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Electromagnetic Wave Absorbing Properties of Cotton Fabric with Carbon Nanotubes Coating

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Abstract
In order to endow cotton fabric with the electromagnetic shielding property while preserving comfort and softness, carbon nanotubes (CNTs) were coated onto NaOH pretreated fabrics via a binder-free dip-coating approach. Scanning electron microscopy (SEM) and Infrared spectroscopy were utilised to investigate the surface morphology and modification of the CNT functionalised fabrics. The effects of the number of dip-coatings, the concentration of carbon nanotubes, and the impregnation temperature on electrical conductivity, electromagnetic (EM) shielding effectiveness (SE), and wave absorbing efficiency of cotton fabrics were evaluated, respectively. The SE value of the CNT functionalised cotton fabrics increased with the dip-coating time and reached 16.5 dB after CNT dip-coating ten times, which indicates that 97.76% of the electromagnetic wave was shielded. Meanwhile, by adding layers of stacking fabrics, the SE of CNT coated fabrics was further improved to 26.4 dB. The shielding mechanism was also studied by comparing its reflection and absorption behaviour, which demonstrates that 65.7% of the electromagnetic wave was absorbed.

Key words: *carbon nanotubes; electromagnetic wave absorbing; coating; cotton fabric.*

Introduction

Electromagnetic waves have found extensive use in a large variety of applications on electronic devices and equipment [1], but they not only interfere with the normal operation of surrounding equipment [2, 3] but also have many adverse effects on human health [4]. Therefore, various electromagnetic shielding fabrics to protect human beings from electromagnetic waves are always in demand. In recent years, the protecting fabrics available have been mainly made of hybridising conductive metal and common fibre/yarn [5, 6]. However, the comfort and softness of these fabrics would be negatively affected due to the existence of stiff and heavy metal [7, 8]. Even worse, secondary or multiple electromagnetic pollutions generated by the reflection of metal on fabric will cause further damage to human health and electronic products. In order to endow common fabric with the microwave absorbing property and weight or flexibility preservation, pioneering studies have been reported on the application of lightweight, electrically conductive materials such as carbon nanotubes, graphene, as well as incorporating polymer in fibres and fabric modification [9].

Carbon nanotubes have drawn substantial interest for fabric modification with its surprising microwave absorption performance because of its outstanding physical, chemical, and mechanical properties [10], as well as high conductivity and light weight [11, 12]. Du et al. [4] studied the electromagnetic shielding and microwave absorbing properties of carbon nanotube composites. Pang et al. [13] prepared a paper (cellulose) fibre and carbon nanotube suspension by the high-speed shearing method, and then rolled it into carbon nanotube-paper fibre composite conductive paper. The surface resistance of the carbon nanotube conductive paper was 28 Ω/Sq; and the electromagnetic (EM) shielding efficiency (SE) reached -24 ~ -37 dB. Zhang and Wu [7] prepared conductive fabrics by coating single-walled carbon nanotubes on the surface of cotton and nylon via the dipping-drying method. The results demonstrated that the conductive network in the fabric became more uniform and concentrated with an increase in the number of dippings, and consequently reduced the resistance of the fabric. In our previous work [14], Nafion-CNTs was coated onto cotton fabric for EM shielding; however, as a polymer, Nafion compromised the cotton fabric's flexibility during the deposition process. In order to preserve the flexibility, the CNT coating process without polymer is required. However, it is still a challenge as to how to improve CNT deposition on fabrics without the polymer binding and preserve their comfort and softness. Qu's group deposited graphene onto fabric via capillarity to fabricate flexible electronic textiles [15-17], which greatly extended the potential application of electronic textile to other smart textiles [18-20].

In this study, the pretreatment of cotton with NaOH was implemented to improve CNT deposition onto fabrics. Multiwalled carbon nanotubes (CNTs) were uniformly coated onto pretreated cotton fabrics by the binder-free approach for electromagnetic shielding and microwave absorption application. Existing dyeing and sizing process equipment is available to prepare electromagnetic shielding fabric with CNT coating without any special equipment required, which is easy to operate and favourable for industrial-scale production. The effects of the number of dip-coatings, CNT concentration and impregnation temperature on the microwave absorbing properties were systematically studied. Scanning electron microscopy (SEM), a digital multi-meter, fabric permeability apparatus, a fabric style meter, and vector network analyser were utilised to investigate their surface morphology, electrical surface resistance, permeability, bending stiffness and electromagnetic shielding properties, respectively. The innovation of this absorbing product was demonstrated by our systematic studies and NaOH pretreatment process, as compared to current materials used for wave absorption.

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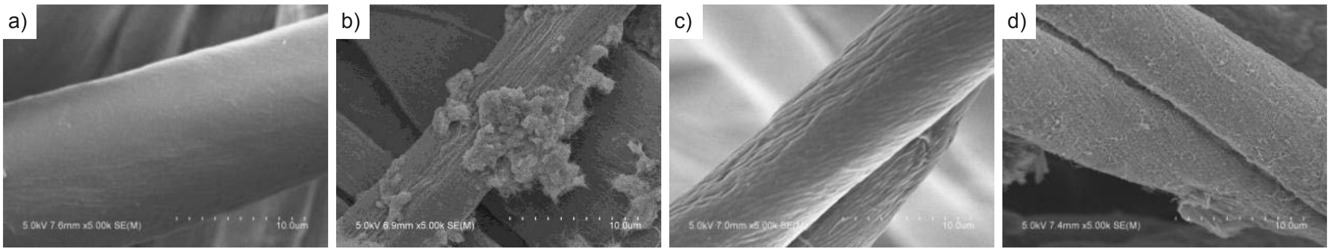

***Figure 1**. SEM images of a) pristine cotton fibre, b) CNT coated cotton fibre, c) NaOH pretreated cotton fibre, d) CNT coated pretreated cotton fibre.*

Materials and methods

Materials

Cotton fabric (Ctn) was provided by Shandong Lutai Co.ltd. Sodium hydroxide (NaOH), sodium dodecylbenzene sulfonate ($C_{18}H_{29}NaO_3S$), and anhydrous alcohol (C_2H_5OH) were purchased from China Pharmaceutical Chemical Reagent Co.ltd. Carboxylated multi-walled carbon nanotubes (CNTs, purity > 95 wt%, density 0.15 g/cm^3, specific surface area > 233 m^2/g, inner diameter 3-5 nm, outer diameter 8-15 nm, length ~ 50 µm) were obtained from Suzhou Hengqiu Technology Co., Ltd.,

Method

Pretreatment of cotton

The cotton fabric cut to a size of 10 cm*10 cm was immersed in 15 g/l of NaOH solution, oscillated at 80 °C for 30 min, and then washed with distilled water several times until the pH was neutral [21]. The surface of the pretreated fabric was cleaned to facilitate the adsorption of carbon nanotubes. After dip-coating with CNTs, the fabrics were dried in an oven at 105 °C and then weighed.

