Functional Fabric with Strain Sensing Based on Foam Finishing

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Abstract. Strain sensing is one of the core parts of smart fabric which can be expressed by electrical signals affected by external forces. In this paper, the strain sensing functional fabric was prepared by using the acidified carbon nanotubes (a-CNTs) as the conductive layer and the waterborne polyurethane (WPU) as the adhesive based on foam finishing method. The results showed that many hydroxyl and carboxyl groups were introduced into the surface of CNTs through acidification, which improved their dispersibility in aqueous solution. The blended film of a-CNTs and anionic WPU had excellent conductive properties. When the ratio of a-CNT to WPU was 9:1, the fabric had the smallest resistivity, about 0.13 Ω·m, and the corresponding tensile sensing sensitivity up to 55.2.

Keywords: Smart fabrics, strain sensing, carbon nanotubes, waterborne polyurethane, foam finishing.

1. Introduction
The rapid development of carbon nanomaterials has opened new avenues for smart textiles [1], including carbon black (CB) [2], carbon nanotubes (CNTs) [3], graphene [4], etc. Compared with the traditional materials of metal [5] and semiconductors [6], conductive textiles made of carbon nanomaterials have many special functions [7, 8], such as excellent flexibility, lightweight, recoverable deformation and washability etc., and can be used as strain sensors [9, 10], electronic skins [11], and wearable heaters [12, 13]. The strain effect of fabrics causes changes in resistance values, and then strains are measured by measuring the resistance changes of fabrics, that is, strain detection is achieved by measuring resistance changes. CNTs have excellent mechanical, electrical and chemical properties. The theoretical elastic modulus is about 1TPa, the tensile strength is about 100 GPa, and the electrical conductivity is 200 to 1.0×10⁹ S/cm. In addition, CNTs also have good piezoresistive properties [14]. When carbon nanotubes are subjected to a tensile force, the resistance will change, so they are mostly used in the field of strain sensing fabrics.

At present, the structural design [15] and advanced assembly technology of new carbon-based composite materials have brought new opportunities for the development of smart textiles in the direction of high performance, high efficiency, and multifunctionality [16, 17]. CNTs can be blended with polymers to prepare the nano to micron composite fibers with good mechanical, thermal, electrical,
and optical performance [18] by electrostatic spinning [19, 20], wet spinning [21, 22], and melt spinning [23, 24]. In addition, composite films with uniform nanomaterial distribution can be prepared by doctor blade coating [25], solvent evaporation [26], vacuum filtration, spin or dipping coating [13], and electrochemical deposition [27, 28]. However, comfort is a factor that cannot be ignored in wearable devices. When the encapsulated sensor is installed on human skin, the encapsulation of elastic polymer reduces air permeability and wearing comfort. At the same time, the tunneling effect between nanomaterials causes the sensor resistance to increase exponentially under tension, which affects the linearity of the strain sensor. Textile strain sensors can integrate conductive nanomaterials into flexible fabrics without the support of elastic polymers and can be used to solve these problems. However, CNTs are prone to aggregate and lack of adhesion on the fiber surface, resulting in poor durability. Therefore, effective assembly methods are needed to enhance the dispersion and the adhesion between CNTs and fiber substrates when using the developed equipment.

In this paper, a smart high-elastic sensing fabric with high sensitivity, wide strain range and stable performance is designed using CNTs as the conductive layer and self-made waterborne polyurethane (WPU) as a dispersant and adhesive by foam finishing method.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. Knitted spandex/polyamide fabric (22% spandex, 78% polyamide), rough multi-walled carbon nanotubes (r-CNT) with an average diameter of 10 nm and a length of 1.5 μm, sodium alginate, acetone and sodium dodecyl sulfate (SDS) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sulfuric acid (H₂SO₄) (95%) and nitric acid (HNO₃) (60%) were provided by Wuhan Operation Fine Chemical Co. Ltd. Chemically pure anionic waterborne polyurethane (WPU) was self-made in the laboratory. Deionized (DI) water was used during the sample treatment.

2.2. Synthesis of Acidified Carbon Nanotubes (a-CNT)

The CNTs were mixed evenly in the mixed acid of H₂SO₄ and HNO₃ (V₅₃₃₄/V₅₃₃₄₅ = 3:1) and then stirred and acidified in a three-necked flask at 60°C for 3 hours. After cooling to room temperature, it was diluted with distilled water, separated by standing layer, the supernatant was filtered off, washed with centrifugal deionized water, and washed several times until neutral to obtain acidified carbon nanotubes (a-CNT).

