Production of CNT Yarns from Methane Gas for Use as Filaments in Incandescent Bulbs: Thermodynamic Properties of As-spun CNT Yarns.

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Abstract

Energy efficiency is a minimal cost energy resource. It is critical in bridging the gap via reducing overall demand, allowing electricity supply to be expanded to meet increasing demand in a timely and sustainable way. Incandescent bulbs with tungsten filaments convert only about 10% of the input energy into light with the rest wasted as heat and resultant carbon dioxide gas emissions. This results in high energy and environmental inefficiency. Carbon nanotubes (CNT) yarns as filaments for replacement of tungsten in incandescent bulbs represent an economic option boosting high energy and environmental efficiency. In this study, CNT yarns were produced from methane, an abundant greenhouse gas currently flared in Africa. Synthesis of CNT yarns were carried out in a Floating Catalyst Chemical Vapour Deposition (FC-CVD) reactor using ferrocene as the catalyst with direct spinning of CNT into yarn. The quality and morphology of the produced yarns at different temperatures (900 – 1000°C) were determined using Scanning Electron Microscope (SEM) and Raman Spectroscopy. The optimum temperature to produce CNT yarns was found to be at reactor temperature of 950°C. The thermodynamics associated with the production of the as-spun CNT yarns were determined by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Heat capacity of CNT yarns was calculated based on the measured heat flow at thermal stable state. A polynomial regression of the form: \( C_p=0.002T^2 - 0.4512T+66.099 \) was proposed for the prediction of the thermodynamic values. Change in thermodynamic quantities of yarn such as entropy and enthalpy were determined based on the heat capacities calculated from fitted polynomial models using relationship of thermodynamic function.

Key words: Carbon nanotube yarn, Kinetic, Thermodynamics,

1. Introduction

Since their rediscovery by Iijima [1], carbon nanotubes (CNTs) are identified as fascinating materials due to their remarkable electrical and mechanical properties. Currently, there is a great effort by researchers to fabricate CNT yarn in order to make use of CNTs remarkable properties. These properties make CNT yarn suitable material to consider in different application, such as, incandescent lamp filament [2], supercapacitor [3], artificial muscles [4], solar cell [5], and many more.

Surfactant-based coagulation spinning, direct spinning, forest spinning, and liquid crystalline spinning are the four most studied methods of manufacturing yarn from CNTs. Surfactant-based
coagulation involves injecting a binder which is polymeric between CNTs to produce a yarn [6]. During the direct spinning method, CNTs and yarns get produced at the same time [7]. In forest spinning, CNTs that are grown on a substrate get drawn and twisted to form a yarn [8]. Liquid-crystalline spinning involves spinning the suspension of CNTs to form a wet-crystalline suspension [9]. Out of all four methods, direct spinning method was found to be advantageous for continuous mass production. It was also found to be the most effective method in producing yarn with good mechanical and electrical properties [6;10].

Studies of thermodynamic properties of a material provide important information for classification of the energy state of the material, sorption, functionalization, calculation of equilibria, etc. Therefore, thermophysical quantities need to be considered when studying material. Thermophysical quantities of individual CNTs has gained interest and their study are been reported in open literature. The source of calculating these thermodynamic properties is by obtaining experimental heat capacities. Heat capacities of material are required in areas such as physics, chemical engineering and in chemistry to determine phase transition, mass balance, entropy and enthalpy. Heat capacities of SWCNTs were found to be higher than that of MWCNTs at a temperature below 275 K. However, at a temperature above 275 K MWCNTs have higher heat capacities than SWCNTs [11]. A study by Muratov showed that the heat capacity of MWCNTs is almost the same as that of graphite at a temperature of 298.15 K, though heat capacity of graphite is slightly higher [12]. As far as could be ascertained, no heat capacities and other thermodynamic properties of CNT yarn reported in open literature until now. Hence this study focused on the thermodynamic properties of yarn produced at different reactor temperatures using the direct spinning method. Effect of production temperature on the thermophysical quantities of the yarn was also investigated.

2. Methodology
2.1 CNT yarn synthesis

A continuous catalytic chemical vapor deposition (CCVD) reactor was used to synthesize CNT yarn. The reactor was equipped with a motor and spindle (Fig.1) to directly spin the CNTs into yarn. Before each experiment, Nitrogen gas (purity: 99.999%) was used to purge the system to remove any contaminants as well as to detect any gas leak around the system. 7 g of Ferrocene (purity: 98%) was used as catalyst, CH4 gas (purity: 99%) was used as carbon precursor at a constant flow rate of 125 ml/min. CH4 gas was chosen as carbon precursor because it produces high quality CNTs as compared to other carbon precursors [13]. At the start of each experiment, ferrocene powder was heated in a vaporiser simultaneously with heating the reactor using the furnace to the desired temperature (900 to 1000°C). During the reaction, CH4 gas was fed into the reaction zone and Argon gas (99.999%) at a constant flow rate of 150 ml/min was used to carry vaporised ferrocene into the reaction zone in the reactor. The electric motor at the reactor outlet was switched on to turn the spindle at a speed of 10 rpm. Each experiment was conducted for 15 mins. CNT yarn was collected from the spindle after the system has cooled down.
2.2 CNT yarn Characterization