Preparation of carbon nanotube coated cotton fabric

A binder-free dip-coating process was adopted to prepare the wave-absorbing fabrics. Dispersions with different CNT concentrations (0.5 mg/ml, 1.5 mg/ml, 2.5 mg/ml) were obtained using sodium dodecylbenzene sulfonate surfactant (SDBS, 10 mg/ml) together with ultrasonication for 30 minutes. The pretreated cotton fabric (Ctn) was soaked in the CNT dispersions prepared for 5 min, whose weigh bath ratio was 1:50. In order to achieve the desirable CNT deposition, the dip-coating operation was repeated multiple times. For convenience, the sample with one CNT deposition was recorded as S1, twice as S2, thrice as S3, four-times as S4, and n-times as Sn. After the treatment with carbon nanotubes, the colour of the cotton fabrics turned from white to black.

Testing and characterisation

FTIR spectra

Fourier Transform-Infrared (FT-IR) transmittance of the NaOH pretreated cotton fibre before and after CNT coating was performed using a Fourier transform-infrared spectrometer (Nicolet 5700) in the spectrum range of 4000-400 cm^{-1}.

Loading of CNTs

The loading of CNTs was obtained by weighing the mass of the Ctn before and after CNT deposition utilising an electronic balance with a sensitivity of 10^{-4} g, as according to the following ***Equation (1)***:

$$W = m_1 - m_0 \quad (1)$$

Where, m_0 and m_1 are the mass of Ctn fabrics before and after CNT coating, respectively.

Thickness of coated fabric

The thickness of the cotton fabrics before and after CNT coating was measured by a fabric thickness gauge (YG141N) according to standard GB 3820-1997.

Electrical surface resistance

According to the AATCC 2005-76 standard, the surface resistance of the coated cotton fabric was measured by a digital multimeter (Fluke 15B) via the two probe method.

Characterisation of surface morphology

Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used to observe the micro-surface morphology of the CNTs on cotton fibres. A thin layer of gold was coated onto the cotton fabrics before the measurement to neutralise the charging issue.

Bending stiffness of fabric

The bending stiffness of the samples before and after CNT deposition were tested by a KES fabric style meter (KES-FB2-S).

Air permeability

Air permeability of the fabrics was measured by a YG(B)461E-III digital fabric permeability instrument according to ASTM D737-2018 Standard Test Method. The tests were performed in the standard atmosphere for testing textiles, which was at 21 ± 1 °C and under 65 ± 2% relative humidity. The values reported were the average of five samples obtained under the same condition.

Microwave absorbing property test

The electromagnetic shielding performance of the cotton fabrics coated with CNTs was tested by a vector network analyser (ROHDE & SCHWARZ ZVL6) at a frequency range of 3.5-6 GHz [21].

Durability test

CNT functionalised cotton fabrics were washed according to standard AATCC 61-2013 test No.1A to estimate its colour fastness and EM SE durability. Samples were sewn together with standard lining fabrics and then washed at 40 °C in an aqueous solution of common laundry detergent (OMO, 0.15 wt%). After washing treatment, the fabrics were cleaned and dried. The discolouration degree of the treated samples was evaluated by the colour-changing grey card. The first grade is the worst and the fifth the best [22]. The EM SE value of the washed fabrics was also assessed.

Results and discussion

The electromagnetic shielding effectiveness represents the attenuation ability of shielding materials with respect to a electromagnetic wave. According to the definition of electromagnetic shielding effec-

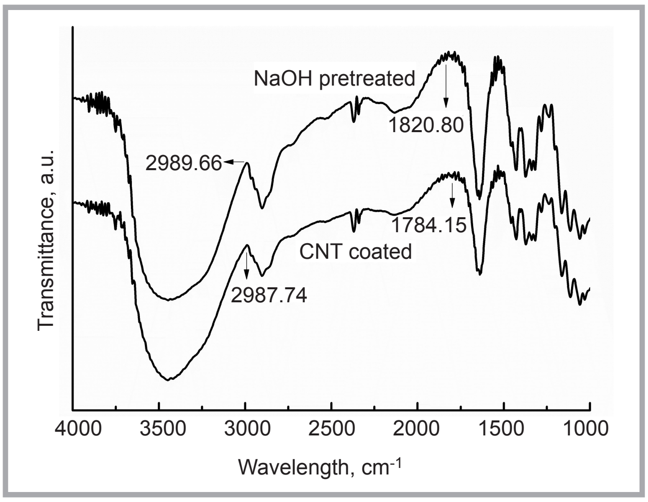

Figure 2. FTIR spectra of cotton fabrics with and without CNTs.

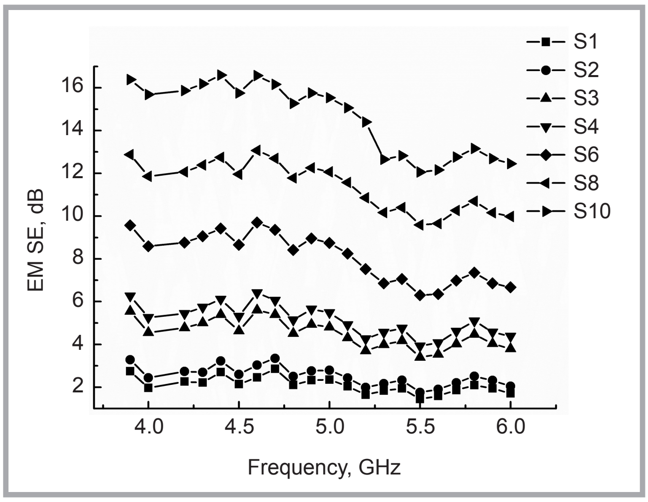

Figure 3. SE of fabrics with different numbers of dip-coatings.

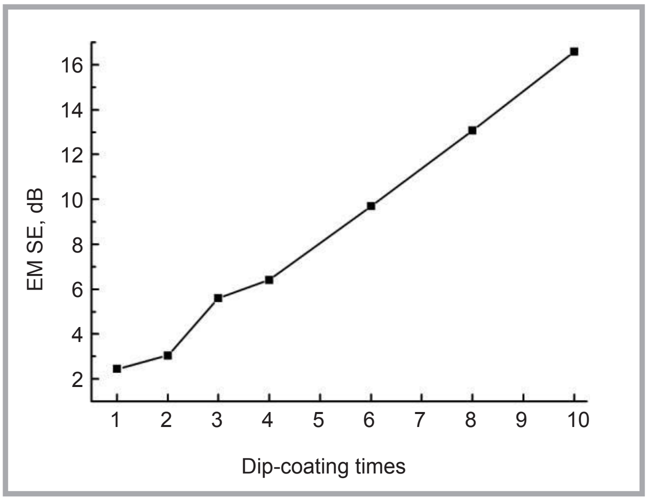

Figure 4. SE of fabrics with different numbers of dip-coatings at a frequency range of 4.6 GHz.

