The effect of plasma modification on the sheet resistance of nylon fabrics coated with carbon nanotubes

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Abstract Low-pressure oxygen and argon plasmas were used to pre-treat nylon fabrics, and the modified fabrics, together with the raw fabrics, were subsequently coated with single walled carbon nanotubes (SWCNTs) by a dip-drying process. Scanning electron microscopy (SEM) and Raman spectroscopy analyses indicated the attachment of SWCNTs onto nylon fabrics. After the coating with SWCNTs, the plasma modified fabrics exhibited sheet resistance of as low as 2.0 k Ω /sq. with respect to 4.9 k Ω /sq. of the raw fabrics, presumably owing to the increase of fibre surface roughness incurred by the plasma modification, which is evidenced by SEM analyses. Fourier transform infrared spectroscopy (FTIR) analysis indicates the incorporation of oxygen functionalities on fibre surfaces in the plasma modification. This is responsible for the variation of the electrical conductance of SWCNT-coated fabrics with the type of plasma and the duration of plasma ablation.

Key words: nylon fabric, carbon nanotube, plasma modification, electronic textile

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1. Introduction

The integration of electronic elements with conventional textiles is essential for the fabrication of intelligent clothes, the applications of which include as diverse as sportswear, foldable displays, portable power, healthcare, military and work wear [1,2]. Owing to their light weight, high surface area, excellent electric and mechanical properties, carbon nanotubes (CNTs) have recently been applied as the electronic element to make wearable electronic textiles by a dip-drying process [3-5]. In these cases, the textiles used are almost exclusively limited to cotton. As constrained by the intrinsic properties of cotton substrates, it is hard for the resultant electronic textiles to offer satisfactory mechanical properties. Nylon, the first man-made fibre, is elastic, tough and resistant to abrasion, implying nylon clothes can last longer. In this aspect, it seems nylon may be an ideal candidate for the manufacturing of electronic textiles. Unfortunately, little information is available at this time on the manufacture of CNT coated nylon by a dip-drying process, and this is the impetus of this study.

Owing to their low surface energy, poor chemical reactivity and the presence of a weak cohesion layer, nylon surfaces are difficult to wet and have poor adhesion with other substances [6,7]. Apparently, this will retard the mobility of surfactant-suspended CNTs and hamper the adsorption of CNTs onto nylon surfaces in a dip-drying process. How to enhance the interactions between CNTs and nylon surfaces is an unavoidable challenge that this technique needs to face. Borcia et al. investigated the effect of plasma treatment on the surface properties of nylon 6 films and concluded that plasma modification represents an attractive technique to improve the wettability and adhesion properties of the films [8,9]. These improvements can be interpreted in terms of synergetic effects, i.e. the removal of the weak cohesive layer, the increase of the cohesion work and the increase of the surface area that is available for subsequent bonding. In line with these, Oh et al. reported that the adhesion of polyaniline on nylon 6 fabrics can be enhanced effectively by modifying the fabrics with plasmas [10]. With these in mind, another

effort here is intended to pre-treat nylon fabrics with oxygen and argon plasmas and then investigate how this modification may affect the attachment of CNTs onto nylon fabrics in a subsequent dip-drying process. It is likely that this study may pave ways for manufacturing electronic textiles with satisfied mechanical and electrical properties.

2. Experimental

2.1. Plasma modification

Nylon 66 fabrics (Whaleys, UK) were first scoured at 60 °C for 15 min in 2 g/cm³ Na₂CO₃ and 1 g/cm³ MFB (non-ionic detergent, BASF, Germany) with a liquid ratio of 1:20. After drying in air, the nylon fabrics were modified with an oxygen or argon plasma (gas flow rate: 20 sccm) on a RF plasma barrel reactor (Emitech K1050X Plasma Asher, Quorum Technologies, UK) at a vacuum of 50 Pa and a 40 W discharge power, and with an exposure time of 0.5, 3, 5, and 10 min.

2.2. Attachment of CNTs

The aqueous mixture of 2 wt. % dodecylbenzenesulfonic acid, sodium salt (Sigma-Aldrich, UK) and 0.1×10^{-3} g cm⁻³ single walled carbon nanotubes (SWCNTs, NanoLab, US) were sonicated in a Cole-Parmer Ultrasonic processor (UK) for 20 min with a power of 120 W. Subsequently, the plasma modified fabrics were immersed and kept in the SWCNT suspension for 1 h. The resulting fabric was then taken out of the SWCNT suspension, air-dried, and the whole procedure was repeated for 4 cycles.

