Functionalization of nylon with carbon nanotubes to make thermally stable fabric and wearable capacitor

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Abstract Single walled carbon nanotubes are dispersed in water and attached to nylon fabric by a simple immersing-drying procedure, which is evidenced by data obtained using Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. Thermalgravimetric analysis reveals the temperature at which the functionalized nylon fabric reaches its maximum weight loss rate increases about 10°C with respect to the pristine nylon. This improvement in thermal oxidation stability can be ascribed to the strong free-radical accepting capacity of nanotubes and their high thermal conductivity. The SWCNT functionalized nylon is then used to make a capacitor structure, which possesses the merits of light weight, little hysteresis, and low power dissipation.

Key words: carbon nanotube, nylon, thermalgravimetric analysis, capacitor

1 Introduction

The first synthetic fiber, nylon, also known as polyamide, is elastic, tough and resistant to abrasion, which means nylon clothes can last longer. This fiber is also light-weight and wrinkle resistant. Additionally, nylon has an absorbency rate of

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about 4%, which is the highest among manmade fibers, implying it is comfortable to wear. As such, nylon has gained great popularity in garment market. However, they melt and adhere to skin at elevated temperatures, one factor that limits their application as protective clothing in military and civilian uses; in these cases, people face the threat of fire and special clothing with high stability with respect to thermal oxidation are desired. To meet such requirements, a range of chemicals have been explored to functionalize nylon, including phosphate ester/ammonia [1], polyurethane [2], formaldehyde/ammonium thiocyanate [3], organophosphorus oligomer/dimethyloldihydroxyethyleneurea/ trimethylolmelamine [4, 5], halogen compounds, ammonium sulfamate, thiourea [6]. Despite these numerous efforts, none of them has achieved any substantial commercial success and research is still necessary to find out an appropriate agent that can be used to improve the thermal stability of nylon fabric. Owing to their unique properties, carbon nanotubes (CNTs) have been used to enhance the thermal stability of polymer matrices, such as polystyrene, polyethylene, polypropylene and poly (vinylidene fluoride), by the formation of composites [7]. In this method, CNTs were ground mechanically with polymer powders, followed by a hot-pressing. Unavoidably, parts of CNTs, if not all, will be damaged due to the shearing forces they experienced. With all of these in mind, in this study, single walled carbon nanotubes (SWCNTs) were dispersed in water and attached to nylon fabric by a simple immersing-drying procedure; we then try to understand how the attached nanotubes can affect the thermal stability of nylon fabric.

On the other hand, the incorporation of functionality into garments represents the development trend of next generation of clothing. Various techniques of manufacturing electronic textiles have been explored, and conductive metal wires and

other rigid fibres have been successfully woven into conventional textiles to make wearable electronics [8, 9]. However, these materials do not provide textiles with sufficient biological compatibility, flexibility, durability and mobile comfort [10]. Herein, SWCNTs were attached to nylon fabric and the functionalized fabrics exhibit reasonable electrically conductive behaviour. It is likely that the resulting fabric can be used to make wearable electronics, overcoming the drawbacks mentioned above. As a proof-of-concept, a fabric based capacitor structure was prepared and its potential applications are also discussed.

2 Experimental

2.1 Functionalization of nylon

The procedure of dispersing SWCNTs in water can be found in our previous communications [11, 12]. Nylon 66 fabric (0.2 g, Whaleys, UK) were immersed and kept in the SWCNT suspension for 30 min. Prior to immersing, nylon was scoured at 60°C for 15 min in Na₂CO₃ (2 g/cm³) and MFB (1 g/cm³, non-ionic detergent, BASF, Germany) with a liquid ratio of 1:20. The resulting nylon was taken out of the SWCNT suspension, air-dried, and the whole procedure was repeated for 5 cycles. Scanning electron microscope (SEM) observations were performed on a FEI Quanta 200 (FEI, US). Raman spectra were obtained on a Renishaw System 2000 microRaman spectrometer (Renishaw, UK). Transmission electron microscopy (TEM) was carried out on a Tecnai G2 20 S-TWIN transmission electron microscope (FEI, US).