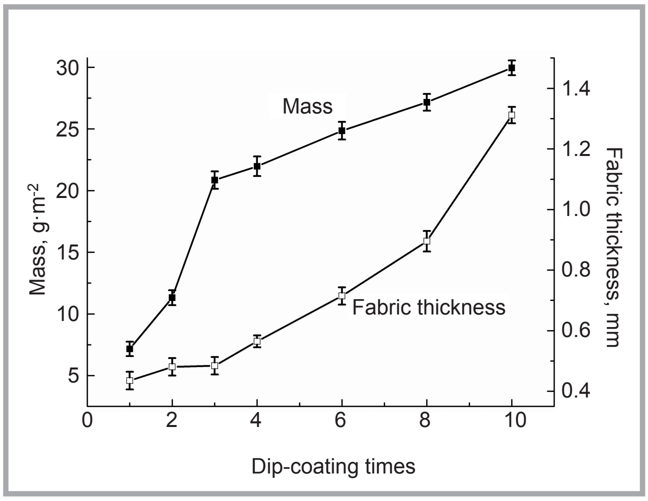

Figure 5. Effect of the number of dip-coatings on mass and fabric thickness.

tiveness, SE = -10 log (P_t/P_i) = -10 logT (where P_t, P_i, and T are the power of the transmitted EM wave, that of the incident EM wave through the shield, and the transmittance respectively). A previous work [14] showed that cotton fabric coated with SDBS-CNTs displayed little shielding effectiveness, because of the obvious aggregation of CNTs on the cotton fabric.

Here, NaOH solution was used to pretreat the cotton fabric, which was beneficial for removing impurities and the sizing agent from the sample [23-25]. In this case, it would promote the uniform adsorption of CNTs onto Ctn, which improves its EM shielding property. As shown in ***Figure 1.a***, impurities can be observed on the surface of pristine cotton fibre, which hinder the uniform adsorption of CNTs (***Figure 1.b***). After the NaOH pretreatment, the surface became cleaner and groove features appeared (***Figure 1.c***), which favours the uniform deposition of CNTs (***Figure 1.d***). Therefore, pretreating the cotton fabrics with NaOH was successful in removing impurities, increasing the roughness of the surface, and then promoting the uniform deposition of CNTs, which would further improve the electromagnetic shielding effectiveness of the fabric.

In order to inspect the interaction between CNTs and Ctn, FTIR measurements were carried out. As shown in ***Figure 2***, a lot of vibrational peaks can be identified. It was obvious that the peaks at 2989.66 and 2987.74 cm^{-1} corresponded to the vibrational signal of -OH, while the peaks at 1820.80 and 1784.15 cm^{-1} corresponded to that of -COOH stretching. It demonstrates that the peaks of carboxyl and hydroxyl groups both redshift slightly with CNT deposition onto fabrics, which proves that there is a strong hydrogen bond interaction between the CNTs and Ctn surface. This force is likely to occur in the combination between CNTs and Ctn. Therefore, NaOH pretreated cotton fabrics were further used to our investigation.

Effect of the number of dip-coatings on electromagnetic shielding effectiveness

The electromagnetic shielding effectiveness of materials is related to their electrical conductivity. The better electrical conductivity of the material, the higher the electromagnetic shielding effectiveness it shows [26, 27].

In order to study the effect of the number of dip-coatings on the electromagnetic shielding performance of the coated cotton fabrics, we chose an immersion temperature of 25 °C and a CNT con-

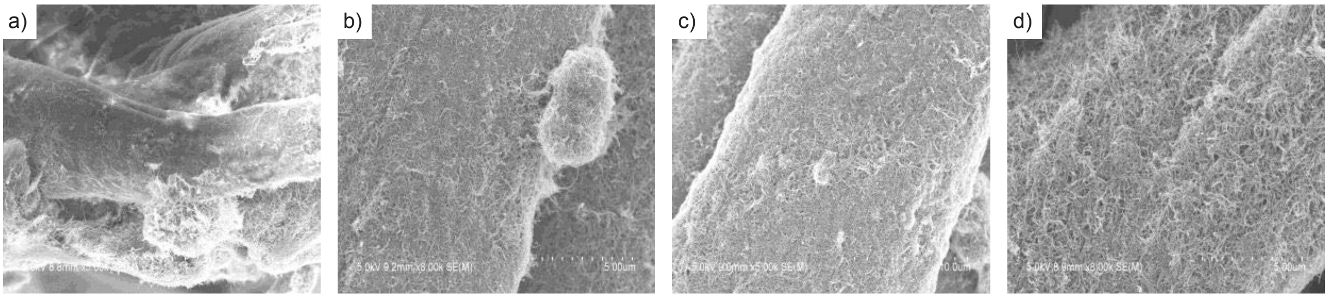

***Figure 6**. SEM of fabrics with different numbers of dip-coatings, a) one, b) two, c) three, d) four.*

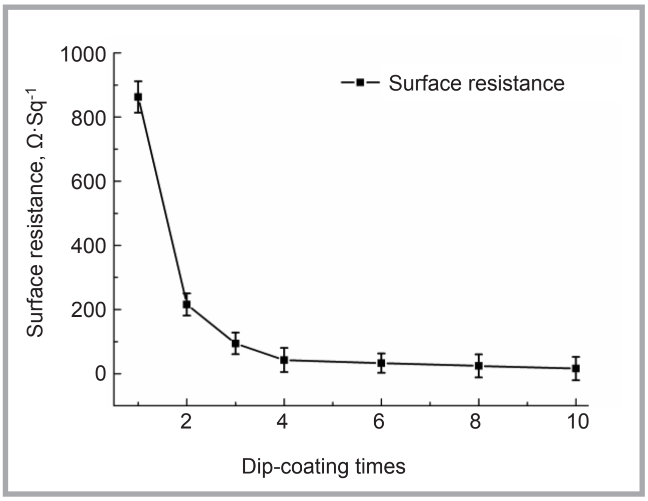

***Figure 7.** Relationship between the numbers of dip-coatings and resistance.*

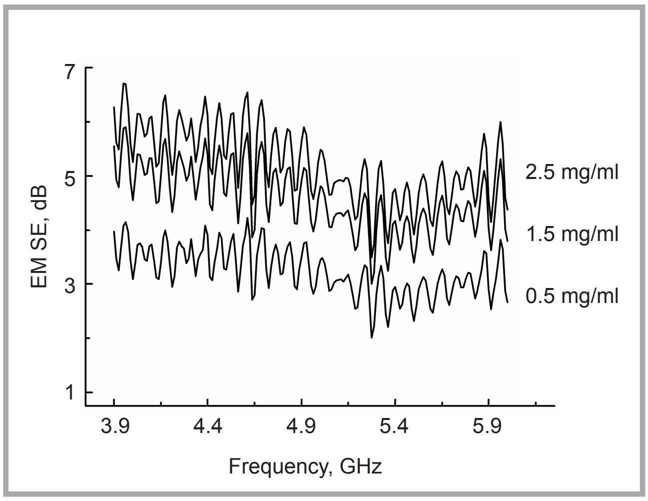

***Figure 8.** SE of fabrics with different concentrations of CNT dispersion.*

centration of 2.5 mg/ml. The relationship between the electromagnetic shielding effectiveness and number of dip-coatings at the frequency range of 3.5-6 GHz is shown in ***Figure 3***. It is obvious that the electromagnetic shielding effectiveness increases with the number of dip-coatings. As shown in ***Figure 4***, the electromagnetic shielding effectiveness with dip-coating once was 2.45 dB, twice – 3.04 dB, thrice – 5.61 dB, four-times – 6.42 dB, and ten-times – 16.47 dB at 4.6 GHz. As a result, the SE value was improved steadily with an increase in the number of dip-coatings.

