

Manufacturing polymer/carbon nanotube composite using a novel direct process

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Abstract. A direct process for manufacturing polymer carbon nanotube (CNT) based composite yarns is reported. The new approach is based on a modified dry spinning method of CNT yarn and gives a high alignment of the CNT bundle structure in yarns. 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. Thus the present method obviates the need of special and complex treatments to align and disperse CNTs in a polymer matrix. The new process allows of producing the polymer/CNT composite with properties that may satisfy various engineering specifications. The structure of the yarn was investigated using scanning electron microscopy coupled with a focused ion beam system. The tensile behavior was characterized using a dynamic mechanical analyzer. Fourier transform infrared spectrometry was also used to chemically analyze the presence of polymer on the composites. The process allows development of polymer/CNT based composite with different mechanical properties suitable for a range of applications by using various resins.

1. Introduction

Carbon nanotube's (CNT) unique properties of high tensile strength and Young's modulus, high aspect ratio, and good electrical and thermal conductivities [1-4] have made possible novel applications, for example, nano-mechanics [5], advanced electronics [6] and bio-technology [7]. The CNTs in fiber-reinforced composites with their very small diameters (4–10 nm) and high aspect ratios (1000–10,000) have received increased attention as reinforcements for polymer composites. Significant effort has focused on fabricating macroscopic structures to make use of the CNT's unique properties, in particular by producing blended polymer/CNT composites with improved physical and mechanical properties [8-9]. Furthermore, it has been theorized that CNTs can enhance the physical properties of polymer composites as well as imparting electrical conductivity at relatively low loadings of nanotubes due to the high aspect ratio and excellent physical and electrical properties [10-13]. In the most recent polymer/CNT composite studies, CNTs have been used as discontinuous reinforcement for polymer matrices, for example, they have been 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 [14-15] and many results have been published [7,16-19]. However, the most difficult and complex problem of these approaches is the alignment and dispersion capability of CNTs because of their easy agglomeration in polymer liquids [20-21]. These issues essentially define the basic challenges for applied CNT composite research.

Recently, CSIRO has successfully developed a modified dry spinning process for converting CNT forest into yarn where the CNT structure is more aligned and the mechanical properties of yarn are significantly improved [22]. The aim of this work was to demonstrate a different approach, based on the modified dry spinning process, for producing the polymer/CNT composite yarns with properties that may satisfy many different engineering specifications, especially in biocompatible applications.

2. Review of the modified dry spinning process

Pure CNT based products (yarns and sheets) have two structural levels, the individual CNTs (molecular level) and bundles of aggregated CNTs held by van der Waals forces [23-24]. When gathered from a CNT forest the CNT bundles form a continuous network, called the web. In CNT structures of web, sliver, sheet or yarn, some free space or porosity is present, even at a high packing factor, that is, there is space not only between the CNTs but also between CNT bundles (see figure 1).

The success of the dry spinning process was attributed in part to the degree of twist applied during spinning [17, 25]. In fact, the role of twist was to increase the van der Waals forces between the CNTs in the bundles as well as the interaction between the CNT bundles, which produced the required inter-bundle lateral cohesion. This cohesion in a macro-structure, however, is only optimal if the alignment and tension is controlled.

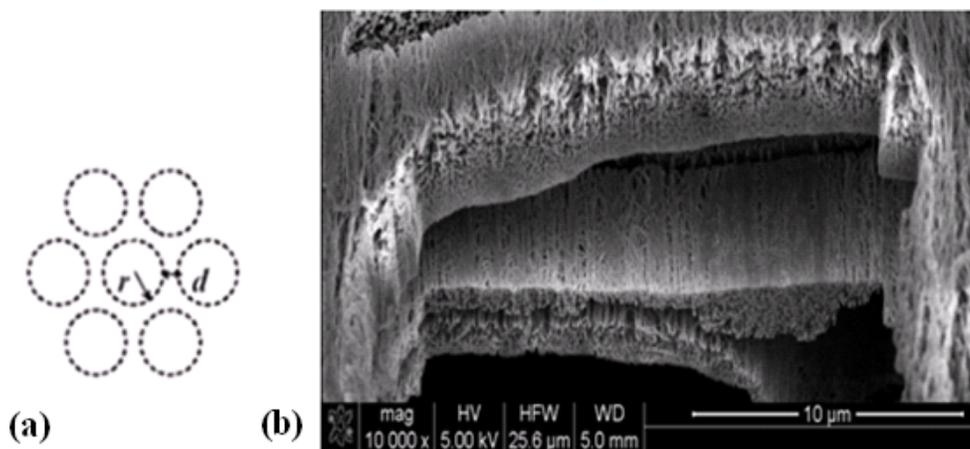


Figure 1. (a) A schematic showing the cross-section of a CNT bundle, where r is the CNT diameter and d is the gap between CNTs. (b) Micrograph of CNT sliver using the modified CNT spinning process: The surface and cross section of a multi-layer sliver.