Fig. 1 demonstrates the results of fastness investigation. The SWCNT coated fabrics were immersed in either water (Fig. 1a) or ethanol (Fig. 1b) and heated to 40°C for 15 min; meanwhile, the fabrics were rolled and squeezed several times. The SWCNT coated fabrics were also adhered with a commercial transparent tape (Fig. 1c).

2.3. Characterization

Scanning electron microscope (SEM) images were obtained on a FEI Quanta 200 (FEI) or a Hitachi S-3200 N (Hitachi). To alleviate the charging phenomena in SEM observations, stemming from the insulating nature of fabrics, the control fabric samples and the plasma pre-treated fabrics were coated with gold in a JLS Sputtering System (JLS Designs) for 2.5 min with the following operating parameters: Power:1000 W, Voltage: 300 V, Current: 60 A. All SWCNT coated fabrics were observed as they were. ATR-FTIR analyses were carried out on a Perkin Elmer Spectrum BX (Perkin Elmer). Raman spectra were obtained on a Renishaw System 2000 microRaman spectrometer (Renishaw) with an excitation at 782 nm. The sheet resistance of SWCNT coated fabrics was measured on a four point probe stand (K&S).

3. Results and discussion

3.1. Effect of plasma modification on the topography of nylon fibres

The control nylon fabrics, together with the plasma modified fabrics, were imaged by SEM to demonstrate the nature of the surface features, wherein only 0.5 min and 10 min plasma modified fabric fibres are shown (Fig. 2). In contrast to the control nylon fibres, it is clear that for an initial exposure to argon or oxygen plasma (Fig. 2b and d), the change in fibre appearance is not distinguishable. With the increase of the exposure time (Fig. 2c and e), the fibre surface is etched more severely due to the bombardment of ions present in the discharge, resulting in more pits in fibres. Additionally, in comparison with argon plasma modified fibres, oxygen plasma treated fibres show a more progressively pitted and etched pattern, in particular for 10 min treated fibres (Fig. 2c vs. Fig. 2e), implying that oxygen plasma is more effective in changing surface topography; this is because argon is an inert gas and has lower ablation efficiency [22].

3.2. Effect of plasma modification on the chemical composition of nylon fibre surfaces

To examine the effect of plasma modification on the surface chemistry of fibres, the infrared transmission spectra of the control nylon and plasma modified nylon fabrics were recorded and are plotted in Fig. 3.

After oxygen plasma modification, the absorption bands of nylon at 1234 cm^{-1} and 1731 cm^{-1} , which can be ascribed to the C-O and C=O stretch respectively, are intensified significantly, indicating the incorporation of oxygen functionalities. It is also interesting to notice that a shoulder peak at around 1234 cm^{-1} is still identifiable for the argon plasma modified nylon fabric. This is because it is hard to evacuate all the air out of the plasma chamber and create an entirely air-free environment in plasma modification, and the present oxygen, even at a fairly small amount, still represents a very surface reactive species and can be implanted onto fibre surfaces [23]. In addition, argon plasma modification may produce surface centred radicals on fibre surfaces, which after exposure to air can be saturated with oxygen, contributing to the incorporation of oxygen functionalities on fibre surfaces.

3.3. Attachment of SWCNTs to nylon fabrics

Fig. 4 displays the SEM images SWCNT coated nylon fibres. Compared with the control nylon fibres, the surfaces of SWCNT coated nylon fibres (Fig. 4a) become fairly rough, and the smooth and fibrillar surfaces of the control nylon fibres (Fig. 2a) are completely hidden, indicating the coating of fibres. One typical high resolution SEM image is shown in Fig. 4b, wherein SWCNTs are clearly visible on the fibre surface as indicated by the block arrows.

To further confirm the presence of SWCNTs in fibre surface coatings, Raman spectroscopies were performed and the Raman profiles of SWCNT coated fabrics are depicted in Fig. 5. The characteristic bands of SWCNTs, namely, radial breathing modes (RBM, $160\text{-}200\text{ cm}^{-1}$), D ($\sim 1310\text{ cm}^{-1}$), G ($\sim 1590\text{ cm}^{-1}$), and G' ($\sim 2600\text{ cm}^{-1}$), are all clearly identifiable, suggesting the incorporation of SWCNTs onto fibre surfaces [24].