Yarn morphology was obtained via SEM using FEI QUANTRA 200 ESEM equipped with Energy-dispersive X-ray spectroscopy (EDS) and operated at a voltage of 30 kV. A small amount of yarn sample was attached on the aluminium stud with an aid of double-sided carbon tape. Gold-palladium was used to coat the mounted sample before the microscope was used to capture images of the coated sample. A Horiba LabRam HR equipped with Olympus BX41 microscope was used to determine the degree of crystallinity of the sample. Raman scattering in the sample was excited at wavelength of 514.5 nm using Lexel argon ion laser. Backscattered light was collected using a 100x objective, which was spread using a 600 lines mm$^{-1}$ grating, on top of liquid nitrogen cooled charge couple device detector. In order to prevent localised heating, the laser at the sample was approximately 0.4 mW.

2.3 Thermophysical measurement of CNT yarn

The Thermogravimetry and heat flow measurements of yarn samples were carried out using thermogravimetric analyser (TGA) equipped with Differential Scanning calorimeter (DSC), model SDT600. Two platinum crucibles were used during the analysis, one for loading sample and the other one was left empty for reference. For each measurement, the initial mass of the sample was about 10 mg. The loaded sample is heated from ambient temperature to a temperature of 900$^\circ$C at a heating ramp of 10$^\circ$C per minute. Nitrogen gas was allowed to flow to the system at a flow rate of 50 ml per minute throughout the measurement.

The heat capacity ($C_p$) of the sample was determined by the dimensional relationships, dividing the heat flow by the rate of heating the sample using equation (1) [14]:

![Process Flow Diagram of experimental set-up to produce CNT yarn](image-url)
Specific heat capacity \( C_{p,m} \) was expressed in terms of heat flow acquired from the DSC curve using Equation (2):

\[
\frac{\Delta Q}{\Delta t} = \frac{1}{m} \frac{\Delta Q}{\Delta T} = C_p
\]  

Where:

\( m = \text{initial sample mass}, \)

\( \frac{\Delta Q}{\Delta t} = \text{heat flow obtained from DSC curve and} \)

\( \frac{\Delta T}{\Delta t} = \text{heating rate} \)

The following thermodynamic functions of CNT yarn were also calculated:

Enthalpy Change using Equation (3):

\[
\Delta H = H[T] - H[25] = \int_{25}^{T} C_{p,m}dT
\]  

Entropy Change using Equation (4):

\[
\Delta S = S[T] - S[25] = \int_{25}^{T} \frac{C_{p,m}}{T} dT
\]  

Whereby 25°C was the initial sample temperature.

3. Result and discussions

3.1 Morphology and crystallinity of CNT yarn

SEM images in Figure 1 depict the formation of a continuous fibrous structure. The diameter of the yarn produced at 900°C, 950°C and 1000°C was approximately 6.5 μm, 12 μm and 25 μm, respectively. These values are greater than that of CNTs which is <100 nm. Therefore, all fibrous structures have a similar structure as a yarn. Comparing the yarn produced at various temperatures, 900°C to 1000°C, Figure 1 indicates that yarn produced at 950°C has a higher degree of alignment with smooth and continuous surface as compared to the yarns produced at 900°C and 1000°C. In addition, increasing reactor temperature from 900°C to 950°C produced CNT yarn with less disorder. These findings agree with other studies that showed that increase in reaction temperature produced high quality yarn [15] and CNTs [16,17]. However, further increase in reactor temperature from 950°C to 1000°C resulted in low quality yarn as compared to those at 950°C but better than those at 900°C. These results agree with the Raman shift results as indicated in Figure 3 and Table 1.
Figure 2: SEM images of CNT yarn produced at reactor temperature of (a) 900°C (b) 950°C (c) 1000°C

Figure 3 shows the spectra of the elemental composition of the produced structure as obtained from EDX. All three spectra indicate that the samples are composed of Carbon, oxygen, and iron impurities. Iron impurities are a result of iron-based catalyst (ferrocene) that was used during synthesis. Therefore, the major components in the samples are carbonaceous in nature. These results only confirm that the fiber shown in Figure 2 is made mainly of carbon. In overall, the reactor temperature of 950°C shows to be the best temperature of producing yarn with good qualities. Poor quality obtained at 900°C could be attributed to the incomplete nucleation of CNTs at the reactor temperature of 900°C for CNT yarn production. In addition, reactor temperature of 1000°C seems to be too high for production of yarn resulting in destruction of the CNTs [18]. This pattern was also observed by other researchers [19]. Edzatty et al. (2016) studied the effect of different reactor temperature (700 to 900°C) on the production of carbon nanomaterial and found the best temperature to be 800°C.
Figure 3: Energy Dispersive X-ray (EDX) of CNT yarn produced at reactor temperature of (a) 900°C (b) 950°C (c) 1000°C