The modified spinning system developed by Tran et al. [22] enhanced the alignment and evenness of the tension of CNTs and CNT bundles in the structures (web, sliver and yarn) along the spinning direction by using a drafting system. The experimental results from this arrangement showed that increased alignment of CNT bundles was obtained (figure 1(b) together with enhanced CNT yarn properties. Furthermore, the partitioning of the modified process into separate zones has now allowed further development of other types of CNT based products (please see [22] for details). Using this modified system, a polymer/CNT composite manufacturing process was set up with simple control of the alignment and tension of the CNT reinforcing structure. In contrast to previous methods where the CNTs were dispersed in polymer solution, in this work, polymer filled the pores between the stretched and aligned CNT web/sliver (defined as compacted bundles at low density and without twist) and formed a polymer/CNT composite.

3. Manufacturing CNT composite yarn using the present process

A composite material, in its basic form, is a heterogeneous combination of two or more materials, differing in form or composition. The structural strength of composites greatly depends on the nature of the bonding at the interface, the mechanical load transfer from the matrix (polymer) to the CNTs and the yielding of the interface. If the interface is weak, a crack formed at the interface will cause fracture and result in failure of the composite. In this aspect, CNTs are better than traditional macro-

fibers due to their ability to inhibit nano and micro cracks. The interfacial interaction of polymer/CNT composites and the benefits for mechanical properties have been published [26-29]. However, the main issue with processing the composites is the inability to align the CNTs in the polymer matrix. In many studies, CNTs served as a filler and were dispersed in a polymer solution [8-9, 14-15]. The difficulties in obtaining uniform dispersion were highlighted, although some solutions have been presented for different resins. For example, covalent functionalization of CNTs with the polymer matrix [30]; utilizing solution-evaporation methods with high-energy sonication [31]; surfactant assisted processing through formation of a colloidal intermediate [32] and stirring CNTs within an epoxy matrix repeatedly at 2000 RPM (rotation per minute) both before and after adding the curing agent [33]. In addition to the problem of uniform dispersion of CNTs within the matrix, it is critical to produce systems with controlled structure and alignment so that the axial load-carrying efficiency of the CNTs can be utilized. In fact, poor dispersion and alignment of CNTs throughout the polymer will not provide the desired mechanical reinforcement. In order to deal with these disadvantages, a dry polymer/CNT composite manufacturing process was developed and will be detailed in the next sections.

In this work, the direct process for manufacturing polymer/CNT composite extends the modified dry CNT spinning process by inserting the extra relevant processing stages. The 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 2).

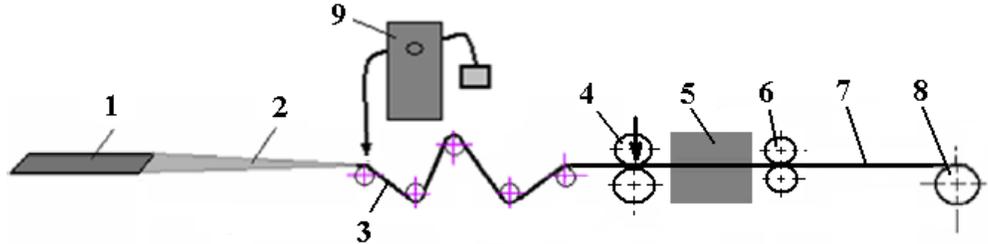


Figure 2. Schematic of the polymer/CNT composite manufacturing process: Wafer (1), web (2), sliver (3), squeeze rollers (4), furnace (5), guide rods (6), yarn (7), bobbin (8) and polymer applicator (9).

3.1. Preparing CNT aligned and drawn web

The CNT web (network of CNT bundles) formed from a CNT forest, ((2), figure 2) is aligned and stretched or drafted when drawn through an arrangement of capstans. The micrograph image (figure 3) indicates that the bundles in the web and sliver structures obtained by the process are parallel and highly aligned in the direction of spinning. Although the web structure is only weakly bonded, its stability and isolation from the later spinning stage were important for allowing polymer to be applied.

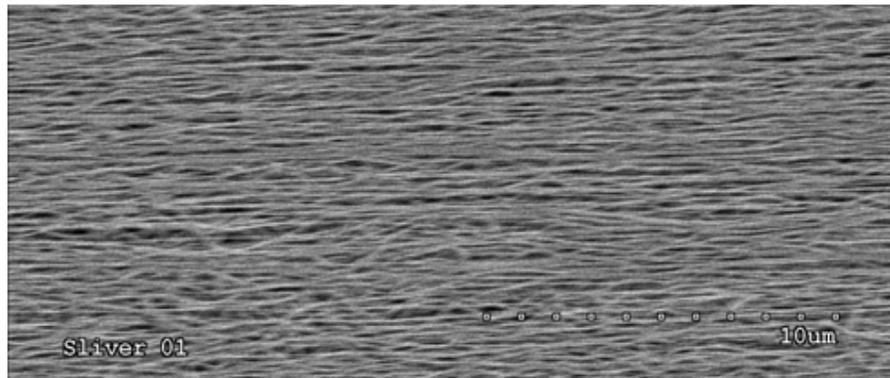


Figure 3. Preparation of CNT web/sliver: Micrograph of a CNT sliver using the modified dry spinning process shows the CNT bundle alignment.

