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Nanocomposite Coatings on Cotton and Silk Fibers for Enhanced Electrical Conductivity

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Abstract: Electrically conducting carbon nanofillers like liquid exfoliated graphite (EG), nanographite (NG), carbon nanotube (CNT) and carbon nanofiber (CNF) were dispersed in thermoplastic polyurethane (TPU) matrix. HRTEM images and SAED patterns confirmed exfoliation of graphite and good dispersion of all nanofillers. The polymer dispersions were used to develop nanocomposite coatings on cotton yarn and silk fibers. These nanocomposite coated fibers showed significant improvements in electrical conductivity. Current-voltage (IV) plots indicated linearity for most of the nanocomposite coated fibers. Among the nanofillers, CNF and CNT have strong potential to impart stable conductivity on such fibers. The electrical conductivity of 10 wt% CNF based nanocomposite coated cotton yarn was 2 S/m; while it was more than 12 S/m for silk filament. 2 wt% CNT dispersed nanocomposite coating on silk also showed very good conductivity of 11 S/m. The large void fraction in coated cotton yarn (~12 %) is attributed for such difference in electrical conductivity. Hence, staple yarns are not suitable to develop such nanocomposite coated fibers. Both the resistance and impedance tests were carried out at different test lengths up to 5 cm and resistance and impedance (at 100 Hz, 120 Hz and 1 kHz) per cm was calculated with variable test length. As variations in test results were not very high it can be concluded that the uniformity in electrical conductivity is achieved through these coatings.

Keywords: Nanocomposite coating, Exfoliated graphite, Carbon nanotube, Carbon nanofiber, Nanographite, Cotton, Silk

Introduction

With the growing interest on wearable electronics devices, electrically conducting yarns are increasingly finding their places as sensors and transmitters [1]. Nanotechnology is under intensive research for last two decades to develop such yarns for textiles and clothing. The functional properties of a fabric can be greatly improved when suitable nano colloidal suspensions are introduced in finishing and coating processes. Fabric or fiber surface can be modified with a thin, precise layer of nanoparticles created by layer-by-layer (LBL), sputter or plasma coating techniques. These methods resulted in durable and more efficient functional properties with less amount of material deposition. However, it is very difficult to ensure durable and stable coating with pure nanoparticles on textile surface using any one of these techniques. The uniform deposition and strong attachment of nanomaterials on the fabric is a topic of research, especially for industrial scale. Three different methods have been suggested to harness nanoparticles on the textile surface. In the first method, a cross linking agent is used to entrap nanomaterials. Secondly, an *in situ* synthesis of nanoparticles on the fabric has been tried as an alternative method of fixation. The third method involves dispersing nanoparticles in the polymer matrix and coating on textiles surface. This method of nanocomposite coating has remarkable processing advantage [2]. The compatibility of coating polymer to the substrate is the key factor for durable and stable performance of such coatings; hence problem of anchoring nanoparticles on the textile can be addressed with more confidence.

Electrically conductive materials are used for various applications like dissipation of static charge, electromagnetic and radio frequency shielding as well as protection against lightning strikes in aircraft, battery components, power cables and even membrane in fuel cells [3,4]. Though most of the commercially viable polymers are insulating materials, electrical conductivity of polymers can be improved by addition of conducting nanofillers [5,6]. This is achieved by continuous network formation among conducting nanoparticles in dielectric polymer matrix. Hence, electrical conductivity of such polymer nanocomposites primarily depends on volume (or weight) content of the nanofiller [7]. The minimum volume or weight fraction to achieve a significant increase in electrical conductivity is termed as percolation threshold [8,9]. The percolation threshold and electrical conductivity of nanocomposites were not only affected by the volume fraction of nanofillers; but also by their electrical conductivity and characteristics like size, shape, aspect ratio, surface area and morphology. Moreover, the distribution and orientation of the nanofillers as well as the filler spacing within the polymer matrix are also important factors to attain high electrical conductivity [10].