A variety of studies have shown that the electromagnetic shielding property is affected by the electrical conductivity, magnetic permeability and thickness of the material [5]. The materials used in this study were all non-magnetic, hence the influence of electrical conductivity and thickness on the absorbing properties was further analysed. As shown in ***Figure 5***, the mass of CNTs and the thickness gradually increased with the number of dip-coatings. Additionally, the CNTs become much denser on the surface of the fabric with the increasing of dip-coatings (***Figure 6***). It is reasonable to speculate that tremendous grooves and -OH groups promote the conformal coating of CNTs onto NaOH pretreated cotton fibre, which, in turn, is beneficial to the formation of a more conductive network on the surface of the cotton fabric and improves its electrical conductivity (***Figure 7***).

As shown in ***Figure 7***, the surface resistance of cotton fabric with CNT coating decreased with an increase in the number of dip-coatings, which means its electrical conductivity increased. Specifically, compared with the fabric with once dip-coating, the electrical surface resistance of the fabric decreased by 75.0% after twice dip-coating and further decreased by 95.1% after four-times dip-coating. This could be attributed to the formation of a more conductive network. Consequently, it could provide more carriers to interact with electromagnetic waves, which improves the electromagnetic shielding performance.

Effect of concentration of CNT dispersion on wave absorbing property

In order to study the effect of CNT concentration on the electromagnetic shielding properties of cotton fabrics, CNT dispersions at concentrations of 0.5 mg/ml, 1.5 mg/ml, and 2.5 mg/ml were chosen to coat cotton fabrics, at an immersion temperature of 25 °C and with four dip-coatings. The result shows that the value of EM SE improves with an increase in the concentration of CNTs. However, it is not an equally proportional increase along with the concentration of CNTs from 0.5 mg/ml to 1.5 mg/ml and to 2.5 mg/ml (***Figure 8***). To analyse the cause, the

***Table 1.** Relationship between the concentration of CNT dispersion and properties of coated cotton fabric.*

Concentration of CNT dispersion, mg/ml	Mass, $g \cdot m^{-2}$	Fabric thickness, mm	Surface resistance, $\Omega \cdot Sq^{-1}$
0.5	13.54 ± 1.27	0.546 ± 0.045	150.03 ± 13.75
1.5	15.17 ± 1.39	0.583 ± 0.051	96.85 ± 8.37
2.5	15.54 ± 1.29	0.586 ± 0.049	82.55 ± 7.61

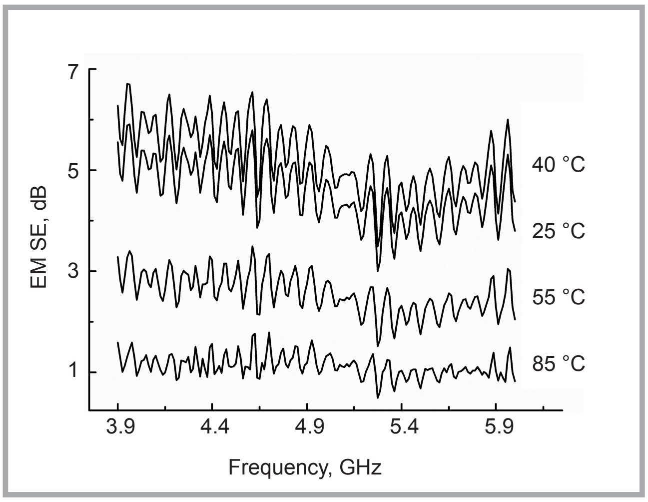

***Figure 9**. SE of fabrics with different dipping temperatures.*

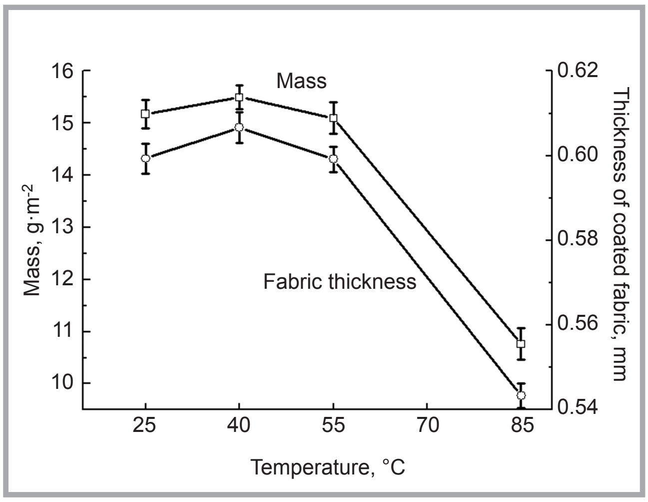

***Figure 10**. Effect of temperature on the unit area upload capacity and fabric thickness*

mass, thickness and electrical surface resistance of the fabrics coated with different concentrations of CNTs were further investigated.

As shown in ***Table 1***, the mass of CNTs and the thickness of the fabric increase with an increase in CNT concentration, whose tendencies are similar to EM SE. Specifically, the mass increased by 1.63 $g \cdot m^{-2}$ and 0.37 $g \cdot m^{-2}$ and the thickness by 0.037 mm and 0.003 mm when the CNT concentration increased from 0.5 mg/ml to 1.5 mg/ml and from 1.5 mg/ml to 2.5 mg/ml, respectively. In this case, the surface resistance of the fabric decreased by 53.15 $\Omega \cdot Sq^{-1}$ and 14.30 $\Omega \cdot Sq^{-1}$. Therefore, we speculate that there is a saturation point of CNT adsorption between 1.5 mg/ml and 2.5 mg/ml. The deposition of CNTs onto the fabric would not increase after approaching the saturation point, and hence the electromagnetic shielding property of the CNTs-coated fabric either. The loading of CNTs and the thickness of the fabrics both increased with an increase in CNT concentration. However, the surface resistance of CNT coated fabrics decreased with CNT concentration, indicating that increasing the concentration of CNT dispersion can improve the conductivity of Ctn/CNTs to some extent [28].