3.2. 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. Four 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) spraying a cloud of nano-particles of PU solution using a fluid dispensing system, (iii) absorbing PU solution using the capillary effect and (iv) 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 (iii) is described with the use of polyurethane (PU) resin. While passing through a capstan effect rod system (CERS), the web/sliver (2) contacts with a membrane of solution of polymer. This solution was applied on the concave surface of the first rod (1) of CERS using a peristaltic pump (3). The mechanism is described in figure 4.

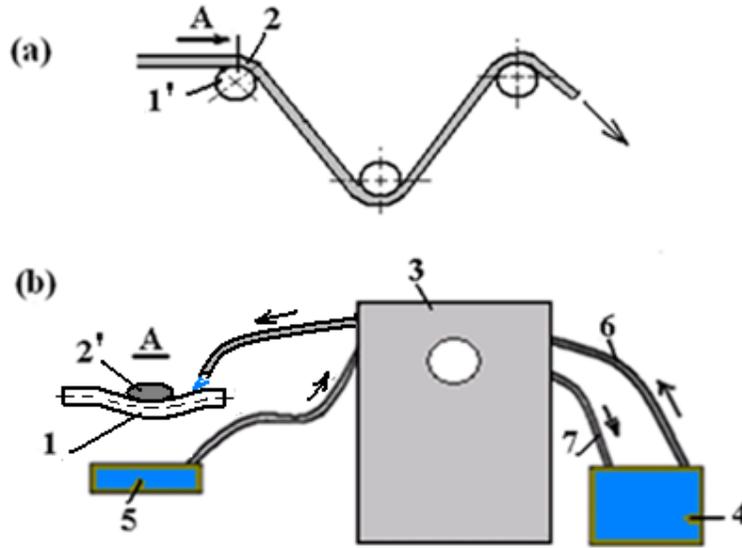


Figure 4. Schematic of polymer applying to web/sliver using the capillary effect: (a) CNT sliver passes through a CERS: cross-section of the first rod of CERS at the position A (1'), sliver (2); (b) Mechanism of polymer applying to web/sliver: the first rod of CERS (1), cross-section of sliver 2 at the position A (2'), peristaltic pump (3), reservoir of polymer solution (4), collector of polymer solution (5) and pipeline (6,7).

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) [34]:

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

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.

The position and number of the polymer applicators located and radial pressure on the capstans of the CERS can qualitatively determine the absorbability of polymer solution in the sliver.

3.3. Squeezing CNT sliver and curing composite

As shown in figure 5, 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 (2) before curing in the furnace (3). The speed of the 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.

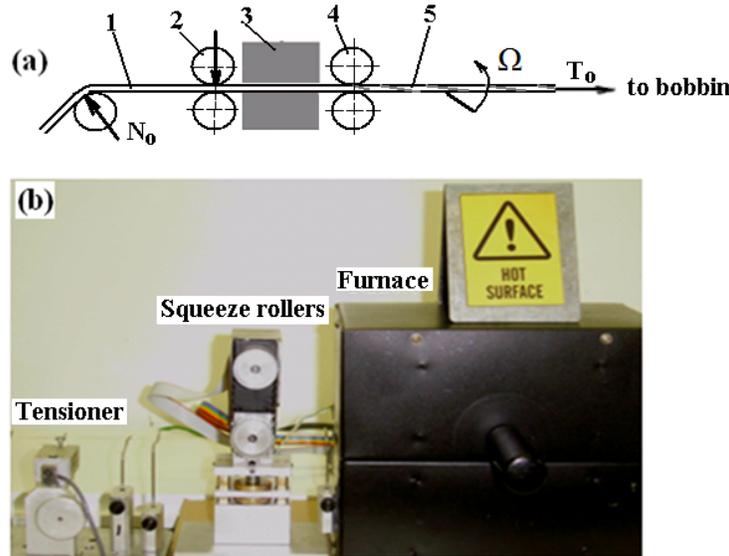


Figure 5. (a) A schematic of the twist zone and final part of CERS showing the twist insertion: Sliver (1), squeeze rollers (2), furnace (3), guide rods (4) twisted yarn (5). N_0 , T_0 and Ω are the radial pressure of a rod on yarn, tension of yarn rolled up on the bobbin and torque caused by twisting, respectively; (b) An actual installation.