Electrically conducting coatings on yarns and fibers offer better strength and low surface resistivity [11,12]. These fibers and yarns can be used as flexible conductive structures in the fields of sensors, heated fabrics, electromagnetic shielding, smart clothing, thermal storage, microwave absorption and intelligent textiles [1,13]. A balance between dispersion

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process and nanofiller content helps to achieve optimized mechanical strength. However, high nanofiller content is required to achieve high electrical conductivity [13]. Among the nanofillers, electrically conducting allotropes of carbon (SP^2 or deformed SP^2 hybridized) are potential reinforcements to attain good electrical and mechanical properties. This group consists of graphite or stacked graphene, carbon nanotube (CNT) and carbon nanofiber (CNF) [14]. Graphene is flat mono layer of graphite containing SP^2 bonded carbon atoms; it is the crystalline allotrope of carbon and has a hexagonal or honey comb structure. High-quality graphene is strong, light, nearly transparent and an excellent conductor of heat and electricity [15]. Graphene sheets stack with inter planar spacing of 0.34 nm to form graphite which is the most stable form of carbon with a layered, planar structure [16]. It has networks of graphene sheets which are parallel to each other and are held together by weak Van der Waals force. Graphite has excellent electrical properties because its π orbital electron is distributed over a graphite plane. However, the bulk electrical conductivity for carbon is lower than most metals [17]. Surface area of graphite can be increased tremendously by exfoliating it into few layer graphene. Among the exfoliation processes, liquid exfoliation in ortho-dichloro benzene (ODCB) is found to be resulted in good quality graphene with less surface defect and high electrical conductivity as compared to other processes [18]. Other conducting nanofillers like CNT and CNF are having cylindrical nanostructures, often defined as rolled or curved graphene (deformed SP^2) [19]. All these carbon nanofillers have very high surface area and good aspect ratio i.e. high length-to-diameter ratio, hence suitable for development of conducting nanocomposites in dielectric polymer matrix at low filler loading [20,21].

In our previous works, carbon nanoparticle based nanocomposite coatings and films show promise to impart stable and uniform electrical conductivity [22-24]. In the present work, carbon based electrically conducting nanofillers such as liquid exfoliated graphite (EG), nano graphite (NG), carbon nano fibers (CNF) and carbon nano tubes (CNT) were used to induce electrical conductivity in thermoplastic polyurethane (TPU) matrix for development of nanocomposite coated conducting cotton yarn and silk filaments.

Experimental

Materials

Extra pure graphite (G) powder (250 microns grain size) was purchased from Loba Chemicals, India. Nanographite (NG) was procured from M/s Kaiyu Inc. Hong Kong, having average platelet size 200 nm. Carbon nanofiber (CNF) (Pyrograf PR24AGLD) was purchased from Applied Sciences Inc. USA, having diameter 60-150 nm and length 30-100 μm. Single wall carbon nanotube (CNT) with diameter 1.4 nm was supplied by Carbolex Inc. USA. ODCB (Loba Chemicals, India) was used as solvent to disperse these fillers properly. TPU was supplied by Bayer Inc. Germany (Texin 945 U, ether type, extrusion grade) and N,N'-Di methyl formamide (DMF, Merck Chemicals, India) was used to dissolve it.

Methods

The objective of present work is to achieve sufficiently high electrical conductivity. For that a strong conducting network formation is essential which can be achieved by dispersing an optimized concentration of nanofillers. However, at high filler loading, the dispersion gets affected. Considering these, weight percentages of the nanofillers were selected based on our previous studies [13,22-24]. The respective fillers were taken in a specific weight ratio with respect to TPU. G was taken at three different weight percentage (20, 30 and 40 wt%). Similarly, 5 and 10 wt% of CNF were used. CNT and NG were taken as 2 and 10 wt%, respectively.

The liquid exfoliated graphite (EG) was prepared by treating G for extended period of high speed mechanical stirring (2000 rpm for 2 h) and ultrasonic treatment at a frequency of 37 kHz for 1 h in the solvent ODCB.

The nanofiller dispersion in ODCB and TPU polymer solution in DMF, were mixed in 2:1 ratio with continuous stirring for 1 h. In final solution, the weight content of polymer is 15 wt%. Finally, it is coated over the cotton and silk of specific length by dip coating using a fiber/yarn coating machine developed at our lab (Figure 1). In the process, the fiber of certain length is rolled in the coating solution at a uniform speed, squeezed and dried before winding.