Lower than the saturation point of CNT concentration [29], an increase in the concentration of CNTs is beneficial to the deposition and the formation of a conductive network. Furthermore, the Van der Waals force and hydrogen bonding promotes the combination between CNT and cotton fibre, thereby enhancing the electrical conductivity [29]. The EM shielding property of CNT-coated cotton fabric increases with the improvement of electrical conductivity, which depends on the uniform deposition of CNTs.

Effect of dipping temperatures on EM shielding property

The finishing process of CNT-coated cotton fabric is similar to the dyeing process. The solution temperature has an important influence on the dye uptake rate during the dyeing process. Therefore, we further studied the effect of the temperature of the CNT loading and explored its effect on the EM shielding property. The concentration of CNT dispersion chosen was 1.5 mg/ml and the number of immersions – four. As shown in ***Figure 9***, the electromagnetic shielding effectiveness of the CNT-coated cotton fabric increased slightly with a temperature rise from 25 °C to 40 °C, but the electromagnetic shielding effectiveness significantly decreased at a higher temperature (85 °C), which suggests that high temperature goes against improving wave absorption performance.

As discussed above, the mass of CNTs loaded onto cotton fabric significantly influences the EM shielding property of CNT-coated cotton fabric. Thus, the mass of CNTs and the thickness of the fabrics were further measured, as shown in ***Figure 10,*** to establish the cause of this result.

Figure 10 displays a trend of first rising and then decreasing. When the temperature rose from 25 °C to 40 °C, the mass of CNTs increased by 2.14%, and the thickness of the fabric increased by 1.24%. However, as the temperature continued to increase, the mass of CNTs and the thickness of fabrics decreased significantly compared to the fabric deposited at 25 °C. Specifically, the mass and thickness of the fabrics decreased by 40.24% and 10.28% at 85 °C, respectively. The probable reason behind this is that the molecular chain of CNTs moves faster at higher temperature, which, on the one hand, is beneficial for the deposition

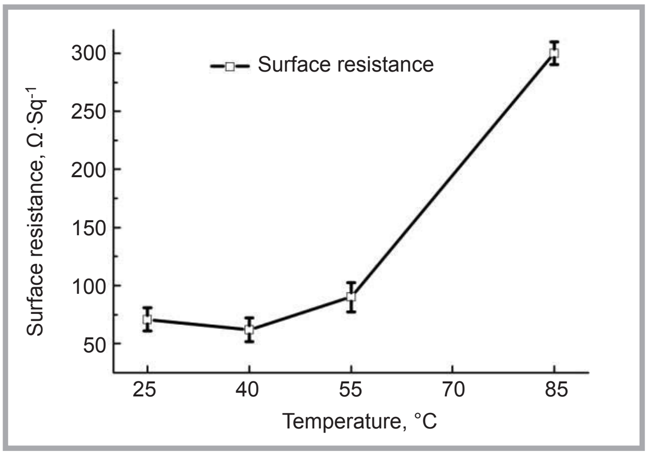

***Figure 11**. Relationship between temperature and resistance.*

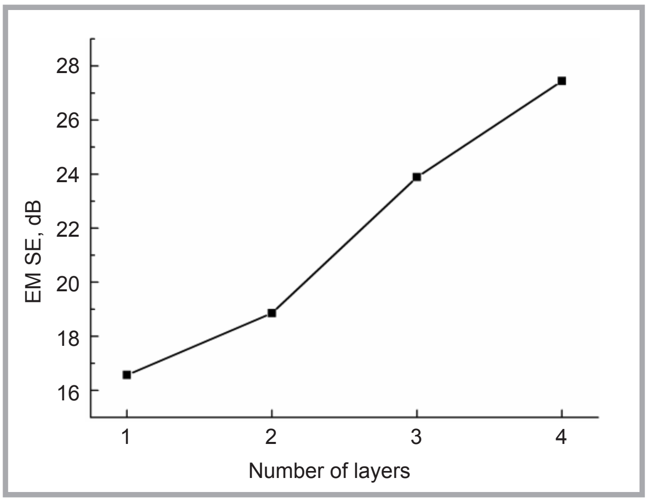

Figure 12. SE with different numbers of layer stackings.

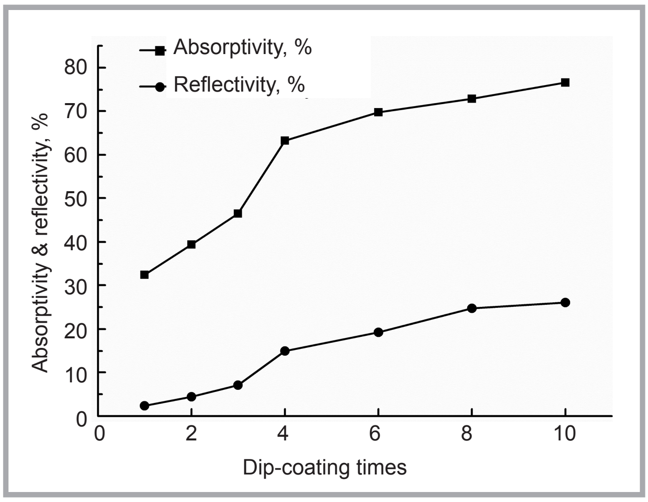

Figure 13. Absorptivity and reflectivity of fabrics with different numbers of dip-coatings.

of CNTs onto cotton fabric, but on the other hand, accelerates CNTs separating away from the cotton fabric. Therefore, there is an optimum temperature that maximizes the mass of CNTs deposited onto cotton. Generally, the internal void volume between the cotton fibres and yarns is constant. When the temperature of CNT dispersion increased, the cotton fibres swelled, which narrowed the gap between the fibres. In this case, it was difficult for CNTs to enter into the gap between fibres, which reduced the deposition of CNTs, and consequently the electrical conductivity of the fabric [30].

The increase in the surface resistance of CNT-coated fabric further confirmed that a much higher temperature of deposition was detrimental to the electrical conductivity of the fabric. It can be seen from ***Figure 11*** that the surface resistance of the cotton fabric with CNT coating first decreased and then rose with the temperature. This means that the conductivity first increases and then decreases. When the temperature was raised from 25 °C to 40 °C, the electromagnetic shielding performance increased slightly, and the surface resistance decreased by 12.3%. At 85 °C, the electromagnetic shielding effectiveness decreased significantly, and the surface resistance increased by 233.1%. Therefore, considering the consumption of energy and practicability of the operation, it is feasible to carry out the dip-coating process at room temperature.

Absorption shielding effectiveness and reflection shielding effectiveness

In order to clarify the main shielding mechanism of CNT-coated cotton fabrics, the absorption and reflection shielding effectiveness, absorptivity and reflectivity of CNT-coated cotton fabric were further studied [31].