3.4. The mechanics of the interface for polymer/CNT composite

Many researchers have attempted to model the polymer/CNT interface using techniques such as multi-scale modelling [35] or a micromechanics model to predict the bulk mechanical properties of the composites as a function of CNT size, orientation, and volume fraction. Generally, the interfacial interactions of polymer/CNT composite yarn consist of (i) the non-covalent bonding such as electrostatic, van der Waals forces and the mechanical interlocking of the CNTs and polymer molecules and (ii) the covalent chemical bonding (not represented in this work). These interactions are mentioned in some recent works of Gou et al [36], Wong et al. [21] and Watts and Hsu [37].

Since the present method is based on the direct process, twist affects the mechanical properties of the reinforcing CNT structure while the surface macro-interfacial interaction (friction and adhesion) and inter-tube corrugation are also the significant factors governing the load transfer at the fibre interface. Hence, the model of mechanical properties in the current case of polymer/CNT composite yarn is different from a traditional composite, for example Halpin-Tsai model mentioned in Thostenson and Chou [38]. Future work will address this model issue.

4. Experimental investigations, results and discussion

The major aims of this section were to investigate the efficacy of the present polymer/CNT yarn manufacturing process such as (i) the polymer distribution in the yarn structure and (ii) evaluation of some mechanical properties of CNT composite yarn. Hence, the influence of different resins as well as their density on properties of the CNT/polymer composite will not be detailed by the authors as an objective of this paper.

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 (manufactured at CSIRO), 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 [39-41]. Polyurethane elastomer (supplied by Urethane Compounds PTY. LTD.) dissolved in dimethylformamide (6% – 10% wt) before being applied into the CNT web/sliver.

4.1. Morphology of the polymer/CNT composite yarn

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 6(a) 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 6(b)). The image depicted in figure 6(b) 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.

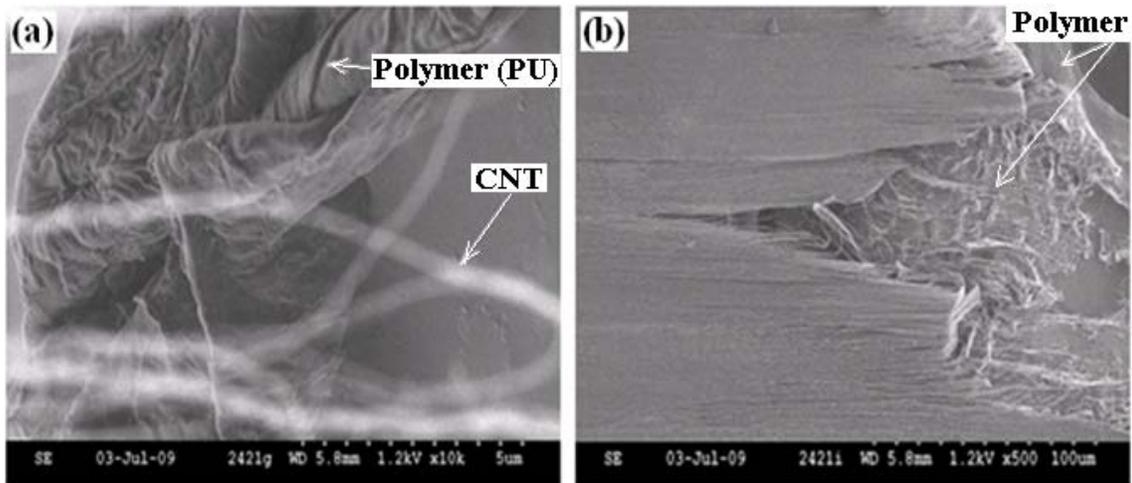


Figure 6. SEM images of PU/CNT structures using the current approach: (a) The initial formation of PU matrix and CNTs; (b) A sliver structure of PU/CNT composite.

After squeezing, the sliver was twisted into a yarn and then dried at 40°C. Figures 7(a) and (b) show the surface of PU/CNT composite and pure CNT yarns, respectively, showing some slight differences in surface character.