The process was repeated four times to get a uniform distribution of coating. The coating is dried at 100 °C and kept at vacuum for 12 h at 50 °C to remove residual solvents. All nanocomposite coated fibers are black in color due to carbon nanofillers. Table 1 gives the abbreviations used in this paper including the uncoated and coated fibers.

Characterizations

The dispersed nanoparticles were imaged at 200 kV in high resolution transmission electron microscopy (HRTEM, Jeol JEM 2100, Japan). Selected area electron diffraction (SAED) pattern were taken on HRTEM for EG and NG to

Figure 1. Fiber/yarn coating set-up used for the study.

Table 1. Sample abbreviate names used in the paper

SI. No.	Sample	Abbreviations
1.	Uncoated	UC
2.	Thermo plastic polyurethane	TPU
3.	Exfoliated graphite	EG
4.	Nano graphite	NG
5.	Carbon nano fiber	CNF
6.	Carbon nano tubes	CNT
7.	Nanocomposite coating with 2 wt% CNT (on weight of TPU)	CNT 2
8.	Nanocomposite coating with 5 wt% CNF	CNF 5
9.	Nanocomposite coating with 10 wt% CNF	CNF 10
10.	Nanocomposite coating with 10 wt% NG	NG 10
11.	Nanocomposite coating with 20 wt% EG	EG 20
12.	Nanocomposite coating with 30 wt% EG	EG 30
13.	Nanocomposite coating with 40 wt% EG	EG 40

assess extent of exfoliation. The coated cotton and silk fibers were observed under optical microscope (LEICA DM750P microscope with DFC295 LEICA Camera, Germany) and their diameters were measured at 10 different places. From that, apparent densities (ρ_{app}) (considering fibers as cylindrical) were calculated to find the void fractions for uncoated and coated fibers. Void fractions were calculated as $(1-\rho_{app}/\rho_{theo})$; where ρ_{theo} is literature reported fiber densities. The nature of bonds and the organic compounds present in the samples were analyzed using FT-IR from Bruker Optik GmbH, Germany. The resistance of the fibers was measured using a computer controlled digital multimeter (GW Instek GDM8246, Goodwill Inc., Taiwan) with alligator clip type test lead. The contact resistance of the leads is approximately 1 Ω. The impedance of the fibers was calculated using Nvis 9304 LCR meter with alligator clip type test lead. For Current-voltage (IV) characteristics, Auto lab electrochemical workstation was used to know the linear relationship between the current and voltage. All the measurements were carried out at laboratory condition of 28 °C and 65 % relative humidity.

Results and Discussion

Dispersed Nanoparticles in HRTEM

Figure 2 shows the dispersed carbon nanoparticles under HRTEM. The liquid exfoliated graphite (EG) has higher flake thickness (Figure 2(a)) than the NG (Figure 2(b)). The SAED patterns shown as insert in Figure 2(a) and (b) confirm more graphene layers for EG as compared to NG. Pure graphite has its multilayered stacked structure without any preferred crystalline orientation which results in continuous ring type SAED pattern. The SAED image of EG gave bright dotted ring like pattern confirming exfoliation of graphite and reduction in layer thickness, evident by transformation from un-oriented continuous ring to dotted rings (Figure 2(a) insert). The d-spacing value of the lattice was calculated using Diffpack software and matched with the standard JCPDS value of hexagonal graphite system (JCPDS-Pdf No:751621). The corresponding d-spacing values of NG in Figure 2(b) (insert) were also confirmed using the Diffpack software. After exfoliation in solvent, very few layers (2-3) were observed for NG as evident from well defined hexagonal spots. However, the size of the flake is higher in case of EG which is prefential for building good conducting network in polymer matrix. From Figure 2(c) and (d), it is evident that the CNT and CNF are also got dispersed nicely in the matrix. Hence, all these dispersed nanofillers are potential to form a continuous conducting network in the polymer matrix.