2.3. Preparation of a-CNT/WPU Composite System

The mixed solutions of the a-CNT and the anionic WPU were prepared by ultrasonically dispersing in an ultrasonic cleaner for 15 minutes. The dry weight ratios of a-CNT to anionic WPU were 9:1, 8:2 and 7:3, respectively. Add a certain amount of sodium alginate and sodium dodecyl sulfate to each solution, mix and shake well.

2.4. Fabrication of Flexible Strain Sensor by Foam Finishing Method

Use the foam instrument to bubble the prepared mixed solution, pour the foam on the elastic fabric washed with acetone, and evenly spread the foam using the coating machine as shown in Fig. 1. After all bubbles were eliminated, the fabric was transferred to a 60°C oven for drying. Install two copper wires on both sides of the fabric strip. Then, drop the silver paste on the installed parts to fix the copper wire and improve the contact between the copper wire and the fabric. After drying the silver paste at 60°C for 15 minutes, the strain sensor was prepared.
2.5. Characterization and Performance Testing

Fourier Transform Infrared spectroscopy (FTIR) test was carried out under the conditions of wave number range 4000-600 cm\(^{-1}\) and resolution 4 cm\(^{-1}\). Thermogravimetric analysis (TGA) test was at a temperature rise of 10°C/min from 30 to 800°C in a nitrogen atmosphere. X-ray diffraction had scanned range 10-80°, test voltage 40kV, test current 40mA. The four-probe instrument was used to measure the a-CNT/WPU film resistance. Finally, the screw micrometre was used to measure film thickness, and the average was measured four times. The final film resistivity = average resistance x average thickness. The fabric dynamic resistance tester can measure the real-time resistance value of fabric during the dynamic deformation process, and obtain the changing trend of the fabric resistance value with tensile deformation.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Fig. 2 is the infrared spectrum of a-CNT and WPU. The FTIR peak frequency and spectral band shape of composite materials are basically the same. This indicates that there is no qualitative change in the main organic functional groups after the reaction, but the peak intensity changes relatively. The a-CNT exhibited typical broad and blunt tensile vibration peaks caused by intramolecular hydroxyl and carboxyl group C=O tensile vibration in the 3200-3500cm\(^{-1}\) and 1500-1700cm\(^{-1}\) regions, respectively. Vibration peaks indicate that carbon nanotubes can generate many hydroxyl and carboxyl groups on the surface of a-CNT after mixed acid treatment. The acidified samples showed very weak C-H vibration peaks near 1380cm\(^{-1}\) and 2900cm\(^{-1}\), indicating that the carbon nanotubes prepared by acidification was not completely acidified, and a small amount of -CH groups remained on the surface.

![Fig. 2. Infrared spectrum curves of CNT and WPU: (a) a-CNT:WPU=9:1, (b) a-CNT:WPU=8:2, (c) a-CNT:WPU=7:3, (d) a-CNT.](image1)

![Fig. 3. Thermal weightlessness curve of CNT and WPU: (a) r-CNT, (b) a-CNT, (c)a-CNT:WPU=9:1, (d) a-CNT:WPU=8:2, (e) a-CNT:WPU=7:3, (f) WPU.](image2)
3.2. Thermogravimetric Analysis (TGA)

It can be seen from Fig. 3 that at 100°C-200°C, the curves a, b, c, d, and e all slightly decreased. Since the temperature at this time has reached the boiling point of water, the evaporation of water in the sample leads to quality decline. From 200°C to 400°C, the a and b curves declined slightly, the c, d, and e curves all declined greatly, and the curve gradually flattened to 400°C. Because the hydrophilic groups such as -COOH grafted on the surface of r-CNTs begin to decompose, and impurities such as metal catalysts remaining in the synthesis of CNTs are also slowly decomposed, so the quality gradually decreases as the temperature rises. However, the f curve dropped sharply, and almost fell to 0 at 400°C, indicating that the anionic WPU decomposed a lot after the temperature reached 200°C, and completely decomposed at 400°C, and a few carbon nanotubes decomposed, which caused the curve to slowly decline.