2.2 Thermal stability

The thermal stability to oxidation of nylon and SWCNT functionalized nylon was assessed by thermalgravimetric analysis (TGA) on a DSC 822/ TGA/SDTA 851

(Mettler–Toledo, Switzerland). The samples were heated in an open platinum pan in an atmosphere of compressed air with a flow rate of 120 ml/min. The temperature was raised from 50°C to 900 °C at a heating rate of 20 °C/min. The percent weight loss of each sample was measured as a function of temperature.

2.3 Capacitor

Two pieces of SWCNT-functionalized nylon (area: 3 mm × 4 mm) are used as the top and bottom electrodes for the capacitive structure. A pristine nylon fabric is used as the dielectric layer that is sandwiched by these two electrodes. To minimize the air trapped within this sandwich structure, these three layers are pressed together mechanically to improve the inter-couplings between the layers. Finally, the capacitance – voltage characteristic is measured using the Kiethley 4200 quasi-static CV measurement setup by physically attaching the capacitor's CNT electrodes to the Kiethley's input terminals via a pair of aluminium/tin coated wire contacts with small footprints. By using small footprints for these contacts, we can ensure the dominant electrodes for the capacitors are due to the CNT electrodes.

3 Results and discussion

3.1 Thermally stable fabric

SEM images display the different surface morphologies of nylon (Fig. 1a and 1b) and SWCNT functionalized nylon (Fig. 1c and 1d). After functionalization, rough fiber surfaces can be observed in sharp contrast to the smooth faces of pristine nylon, suggesting the attachment of SWCNTs.

To further corroborate the evidence of attachment of SWCNTs to nylon, the resulting nylon fabric was characterized using Raman spectroscopic technique. As it is shown

in Fig. 2, the Raman profile of functionalized nylon fabric displays the typical SWCNT features: radial breathing mode bands (RBM, 160-200 cm^{-1} , implying the diameters of nanotubes lie in the region of 1.24-1.55 nm), D-band ($\sim 1310 \text{ cm}^{-1}$), G-band ($\sim 1590 \text{ cm}^{-1}$) and the second order band (G', $\sim 2600 \text{ cm}^{-1}$). These Raman signals are indicative of the presence of SWCNTs, which, in turn, confirms the incorporation of SWCNTs to nylon fabric.

To further visualize SWCNTs on nylon fibers, TEM images of the functionalized nylon were taken and are shown in Fig. 3. The tubular structures, as denoted by the red block arrows, are recognized to be nanotubes. In addition, some circular features can be observed, as denoted by the blue block arrow in Fig. 3a, which may represent the broken ends of nanotubes. In SWCNT dispersion procedure, sonication energy is provided to overcome the attractive van der Waals forces between nanotubes; in the meantime, however, this high and localized ultrasonic power can be a new source of nanotube fragmentation by creating new defects and/or even cutting nanotubes [13, 14], resulting in the appearance of broken-end nanotubes.

The SWCNTs attached to nylon fabrics show reasonable mechanical adhesion properties to the fabrics; after adhesion test with transparent adhesive tape, the tape is still transparent and no visible nanotubes were observed on the tape (see Fig. 4a). Additionally, after the functionalized fabrics were soaked, squeezed and twisted in water, the SWCNTs stick firmly to fabric without peeling off and precipitating in water, and the water remains transparent and colourless (see Fig. 4b). These results indicate the robust interactions among SWCNTs, nylon fabric and dye molecules.

The TGA thermograms of nylon and functionalized nylon are plotted in Fig. 5, where it can be found that nylon starts to lose weight at *ca.* 350°C, and its weight loss rate reaches a maximum (T_{max}) at 446.3 °C, as indicated by the inflection point in the derivative weight curve. The weight loss of nylon can be attributed to the thermal decomposition of polymer chains and subsequently the evaporation of resulting products such as NH₃, H₂O, CO, CO₂, and hydrocarbons [15]. For SWCNT functionalized nylon, the onset decomposition temperature does not differ significantly from pristine nylon fabric (*ca.* 350°C), but its T_{max} increases to 456.4 °C due to the effect of SWCNTs, which means an increase of *c.a.* 10 °C in thermal oxidation stability of the polyamide chains.