To investigate the robustness of the attachment of SWCNTs to nylon fabrics, the SWCNT coated fabrics were rolled up and squeezed in water and ethanol in conjunction with heat treatment, no clear SWCNT precipitating was observed (Fig. 1a and b). The SWCNT coated fabrics were also adhered with a commercial transparent tape; no obvious peeling off of SWCNTs from fabric was visible on the transparent tape (Fig. 1c). These results indicate the intimate interactions between SWCNTs and fabric fibres.

3.4. Sheet resistance of SWCNT coated fabrics

The sheet resistance of SWCNT coated fabrics after 4 times of immersion was measured and is plotted in Fig. 6 as a function of the plasma exposure duration. As Fig. 6 demonstrates, the sheet resistance values of all the plasma-modified fabrics, ranging from 2.0 to 4.2 k Ω /sq., are lower than the corresponding untreated fabrics of 4.9 k Ω /sq., which may be ascribed to the effect of plasma modification on the surface topography of fabric fibres. As Fig. 2 displays, the nylon fibre surfaces are etched to some extent and many pits are created on fibre surfaces after the plasma modification. This gives rise to the increase of surface roughness, which is beneficial for the attachment of SWCNTs. The more rough the fibre surfaces are, the larger quantity of SWCNTs are attached onto fibre surfaces, facilitating the development of electrically conductive networks in nylon fabrics and enhancing the electrical conductance.

The sheet resistance of SWCNT coated nylon fabrics is dependent of plasma exposure time. The sheet resistance drops considerably on the initial exposure to plasma within 0.5 min, and then the dropping rate becomes sluggish from 0.5 min to 5 min. A further extension of plasma ablation up to 10 min results in the increase of sheet resistance, and this trend is particularly apparent for the argon plasma modified fabrics.

This is presumably owing to another profound effect of plasma modification on the fibre surfaces, i.e. anchoring oxygen containing moieties onto fibre surfaces. Plasma, partially ionized gas, is composed of highly excited atomic, molecular, ionic and radical species with free

electrons and photons, which can abstract hydrogen from the fibre polymer chain to generate radicals. The resultant radicals can then react with a present oxygen species and form oxygen-containing functional groups on fibre surfaces [25]. As discussed in Section 3.2, the absorption bands of nylon fabrics corresponding to the stretch of oxygen functionalities are intensified after the plasma modification.

The incorporation of oxygen functionalities onto fibre surface will influence the attachment of SWCNTs adversely. These oxygen containing groups are hydrophilic in nature, while SWCNTs are hydrophobic, creating a higher energy barrier for SWCNTs from getting close and becoming attached to fibre surfaces. On the other hand, the resulting carboxyl group may become dissociated in water, while the dispersed SWCNTs also carry negative charges due to the dissociation of sulfonate groups in dodecylbenzenesulfonic acid (sodium salt), increasing the electrostatic repulsion-forces between dispersed SWCNTs and fabrics.

As the plasma exposure duration increases, the increase in fibre surface roughness and the incorporation of polar oxygen functionalities will occur simultaneously. This will bring about two competing effects on the attachment of SWCNTs to fabrics, and the overall outcome will be governed by the predominant one. And this can be invoked to explain the observed variation in sheet resistance with exposure time in Fig. 6. With the initial increase of plasma ablation, the increase in surface roughness prevails and more SWCNTs become attached onto nylon fabrics. Consequently, electrically conductive networks enrich in the fibre surface coatings, leading to a lower resistance value. On the contrary, further increase in the extent of plasma ablation gives rise to the abundance of hydrophilic oxygen groups on fibre surfaces, slowing down the attachment of SWCNTs and increasing resistance values. It is also noticeable that for 10 min plasma modified fabrics, the increase in sheet resistance is more pronounced for argon plasma modified ones in contrast to oxygen plasma modified ones. This is because a longer plasma ablation in oxygen incurs more severe damage on fibre surfaces than in argon, as demonstrated

by SEM images (Fig. 2c and e); this significant increase in fibre surface area partially offsets the detrimental effect on the attachment which arises from the increase in the hydrophilicity of fibre surface and the electrostatic repulsion between the dispersed SWCNTs and the fibre surfaces. As the argon plasma modified fabrics are concerned, a prolonged plasma treatment does not result in a substantial increase in fibre surface roughness (Fig 2b and c) and thereby can not counteract the deconstructive effect on the development of SWCNT conductive networks in fabrics.