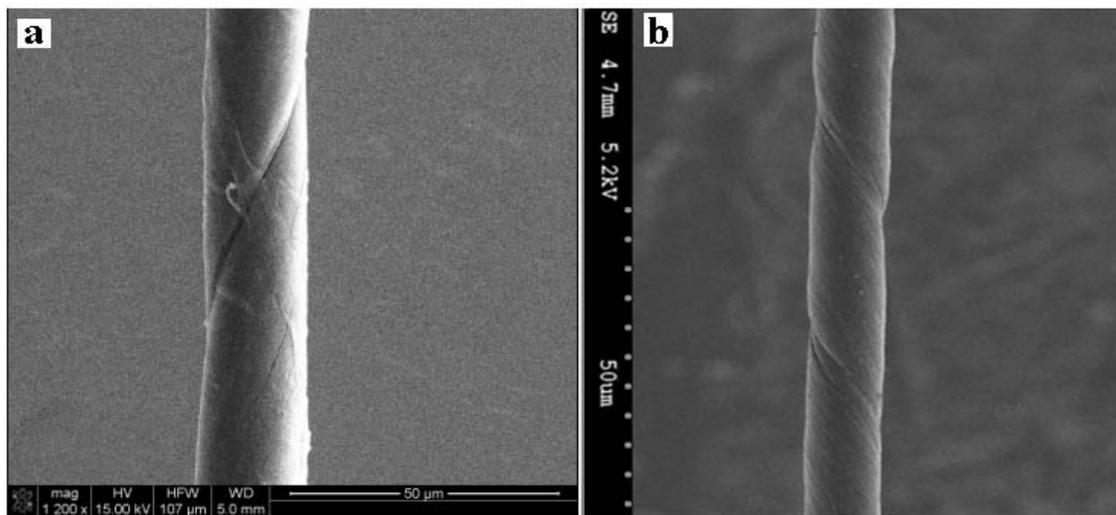


Figure 7. Micrograph (SEM images) of the surface layer for CNT yarn using the modified process: (a) PU/CNT composite yarn and (b) pure CNT yarn.

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 . While the surface of pure CNT (figure 7(b)) yarn is not significantly different from the PU/CNT yarn's surface (figure 7(a)), large differences in appearance of the cross-section were very obvious.

Figure 8(a) 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 8(a) near the defect (I) was enlarged to the figure 8(b).

The penetration and distribution of polymer in the yarn core are the important factors to evaluate the effectiveness of the method. Figures 8(b) and (c), whose magnifications are around 80000, compare SEM images of PU/CNT composite with pure CNT yarn sections. The pure CNT yarn (figure 8(c)) shows individual CNT bundles whereas the PU/CNT section shows the PU has filled the spaces between the bundles. Although further investigations are required for a quantitative distribution of polymer in CNT/polymer composite yarns, the morphology of yarn's cross-section obtained from the FIB & SEM method showed the significant presence of PU in the pores of CNT/composite.

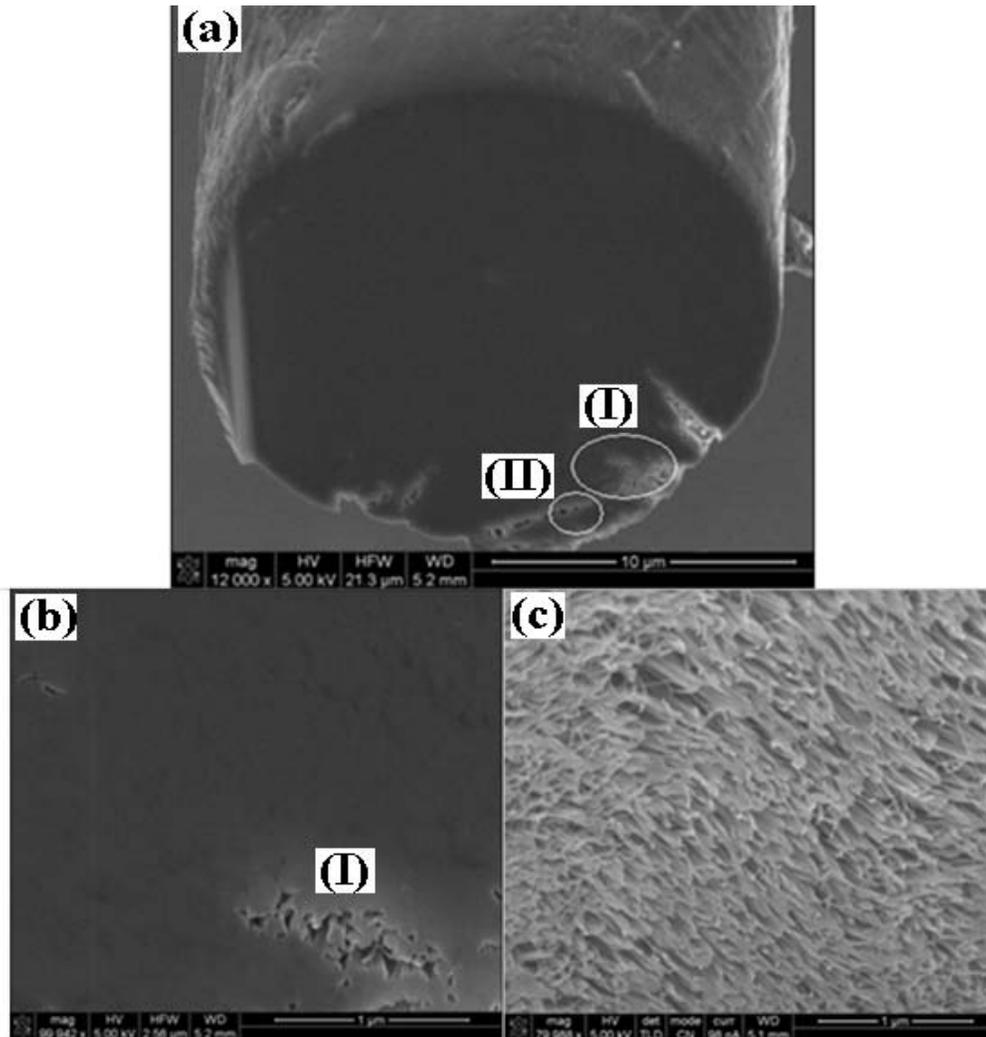


Figure 8. Morphology of the cross-sections of pure CNT and PU/CNT composite yarns using SEM-FIB: (a) Cross-section of a PU/CNT composite yarn with some defects (I, II) near the circumference; (b) An enlargement of the cross-sections extracted from (a) at the position near the defect (I) and (c) Cross-sections of a pure CNT yarn.