Absorptivity (A, the percentage of absorption to incidence of EM weave), reflectivity (R, the percentage of reflection to incidence of EM weave), absorption shielding effectiveness (SE_A) and reflection shielding effectiveness (SE_R) were calculated according to the scattering parameters S_{11} and S_{21} measured by a vector network analyser, the computational formula is as follows:

$$S_{21} = 10\log T \quad (2)$$

$$T = 10^{\frac{S_{21}}{10}} \quad (3)$$

$$S_{11} = 10\log R \quad (4)$$

$$R = 10^{\frac{S_{11}}{10}} \quad (5)$$

According to the principle of conservation of energy, the value of absorptivity can be calculated as (A):

$$A = 1 - R - T \quad (6)$$

In addition, the electromagnetic wave that can enter the inside of the shielding material needs to be subtracted from the reflected portion, which is 1-R, hence the effective absorption rate A_{eff} is:

$$A_{eff} = \frac{1-R-T}{1-R} \quad (7)$$

Based on the above analysis, the reflection shielding effectiveness SE_R and absorption shielding effectiveness SE_A can be expressed as

$$SE_R = -10\log(1-R) \quad (8)$$

$$SE_A = -10\log(1-A_{eff}) = -10\log\frac{T}{1-R} \quad (9)$$

According to ***Equations (8)*** and ***(9)***, the reflection shielding effectiveness SE_R and absorption shielding effectiveness SE_A were calculated, respectively. The absorption shielding effectiveness and reflection shielding effectiveness of CNT-coated cotton fabric with different numbers of dip-coatings are shown in ***Table 2***, demonstrating that as the number of dip-coating increases, both the absorption shielding effectiveness and reflection shielding effectiveness increase, which could attribute to the formation of a more conductive network. For those samples, SE_A was more than four-times larger than SE_R at most frequency points, which indicates that the shielding mechanism of CNT-coated cotton fabrics is mainly caused by absorption. This result

Table 2. *SE_A (dB) and SE_R (dB) of cotton fabrics with various numbers of dip-coatings.*

Sample	S1		S3		S5		S7	
Frequency, GHz	SE_A	SE_R	SE_A	SE_R	SE_A	SE_R	SE_A	SE_R
4.0	1.29	0.28	3.28	1.64	5.26	2.18	12.3	3.06
4.5	1.44	0.17	3.59	1.09	5.81	2.2	13.5	3.21
5.0	2.09	0.11	3.89	0.92	6.48	2.34	14.5	3.46
5.5	0.69	0.24	2.7	0.8	4.38	1.96	12.1	2.82
6.0	1.08	0.21	2.95	0.65	4.76	2.09	12.9	3.35

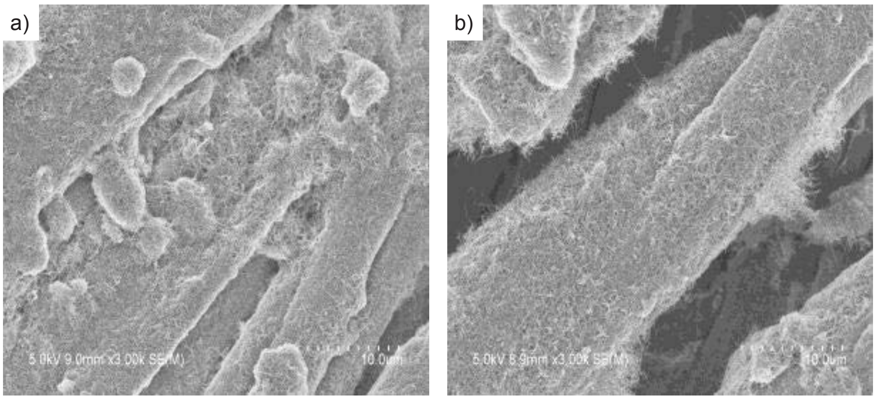

***Figure 14**. Micromorphology of carbon nanotubes: a) between cotton fibres, and b) on a single cotton fibre.*

***Table 3.** Bending rigidity and air permeability of CNT-coated fabric.*

Number of dip-coatings	0	1	2	3	4	6	8	10
Bending stiffness, 10^{-2} cN·cm^2/cm	3.36	3.91	4.52	5.25	5.93	6.98	7.89	8.71
Air permeability, mm/s	2295	2127	1915	1693	1421	1154	907.9	751.3

also proves that CNT-coated cotton fabric has great potential for application in flexible absorbing materials.

Besides increasing the number of dip-coatings, the stacking of CNT-coated fabric also improves its EM shielding effectiveness. As shown in ***Figure 12***, the EM SE value increased with the augmenting of the stacking layer, which is consistent with the result of previous studies [6, 32]. The SE value reached 26.4 dB when four layers were stacked, which meet the requirement of commercial utilisation. Besides this, the EM absorbing ability of flexible materials can be improved by adjusting the stacking angle, stacking space and stacking mode of fabrics [8, 32].

Absorptivity and reflectivity

Furthermore, the reflectivity R (%) and absorptivity A (%) of the CNT-coated fabrics were compared at 5 GHz (***Figure 13***). The CNT concentration and the immersion temperature used were 1.5 mg/ml and 25 °C (room temperature), respectively. ***Figure 13*** indicates that the absorptivity increases with an increase in the number of dip-coatings. When the number of dip-coatings was one, the absorptivity was the lowest because the carbon nanotubes deposited on the fabric were too few to form a uniform conductive network [33]. Moreover, there were not enough electrical carriers to interact with the EM wave, and the fabric itself is an EM wave-transparent material [34]. Therefore, most of the EM waves passed through the fabric without being absorbed or reflected. With an increase in the number of dip-coatings, the absorptivity and reflectivity increased, but the reflectivity was still relatively less than the absorptivity. The relatively low reflectivity indicates that the impedance of the fabric with the carbon nanotube coating matches well with that of an EM wave in airspace, which allows more EM waves to enter the interior of the fabric. It provides the necessary condition for the absorption of EM waves inside the fabric.

Bending rigidity of the fabric

In order to learn the change in flexibility of fabric after coating with CNTs. The bending rigidity of the NaOH pretreated fabric and the fabric with different numbers of CNT dip-coatings was investigated. As shown in ***Table 3***, the bending rigidity of fabric with CNTs increased with an increase in the number of dip-coatings. When the number of dip-coatings reached 10, the bending stiffness increased from 0.0336 to 0.0871 cN·cm^2/cm, which was still flexible enough compared with the fabric coated with (CNT/PAH, PAH is a high-molecular polymer)*10, whose bending rigidity reached 0.3835 cN·cm^2/cm [35, 36]. Therefore, it is feasible to coat a cotton fabric with CNTs instead of polymer so as to improve the electromagnetic shielding property while retaining the fabric's flexibility.

Air permeability of fabric

The air permeability of fabric without and with different numbers of CNT dip-coatings was also investigated. As shown in ***Table 3***, the air permeability of fabric with CNTs decreased with the number of dip-coatings. When the number of dip-coatings reached 10, the air permeability decreased to 751.3 mm/s, but it was still permeable enough compared with other wave absorbing materials. For instance, the air permeability of woven fabric with 30 weft yarns per centimeter is 400 mm/s [37]. In our study, the addition of CNTs in cotton fabric can form numerous nano pores, which can also improve air permeability. Therefore, CNT coated cotton fabrics are promising alternatives in the electromagnetic shielding field.