4. Conclusions

It was demonstrated that nylon fabrics can be coated with carbon nanotubes by a dip-drying process. The sheet resistance of carbon nanotube coated nylon fabrics drops from 4.9 k Ω /sq. to as low as 2.0 k Ω /sq. when the nylon fabrics were pre-treated with argon and oxygen plasmas. The sheet resistance of carbon nanotube coated nylon fabrics decreases and then increases with plasma modification time. Plasma modification can create pits on nylon fibre surfaces and increase fibre surface area, facilitating the attachment of carbon nanotubes onto fibre surfaces. Meanwhile polar oxygen functionalities can be incorporated onto fibre surface, which cause the increase in the hydrophilicity of fibre surfaces, impairing the attachment of carbon nanotubes. The attachment of carbon nanotubes onto nylon fabrics is affected by fibre surface morphology and fibre surface composition, and the overall outcome is the balanced result of these two competing factors.

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References

- [1] S. Park, S. Jayaraman, Smart textiles: Wearable electronic systems, *MRS Bull.* 28 (2003) 585-591.
- [2] K. Gniotek, I. Krucinska, The basic problems of textronics, *Fibres Text. East. Eur.* 12 (2004) 13-16.
- [3] B. S. Shim, W. Chen, C. Doty, C. Xu, N. A. Kotov, Smart electronic yarns and wearable fabrics for human biomonitoring made by carbon nanotube coating with polyelectrolytes, *Nano Lett.* 8 (2008) 4151–4157.
- [4] M. Panhuis, J. Wu, S. A. Ashraf, G. G. Wallace, Conductive textiles from single-walled carbon nanotubes, *Synth. Met.* 157 (2007) 358-362.
- [5] T. J. Kang, A. Choi, D. H. Kim, K. Jin, D. K. Seo, D. H. Jeong, S. H. Hong, Y. W. Park, Y. H. Kim, Electromechanical properties of CNT-coated cotton yarn for electronic textile applications, *Smart. Mater. Struct.* 20 (2011) 015004.
- [6] C. Canal, R. Molina, E. Bertran, P. Erra, Wettability, ageing and recovery process of plasma-treated polyamide 6, *J. Adhesion Sci. Technol.* 18 (2004) 1077-1089.
- [7] A. Das, Shabaridharan, B. Biswas, Study on heat and moisture vapour transmission characteristics through multilayered fabric ensembles, *Indian J. Fibre Text. Res.*, 36 (2011) 410-414.
- [8] G. Borcia, N. Dumitrascu, G. Popa, Influence of dielectric barrier discharge treatment on the surface properties of polyamide-6 films, *J. Optoelectron. and Adv. M.*, 7 (2005) 2535-2538.
- [9] G. Borcia, C. A. Anderson, N. M. D. Brown, Surface treatment of natural and synthetic textiles using a dielectric barrier discharge, *Surf. Coat. Technol.* 201 (2006) 3074-3081.
- [10] K. W. OH, S. H. Kim, E. A. Kim, improved surface characteristics and the conductivity of polyaniline-nylon 6 fabrics by plasma treatment, *J. Appl. Polym. Sci.*, 81 (2001) 684-694.

Figure Captions:

Fig. 1 SWCNT coated nylon fabrics washed in water (a) and ethanol (b). The SWCNT coated nylon fabric after adhesion with a transparent tape (c).

Fig 2 SEM images of control nylon fibres (a) and plasma modified nylon fibres: (b) Ar 0.5 min, (c) Ar 10 min, (d) O₂ 0.5 min, (e) O₂ 10 min. HV: 30kV.

Fig. 3 Normalized infrared transmission spectra of control nylon fabrics and plasma modified fabrics after 10 min treatment.

Fig. 4 SEM images of SWCNT coated nylon fibres: (a) low magnification, (b) high magnification

Fig.5 Raman spectra of pristine SWCNTs and SWCNT coated nylon fabrics.

Fig. 6 Sheet resistance of SWCNT coated fabrics after 4 times of immersion against plasma exposure time.