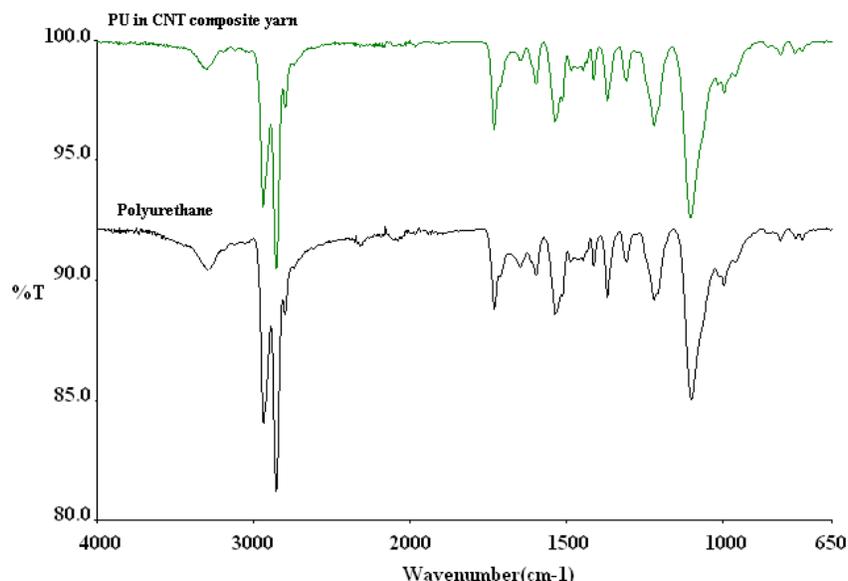


Figure 9. Fourier transform infrared spectroscopy of the polyurethane sample and PU/CNT composite yarn.

Fourier transform infrared spectroscopy (FTIR) was also used to confirm the presence of polymer in the CNT yarn and investigate the bonding mechanism. Infrared spectra were collected using a single bounce universal attenuated total reflectance (UATR) accessory in a Perkin Elmer Spectrum 100B spectrometer. Each spectrum was the result of five repeat co-added scans collected at 4 cm^{-1} resolution. Spectra were baseline corrected and corrected for variation in penetration of the sample with incident radiation wavelength. Two samples were prepared for analysis; a slide coated with a thin film of polyurethane, dried at $40\text{ }^{\circ}\text{C}$ and a CNT composite yarn sample. The CNT yarn sample consisted of approximately $100 \times 15\text{ }\mu\text{m}$ diameter yarns twisted together then flattened to form a sample approximately 1mm in width. The sample was held on the crystal using force of 80% by the instrument pressure gauge. Typical infrared spectra of the PU film and composite yarn are shown in figure 9.

In spite of some small differences, both spectra are similar and show the CNT yarn contains a significant quantity of polyurethane. The minor differences in these spectra are instrumental variation due to the sampling and analysis techniques. In fact, the micro ATR accessory used a single bounce of the infrared beam to obtain the spectra and the quality is therefore dependant on the contact of the sample with the crystal. As we are looking at yarn samples, the contact area varied between samples, introducing some noise and loss of resolution into the spectra. Hence, the small variation between the spectra is a result of this variation in contact. Furthermore, there is no evidence of covalent bonding between the CNTs and PU because there are not significant changes in the $1740 - 1690\text{ cm}^{-1}$ region of the spectra.

4.2. 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 4 m/hour), polymer add-on of 20-30 wt% and test gauge length of 10mm as described in [22]. The tensile strength and strain data measured on the tensile tester Chatillon at CSIRO (0.2 mm/min, room temperature) cover a range from 1.6 GPa to 2 GPa and 1.8% - 2.5%, respectively (figure 10). 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 whose tensile strength is around 1.2 MPa (see figure 11, ref [22] for details). From Figures 10(a)&(b), it is interesting to appreciate that the variability of tensile strength of a polymer/CNT composite yarn is smaller than one of a pure CNT yarn. Although further investigations are required, the initial results have shown that the tensile strength decreases and the

strain tends to reach the higher values as polymer add-on is increased (figures 10(a) and 10(b)). However this issue is not a main objective of this work.

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 (0.02 N/min, 25°C). The results show a good agreement with the results from the tensile tester (figure 10). A typical stress/strain curve of PU/CNT composite yarn on DMA is shown in figure 11.