EM SE durability of CNT coated fabric

AATCC 61-2013 standard test No.1A was used for evaluating the EM SE durability of CNT coated fabric. The S8 and S10 samples were washed at 40 °C in an aqueous solution with common laundry detergent (OMO, 0.15 wt%). After washing, the EM SE of the fabrics had decreased insignificantly, and remained at 8.91 dB and 10.61 dB, corresponding to retention rates of 91.79% and 90.77%, respectively.

The washing colour fastness of CNT coated fabrics was assessed via comparing with the standard grey card. After washing, the colour of the CNT coated fabric had changed a little bit, and the carbon nanotubes had not significantly fallen off. It was observed that the washable fastness of both sample S8 and S10 is 4. The reasons of the moderate durability may be as follows: (1) the grooves of the cotton fibre act as "anchors", which favours the deposition of CNTs [38]; (2) the carboxyl group of CNTs can combine with the hydroxyl group of the cotton fabric to form hydrogen bonds [39], which increases the binding fastness between the CNTs and cotton fabric. The fastness of the coated fabrics can be further increased by plasma treatment [40].

Further observation of SEM images of the washed cotton fabric revealed that a little agglomeration existed, as shown in ***Figure 14 (a)*** and ***(b),*** which may be due to the rearrangement of CNTs, drived by the large Van der Waals force.

In fact, the rearrangement of CNTs not only promoted their aggregation but also built “bridges” between fibres. The aggregation of CNTs formed a conductive network with many nano-holes, which was similar to the micro-porous structure of the fabric. The nano- and micro-porous structure enhanced the chance of EM wave reflection and, consequently, extended the path of EM propagation, dissipating more EM energy. The “bridges” connecting fibre to fibre are beneficial in constructing a more conductive network structure in the cotton fabric, thereby improving the wave absorbing performance.

Conclusions

In this paper, NaOH pretreated cotton fabric (Ctn) was dip-coated with CNTs for EM shielding application. The effects of the numbers of dip-coatings, CNT concentration and temperature of the dip-coating on EM shielding properties were discussed. The results show that the EM shielding effectiveness increased with the number of dip-coatings. The EM shielding effectiveness obviously increases when the CNT concentration increases from 0.5 mg/ml to 1.5 mg/ml, while the EM shielding effectiveness decreased significantly at high temperature. Based on this, the process of CNT dip-coating can be carried out at room temperature, which is simple and convenient. Moreover, the EM SE of Ctn fabric after ten dip-coatings reached 16.5 dB, which shielded 97.76% of EM energy. By stacking four layers of Ctn fabric with CNTs, the EM SE was further improved to 26.4 dB, and we found that the EM wave absorption is the major contributor to the shielding mechanism. After washing, the EM SE value of CNT coated Ctn fabrics remained more than 90%, and the washing fastness was fourth grade. Therefore, it can be concluded that carbon nanotube coated cotton fabric is a flexible material which has great potential for application in wave absorbing protective clothing.

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References

1. Li Y, Xu F, Lin Z, Sun X, Peng Q, Yuan Y, et al. Electrically and Thermally Conductive Underwater Acoustically Absorptive Graphene/Rubber Nanocomposites for Multifunctional Applications [J]. *Nanoscale* 2017; 9(38): 14476-14485.
2. Xie S, Ji ZJ, Shui ZH, Li B, Wang J, Hou GY, et al. Design and Manufacture of a Dual-Functional Exterior Wall Structure for 1.1-5 Ghz Electromagnetic Radiation Absorption [J]. *Composite Structures* 2018; 201: 608-615.
3. Chung DDL. Carbon Materials For Structural Self-Sensing, Electromagnetic Shielding And Thermal Interfacing[J]. *Carbon* 2012; 50(9): 3342-3353.
4. Du L, Zhang HY, Huang YL, Zhang M. Study on Composite Electromagnetic Shielding Coatings With Cnts [J]. *Materials Research and Application* 2010; 4(4): 414-417.
5. Liu Z, Su Y, Pan Z, Li Y, Wang X, Zhou Z. Parameter Description of the Surface Metal Fiber Arrangement of Electromagnetic Shielding Fabric. *FIBRES & TEXTILES in Eastern Europe* 2017; 25, 2(122): 62-67. DOI: 10.5604/12303666.1228174.
6. Xu YD, Yang YQ, Duan HJ, Gao JF, Yan DX, Zhao GZ, et al. Flexible and Highly Conductive Sandwich Nylon/Nickel Film for Ultra-Efficient Electromagnetic Interference Shielding [J]. *Applied Surface Science* 2018; 455: 856-863.
7. Zhang W, Wu CW. Preparation and Application of Flexible Conductive Fabric Based on Sing – Wall Carbon Nanotube[J]. *Modern Chemical Industry* 2013; 331(12): 39-42.
8. Ozen MS, Usta I, Yuksek M, Sancak E, Soin N. Investigation of the Electromagnetic Shielding Effectiveness of Needle Punched Nonwoven Fabrics Produced from Stainless Steel and Carbon Fibres. *FIBRES & TEXTILES in Eastern Europe* 2018; 26, 1(127): 94-100. DOI: 10.5604/01.3001.0010.5636.
9. Shen QL, Li HJ, Lin HJ, Li L, Li W, Song Q. Simultaneously Improving The Mechanical Strength and Electromagnetic Interference Shielding of Carbon/Carbon Composites by Electrophoretic Deposition of Sic Nanowires [J]. *Journal of Materials Chemistry C*. 2018; 6(22): 5888-5899.
10. Peng B, Takai C, Razavi-Khosroshahi H, Salmawy MSE, Fuji M. Effect of Cnts on Morphology and Electromagnetic Properties of Non-Firing Cnts/Silica Composite Ceramics [J]. *Advanced Powder Technology* 2018; 29(8): 1865-1870.
11. Xia QS, Zhang ZC, Liu YJ, Leng JS. Self-Assembly of Cross-Linked Carbon Nanotube Films for Improvement on Mechanical Properties and Conductivity [J]. *Materials Letters* 2018; 231: 190-193.
12. Singh SK, Akhtar MJ, Kar KK. Hierarchical Carbon Nanotube-Coated Carbon Fiber: Ultra Lightweight, Thin, and Highly Efficient Microwave Absorber [J]. *ACS Appl Mater Interfaces* 2018; 10(29): 24816-24828.
13. Pang ZP, Sun XG, Cheng XY, Cao HH, Wu XY, Fu Q. Preparation and Emi Shielding Performance of Carbon Nanotubes Conductive Paper [J]. Journal of Synthetic Crystals 2014; 43(10): 2635-2645.
14. Zou LH, Yao L, Ma Y, Li XP, Sailimujiang S, Qiu YP. Comparison of Polyelectrolyte and Sodium Dodecyl Benzene Sulfonate as Dispersants for Multiwalled Carbon Nanotubes on Cotton Fabrics for Electromagnetic Interference Shielding [J]. *Journal of Applied Polymer Science* 2014; 131(15): 1-9.
15. Hu XL, Tian MW, Pan N, Sun B, Li ZQ, Ma YL, et al. Structure-Tunable Graphene Oxide Fibers Via Microfluidic Spinning Route for Multifunctional Textiles [J]. *Carbon* 2019; 152: 106-113.
16. Hu XL, Tian MW, Xu TL, Sun XT, Sun B, Sun CC, et al. Multiscale Disordered Porous Fibers for Self-Sensing and Self-Cooling Integrated Smart Sportswear [J]. *ACS Nano* 2020; 14(1): 559-567.
17. Li ZQ, Ma YL, Wang LH, Du XJ, Zhu SF, Zhang XS, et al. Multidimensional Hierarchical Fabric-Based Supercapacitor with Bionic Fiber Microarrays for Smart Wearable Electronic Textiles [J]. *ACS Appl Mater Interfaces* 2019; 11(49): 46278-46285.
18. Sun F, Tian M, Sun X, Xu T, Liu X, Zhu S, et al. Stretchable Conductive Fibers of Ultrahigh Tensile Strain and Stable Conductance Enabled by a Worm-Shaped Graphene Microlayer [J]. *Nano Lett* 2019; 19(9): 6592-6599.
19. Li Z, Tian M, Sun X, Zhao H, Zhu S, Zhang X. Flexible All-Solid Planar Fibrous Cellulose Nonwoven Fabric-Based Supercapacitor via Capillarity-Assisted Graphene/Mno2 Assembly [J]. *Journal of Alloys and Compounds* 2019; 782: 986-994.
20. Lu Y, Tian M, Sun X, Pan N, Chen F, Zhu S, et al. Highly Sensitive Wearable 3D Piezoresistive Pressure Sensors Based on Graphene Coated Isotropic Non-Woven Substrate [J]. *Composites Part A: Applied Science and Manufacturing* 2019; 117: 202-210.
21. Xu Y, Wang J, Hu JP, Tong XC, Zhang MX. Purification of Multi-Walled Carbon Nanotubes and Its Surface Modification [J]. *Sciencepaper Online* 2010; 5(6): 423-426.
22. Ji Y. A Methodological Contrast of Textile Washing Color Fastness Testing [J]. *Journal of Jiangsu College of Engineering and Technology* 2017; 17(3): 20-23.
23. Kaitsuka Y, Goto H. Synthesis of Conductive Cocoon Silk Composites. *FIBRES & TEXTILES in Eastern Eu-*