3.3. X-ray Diffraction (XRD) Analysis

Since the components of b, c, and d in Fig. 4 are both a-CNT and WPU, and only the mass ratio between the two is changed, the atomic structure of the substance will not occur change, the obtained b, c, d, e diagrams are almost the same. It can be seen from the figure that the angle corresponding to the diffraction peak of the a-CNT has changed and the diffraction peak has broadened, resulting in an increase in the interplanar spacing, larger grain size, and smaller size. According to Bragg's law, \(2\lambda\sin\theta=\lambda\), (d is the distance between parallel atomic planes, \(\lambda\) is the wavelength of the incident wave, and \(\theta\) is the angle between the incident light and the crystal plane). The XRD diffraction peaks are all shifted to the left, indicating that \(\theta\) becomes smaller, but \(\lambda\) is unchanged, so it can only be the reason for the increase of d. The reason for the increase in the value of d is most likely due to the elongation of the crystal lattice due to the stress of the interstitial atoms.

![X-ray diffraction curves of CNT and WPU](image)

3.4. Flexible Strain Sensor Performance

3.4.1. Conductive Resistivity. Because polyamide fiber is hydrophilic and easily absorbs water due to its abundant amine and carbonyl groups. On the other hand, the CNT solution easily penetrates into the fabric due to surface diffusion caused by capillary action. In the dipping process, a-CNT not only adsorbs on the surface of the fabric, but also on its single fiber, so the fabric has a good conductive effect. From table 1, it can be seen that when a-CNT:WPU=9:1, the fabric resistivity is the smallest, and the conductivity is the best. When a-CNT:WPU=7:3, the fabric resistivity is the largest, and the conductivity is the worst. Therefore, a-CNT:WPU treated elastic fabric can make the fabric have excellent conductivity, and the greater the ratio of acidified carbon tube to anionic WPU, the better the conductivity.
Table 1. The square resistivity of fabrics treated with different ratios of CNT/WPU.

| Sample        | Resistance($R_{\square}$) [kΩ] | Thickness(L) [mm] | Resistivity($R_{\square}$×L) [Ω·m] |
|---------------|---------------------------------|-------------------|-----------------------------------|
| a-CNT:WPU=7:3 | 8.01                            | 0.043             | 0.34402                           |
| a-CNT:WPU=8:2 | 4.05                            | 0.041             | 0.16605                           |
| a-CNT:WPU=9:1 | 5.78                            | 0.022             | 0.12716                           |

3.4.2. Strain Sensing. Due to the unique continuous interlocking loops of knitted fabrics and the combination of spandex filaments in the yarn, the textile has excellent elasticity and recoverability. CNTs have uniform distribution and high density of CNTs in the matrix, showing a good nano-scale percolation network and a large number of contact connections between CNTs, thereby forming an excellent electrical path. In this experiment, the original resistance value $R_0$ of the sample fabric and the resistance values ($R_x$) stretched to 30%, 40%, 50% and 60% of the strain were measured to obtain $(R_x-R_0)/R_0$ and stretch degree of linear fit between images.

Fig. 5 showed that as the WPU content on the fabric increased, the resistance sensitivity on the fabric became smaller. As the stretching rate continues to increase, the electrical resistance of the fabric also increased. It indicated that after the fabric is stretched by an external force, the conductive network on the fabric is destroyed, the resistance value becomes larger. $\Delta R/R_0$ is linearly related to the strain, when a-CNT:WPU=9:1, it has the best tensile sensitivity, GF=55.2. In this paper, the fabric sensing properties are achieved by the elastic properties of WPU and the formation of a good interface between the carboxyl group on CNT and the functional group of WPU. In addition, the elastomer layer used as the support layer on the fabric is essential for keeping the strain sensor firmly attached to the fabric, preventing cracks on the conductive layer during stretching, and making the strain sensor have good stretchability.

4. Conclusions

Conductive materials need to be able to adhere to the fabric and have high stretchability while maintaining high electrical conductivity. Strain sensors on wearable textiles are challenging. CNTs can be tightly adhered to the textile through an adhesive, which ensures the stability of the prepared strain sensor. Polyamide fiber is hydrophilic due to its abundant amine and carbonyl groups. After the carbon nanotubes are treated with mixed acid, a large number of hydroxyl groups and carboxyl groups can be introduced on the surface of the carbon tubes, which can continue to undergo grafting or surface modification reactions with other reagents to improve the dispersibility and solubility of the carbon nanotubes. The acidified CNT can easily penetrate into the fabric and adsorb on the fiber through foam finishing. On the other hand, polyamide fiber has good wear resistance and strength, which also ensures
the stability of the sensor. The functional fabric with high strain sensing sensitivity, wide strain range and stable performance was fabricated using a-CNT as the conductive layer and anionic WPU as a dispersant and adhesive by foam finishing method. The range of strain range is 0-60%, and the maximum sensitivity (GF) is 55.2.

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