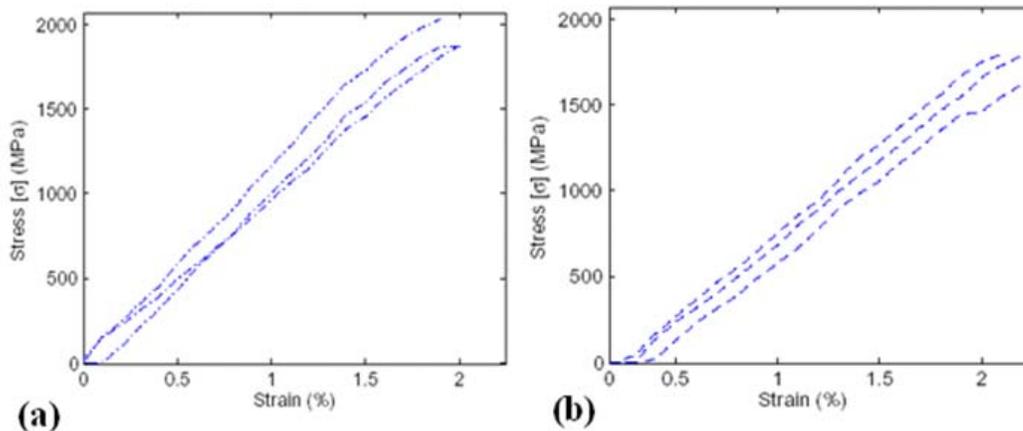


Figure 10. The tensile strength of PU/CNT composite yarns: Stress-strain curves of samples on the tensile tester Chatillon (0.2 mm/min, room temperature, 25°C); (a) PU add-on of 20 wt%; (b) PU add-on of 30 wt%.

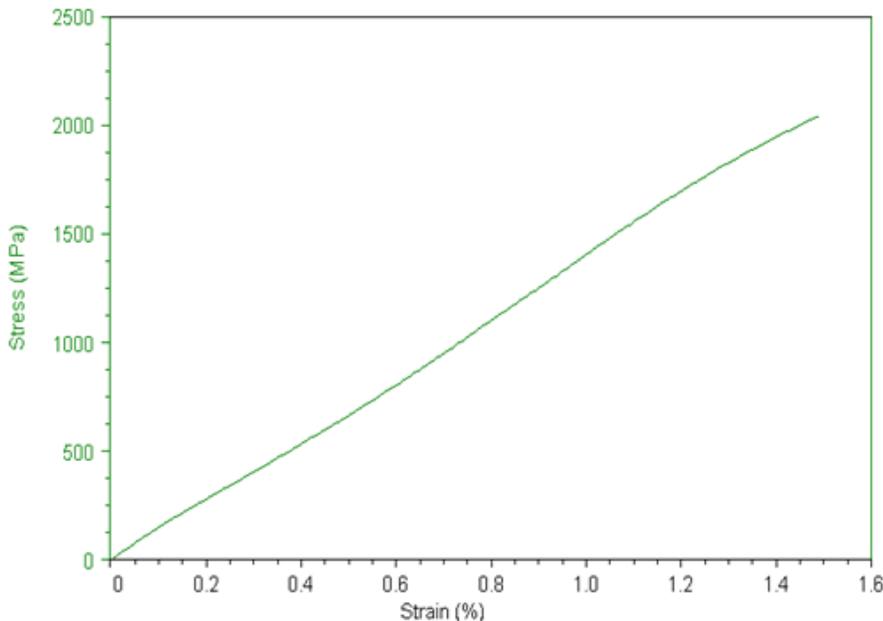


Figure 11. The stress-strain curve of a typical PU/CNT composite yarn (with PU add-on of 20 wt%) using DMA under controlled force mode (0.02 N/min, 25°C).

Figure 12 depicts a result of the constant frequency temperature scan mode (1 Hz, 5°C/min) on the elastic and damping behavior of the PU/CNT composite yarns (with PU add-on of 20 wt%). It shows to interested parties that the response of material to DMA measurement is possible but more extensive studies are necessary. 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. In general, a drop in storage modulus and peak in loss modulus come about because

the material goes through a glass transition. Normally, the drop is stiff (from GPa down to MPa [26]) and depends on how much PU is in the CNT composite. However, the result showed that the drop is low (from 150 GPa down to 120 GPa). Although extensive investigations are required, the very low density (add-on) of PU in CNT composite as well as the interaction of CNTs in twisted yarn's structure could be its reasons. We will return to this problem and others related to the DMA measurement of CNT/polymer composites in next papers.