Figure 4 depicts the Raman Spectra of CNT yarn produced at reactor temperature of 900°C, 950 and 1000°C. The Raman spectra revolves around assigning, the G-band (between 1579 cm⁻¹ and 1581 cm⁻¹) which represents graphitisation degree of CNT yarn, and the D-band (between 1100 to 1500 cm⁻¹) which shows the structural defects of CNT yarn [20]. Figure 4 shows the D-band and G-band at 1300 cm⁻¹ and 1590 cm⁻¹, respectively. The I_D/I_G ratio represents the relative intensity of deformation and graphitisation of the CNT yarn [21]. As indicated in Table 1, CNT yarn produced at reactor temperature of 900°C, 950°C and 1000°C have a ratio of 0.36, 0.18 and 0.29, respectively. These values indicate that the CNT yarn maintains a remarkable crystallinity structure as the reactor temperature increases from 900 to 950°C then the crystallinity gets slightly deformed when the temperature increased further to 1000°C.
Figure 4: Raman shift of CNTs yarn produced at (a) 900°C; (b) 950°C and (c) 1000°C.

Table 1: ID/IG ratio of CNT yarn produced at 900°C, 950°C and 1000°C.

| Graph | Reactor Temperature [°C] | ID/IG  |
|-------|--------------------------|--------|
| (a)   | 900                      | 0.36   |
| (b)   | 950                      | 0.18   |
| (c)   | 1000                     | 0.29   |

3.2 Thermophysical quantities of CNT yarn

Figure 5 represented TGA/DSC curve for CNT yarn produced at best reactor temperature (950°C). From the graph shown in Figure 5, the area of weight stability was identified i.e. where no phase change, decomposition or association occurred. Yarn produced at reactor temperature of 950°C is thermally stable at temperatures between 200°C and 330°C as depicted in Figure 5. The thermal stability of the samples was determined based on the weight % curve. The corresponding heat flow of the sample at thermal stable state was used to determine heat capacities of the sample [22,23,24]. Equation (2) was used to calculate heat capacities of yarns based on the heat flow of yarn at their thermal stable state. Figure 6 represents the heat capacities of yarn produced at reactor temperature of 950°C.
Analysis from Figure 6 indicates that heat capacities of the sample increase with the increase in experimental temperature. At the stable DSC temperature of the yarn, a polynomial equation of specific heat capacities was obtained using Least Square Estimation method. Equation (5) was
obtained as polynomial model to predict the heat capacities of CNT yarn that is produced at reactor temperature of 950°C.

\[ C_{p,m}[J \cdot g^{-1} \cdot \text{C}^{-1}] = 0.002T^2 - 0.4512T + 66.099 \]  

Equation (5) was used to determine smoothed specific heat capacities of yarn produced at reactor temperature of 950°C. At DSC temperature of 200°C, the specific heat capacity of yarn was found to be 55.9 J/K·g which is higher than the specific heat capacity of both MWCNTs and SWCNTs which were reported to be 1.1852 J/K·g [25] and 1.02 J/K·g [26], respectively. The heat capacities of yarn and CNTs are expected to be different because of their difference in diameter and purity. From the calculated specific heat capacities, thermodynamic function such as change in Entropy (\(\Delta S\)) and Change in Enthalpy (\(\Delta H\)) was determined and shown in Figure 7. Change in entropy increases with the increase in temperature, indicating the degree of disorder of material increases with temperature. Change in enthalpy increased with the increase in temperature, indicating the heat content of material increased with increase in temperature. This behaviour is in agreement with other studies for CNTs [11; 25].

![Figure 7: Thermodynamic property of CNT yarns and calculated heat capacities](image-url)
4. Conclusion
CNT yarn was successfully produced using direct spinning method at reactor temperatures of 900°C, 950°C and 1000°C. The SEM micrographs revealed that yarn produced at 950°C has high degree of CNT alignment as compared to the yarn produced at reactor temperature of 900°C or 1000°C. Since the reactor temperature of 950°C yields yarn with good qualities, their thermodynamic properties were studied in this article. The TGA curve of the CNT yarn show that the yarn was stable at a TGA experimental temperature range of 200 and 330°C. The heat flow of sample at thermal stable state was used to calculate the heat capacities of the sample. The heat capacities of CNT yarn increase with the increase in experimental temperature. The function of heat capacities with respect to the experimental temperature was developed. Thermodynamic functions such as change in entropy and change in enthalpy of the best as-produced yarn were derived based on the established heat capacity equation. Further studies should consider thorough studies on CNT yarn purification and results obtained thereof should be compared with the as-produced yarn.

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