benefit a load transfer mechanism between CNTs and polymer. Similarly, in principle, the technique may be easily extended to multi-layer CNT composites with potential for innovative properties, for example high thermal and electrical conductivities or/and super-strong tensile strength.

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