Based on the data above presented, it is clear that the presence of nanotubes on nylon retards its thermal oxidation. It is reported that the oxidative degradation of polymer usually involves free radical chain reactions and the introduction of radical inhibitor/scavenger can improve the antioxidative properties of polymer effectively [6,16]. Distinguishable D-band and G' band can be observed in the Raman spectra of nanotubes used in this study (see Fig. 2), which indicates the existence of defects (such as vacancies, OH and CO attachments) on nanotubes. Owing to the presence of these defects, nanotubes contain localized states, which are believed to be electron acceptor-like [17]. Thus, in polymer degradation procedure, nanotubes can trap the free radicals and inhibit the propagation of the chain cleavage reaction, stabilizing the polyamide chains. Additionally, the high thermal conductivity of CNTs can facilitate the energy transfer in fabric upon heating and reduce the possibility of localized energy accumulation, which may also contribute to the rise of oxidation temperature.

3.2 Wearable capacitor

The SWCNT functionalized fabrics exhibit electrically conductive behavior and the sheet resistance of a typical functionalized nylon is around $5 \text{ k}\Omega/\text{sq}$. By sandwiching the original nylon sheet between two SWCNT functionalized nylon sheets, we succeeded in fabricating a capacitor structure, the structure of which is shown in inset of Fig. 6a schematically, wherein the original nylon fabric serves as a dielectric and the SWCNT functionalized ones function as electrodes.

Capacitance-frequency and capacitance-voltage measurements of the capacitive structure were carried out at a Keithley 4200 unit under ambient conditions and the results are plotted in Fig. 6a and 6b, respectively. Fig. 6 shows that for low frequency operations, the area of the hysteresis loop of the investigated device structure is fairly small, indicating a small amount of hysteresis and thereby a marginal power loss when it is used as an energy storage device. This means that our fabric structures may be used as a charge storage system, particularly in a DC/low frequency operation, for subsequent electrical charging of electronic devices, since low power dissipation implies a high efficient energy-storage. Another distinct advantage of this capacitor structure is its super-light weight, which makes it suitable for the manufacture of wearable electronics. Assuming the weight of a typical nylon t-shirt is $\sim 0.5 \text{ kg}$, a fabric based capacitor with the structure described here has the potential to store a total charge of $\sim 40 - 50 \text{ nF}$ or 10 nW of power. And it is believed that the performance of the capacitor structure can be further improved by employing a dielectric with a higher relative permittivity. As a consequence, there are reasons to believe that when such an energy storage structure is integrated into clothing, it will be able to power portable electronic devices (*e.g.* an MP3 player).

4 Conclusions

Carbon nanotube functionalized nylon fabric exhibits improved thermal stability to oxidation, which can be interpreted in terms of the strong free-radical capture ability of nanotubes and their high thermal conductivity. It is likely that this general picture is applicable to other nanotube functionalized fabrics, and carbon nanotubes can be used as a novel agent to improve the thermal stability of fabrics. It is also demonstrated that the SWCNT functionalized fabric can be applied to make a capacitive structure, which may be integrated into future clothing to power portable electronics.

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Figure captions:

Fig. 1 SEM images of nylon fibres (a, b), and SWCNT functionalized nylon fibres (c, d).

Fig. 2 Raman spectra of SWCNTs and SWCNT functionalized nylon fabric, normalized to G band. Excitation at 782 nm (red).

Fig. 3 TEM images of SWCNTs on nylon fiber (note the different scale bars).

Fig. 4 a) The adhesion test for SWCNTs to fabric by transparent adhesive tape, and b) the washing test of functionalized fabric.

Fig. 5 TGA mass loss (dash dot lines) and its derivative (solid lines) for nylon and functionalized nylon.

Fig. 6 a) shows the measured capacitance against frequency sweep. A relatively higher capacitance is observed at lower frequency. **b)** shows the measured capacitance as a function of an applied sweeping voltage (1 kHz).