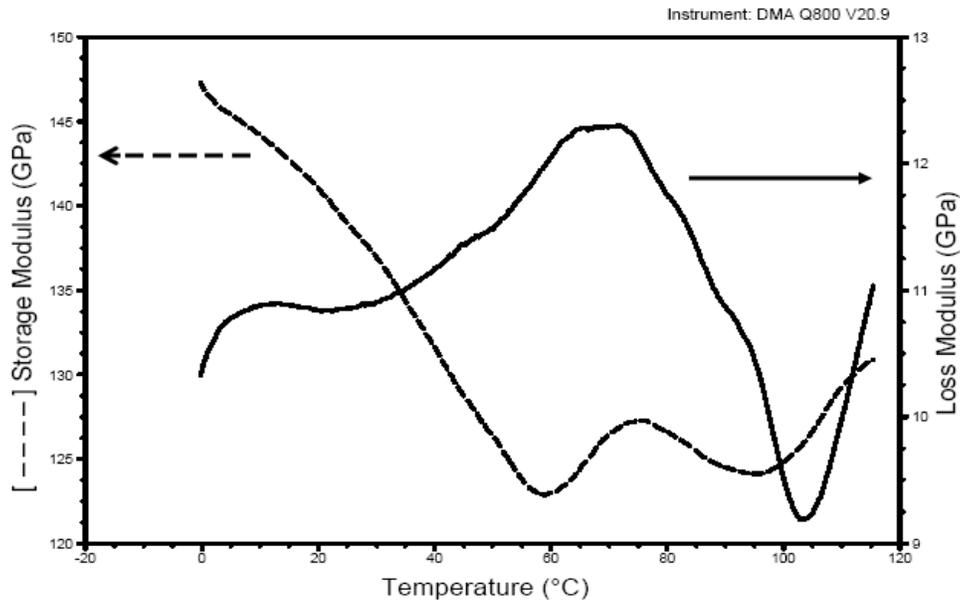


Figure 12. DMA results for a PU/CNT composite yarn (with PU add-on of 20 wt%): Storage and loss modulus plotted against temperature using the constant frequency mode.

4.3. 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. Two typical applications are foreshadowed in the following.

(i) Improvement of 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 [42-44]. A plasma torch using helium and operating at atmospheric pressure has been installed to functionalize the CNT web (figure 13(a)) prior to the polymer application. The presence of polymeric bonding to CNTs can be detected using analytical techniques (for example FTIR) and will be mentioned in our next work. An alternative approach was to charge a web with static electricity, produced from a Van der Graaff generator to enhance the absorption of the conducting polymer (see figure 13(b)).

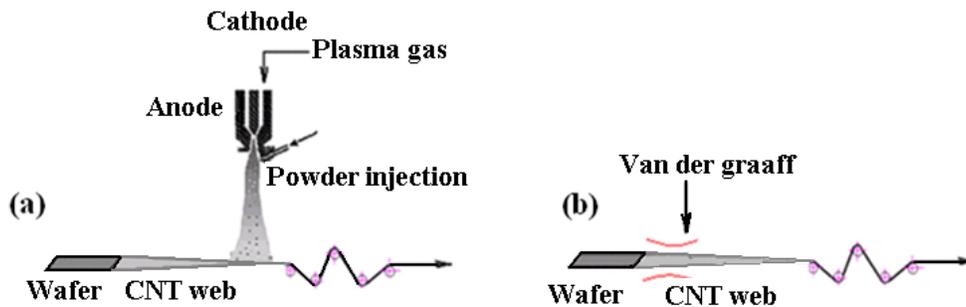


Figure 13. Web treatments before being applied polymer: (a) Schematic of plasma torch configuration applied to the CNT web/sliver and (b) Schematic of web vibration using Van der Graaff.

(ii) The multi-web spinning from multi-wafers (figure 14) allows of development of multi-layer composite yarns and multi-layer or sandwich composite constructions which can respond to various requirements.

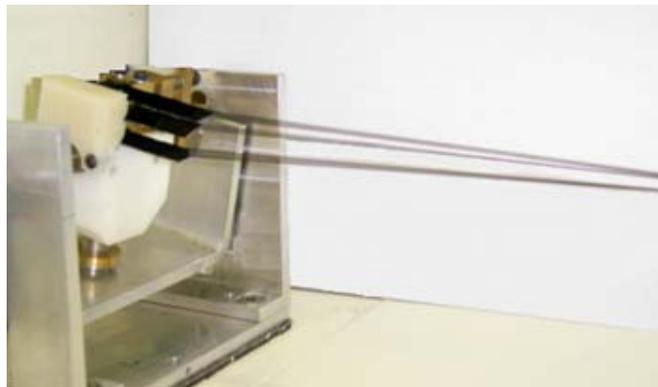


Figure 14. CNT Multi-web spinning from multi wafers used in the present process

5. 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 spinning approach to obtain new CNT yarn properties. For example, the technique may be easily extended to multi-layer CNT composites with potential for innovative properties, such as high thermal and electrical conductivities or/and super-strong tensile strength. Other treatments may be compatible with this system include on-line functionalization, magnetic and Ultraviolet treatments or static electricity processing. Those may provide favorable interactions between the polymer matrix and the CNTs to benefit a load transfer mechanism between CNTs and polymer.

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