rope 2017; 25, 1(121): 17-22. DOI: 10.5604/01.3001.0010.1705.
24. Jiang LQ, Gao L. Effect of Chemical Treatment on The Dispersion Properties of Carbon Nanotubes [J]. Journal of Inorganic Materials 2003; 18(5): 1135-1138.
25. Xu J, Zhou X, Xing ZQ, Tu TM, Wu YR. Flame Retardant Finish of Cotton Fabric with Dimethyl Phosphite Modified Carbon Nanotubes [J]. *Dyeing & Finishing* 2016; 42(12): 16-21.
26. Kim CJ, Choi HD, Suh KS, Yoon HG. Electrical Properties and Electromagnetic Shielding Effectiveness of Milled Carbon Fiber/Nylon Composites [J]. *Polym -Korea* 2003; 27(3): 201-209.
27. Sun YM, Luo SH, Sun HL, Zeng W, Ling CX, Chen DG, et al. Engineering Closed-Cell Structure in Lightweight and Flexible Carbon Foam Composite for High-Efficient Electromagnetic Interference Shielding [J]. *Carbon* 2018;136:299-308.
28. Al-Saleh MH. Influence of Conductive Network Structure on the Emi Shielding and Electrical Percolation of Carbon Nanotube/Polymer Nanocomposites[J]. *Synthetic Metals* 2015; 205: 78-84.
29. Wang ZF, Shi XM, Yu ZB, Li GB. Study on Infrared Emittance of Carbon Nanotube Coating [J]. Ordnance Material Science and Engineering 2009; 32(1): 21-23.
30. Feng M, Zhang YH, Wang XL. Research on Conductive Properties of Carbon Nano Capsule Filled Electromagnetic Shielding Coatings [J]. SAFETY & EMC 2010; 4: 67-68.
31. Cheng YC, Zhao XM, Wang R, Song BT. The Development Status and Shielding Effectiveness of Electromagnetic Shielding Fabric [J]. *Light and Textile Industry and Technology* 2013; 42(1): 58-60.
32. Palanisamy S, Tunakova V, Militky J. Fiber-Based Structures for Electromagnetic Shielding – Comparison of Different Materials and Textile Structures [J]. *Textile Research Journal* 2017; 88(17): 1992-2012.
33. Al-Saleh MH, Sundararaj U. Electromagnetic Interference Shielding Mechanisms of Cnt/Polymer Composites [J]. *Carbon* 2009; 47(7): 1738-1746.
34. Cai YH, Li XM, Dong JH. Properties of Porous Si_3N_4 Ceramic Electromagnetic Wave Transparent Materials Prepared by Technique Combining Freeze Drying And Oxidation Sintering [J]. *Journal of Materials Science: Materials in Electronics* 2014; 25(4): 1949-1954.
35. Lan CT, Li CL, Hu JY, Yang SG, Qiu YP, Ma Y. High-Loading Carbon Nanotube/ Polymer Nanocomposite Fabric Coatings Obtained by Capillarity-Assisted “Excess Assembly” for Electromagnetic Interference Shielding [J]. *Advanced Materials Interfaces* 2018; 5(13).
36. Sisodia N, Parmar MS, Jain S. Effect of Pretreatment on the Smoothness Behaviour of Cotton Fabric. *FIBRES & TEXTILES in Eastern Europe* 2019; 27, 5(137): 47-52. DOI: 10.5604/01.3001.0013.290.
37. Ogulata RT. Air Permeability of Woven Fabrics [J]. *Journal of Textile and Apparel, Technology and Management* 2006; 5(2): 1-10.
38. Zheng G, Juan X. Preparation of Copper Sulfide Deposition on Modified Poly (Ethylene Terephtalate) Fibres with Good Conductivity. *FIBRES & TEXTILES in Eastern Europe* 2018; 26, 1(127): 25-29. DOI: 10.5604/01.3001.0010.7792.
39. Li LQ, Fan T, Hu RM, Liu YP, Lu M. Surface Micro-Dissolution Process for Embedding Carbon Nanotubes on Cotton Fabric as a Conductive Textile [J]. *Cellulose* 2016; 24(2): 1121-1128.
40. Mojtahed F, Shahidi S, Hezavehi E. Influence of Plasma Treatment on cnt Absorption of Cotton Fabric and Its Electrical Conductivity and Antibacterial Activity [J]. *Journal of Experimental Nanoscience* 2015; 11(3): 215-225.

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