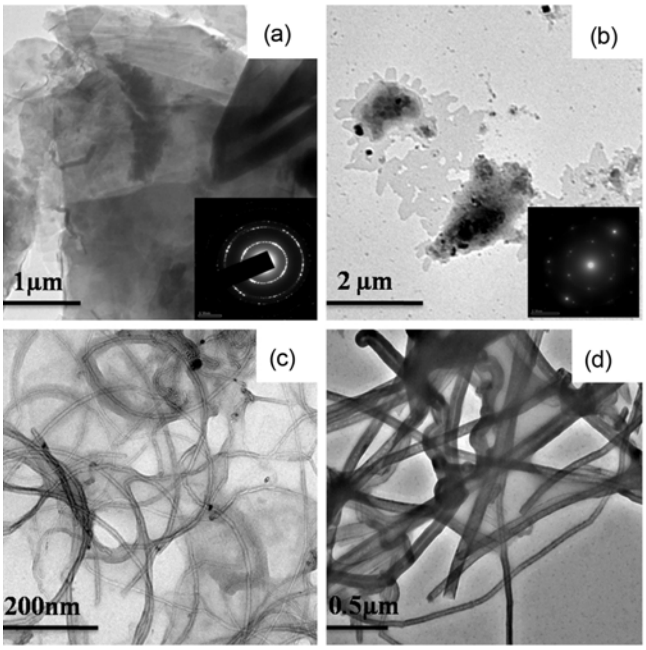

Figure 2. TEM images of (a) EG 20 (with SAED pattern), (b) NG 10 (with SAED pattern), (c) CNT 2, and (d) CNF 5.

Coated Fiber Diameter and Coating Add-on

Figure 3 shows optical images of cotton and silk fibers. The diameter of cotton yarn was reduced after coating. Cotton yarn has sponge like structure with lots of air gaps. The measured porosity or void was ~86.5 % in case of cotton yarn. During coating, compactness of the cotton yarn was increased as the coating solution was squeezed over the cotton yarn to make them adhere to the surface. The squeezing process resulted in penetration of the coating solution from surface to yarn pores. Despite repeated coating, the final void was ~12 % for coated cotton yarns. The air gap in uncoated silk fiber was less as it is a continuous filament (calculated as ~15 %). The diameter of silk gets increased by coating as

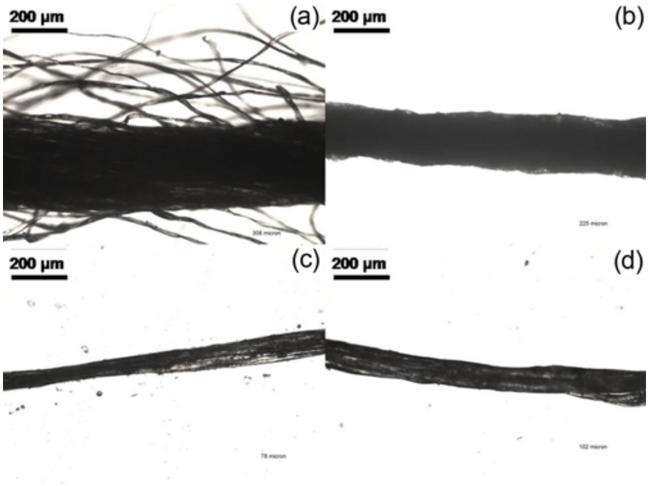

Figure 3. Optical images of (a) uncoated cotton yarn, (b) TPU coated cotton yarn, (c) uncoated silk fiber, and (d) TPU coated silk fiber.

Table 2. Diameter and add-on of cotton and silk coated fibers

Sample name	Cotton diameter (μm) (Mean±S.E.)	Add on (g) per gram of cotton	Silk diameter (μm) (Mean±S.E.)	Add on (g) per gram of silk
UC	310±2	-	78±2	-
TPU	225±5	5.0	110±8	5.0
EG 20	230±1	9.0	110±7	7.3
EG 30	210±3	9.3	90±1	7.0
EG 40	220±8	8.7	90±2	7.0
NG 10	260±8	9.0	130±1	7.0
CNT 2	290±2	11.0	110±1	12.0
CNF 5	270±8	8.3	110±7	10.0
CNF 10	250±7	7.7	90±3	9.3

there is little access of the coating solution inside the fiber. The apparent densities of coated silk fibers were found to be almost similar to the theoretically calculated densities; hence the void is very less for coated silk fibers. Table 2 describes the diameter and add-on per gram of both the fibers. The add-on increased for nanocomposite coatings. This may be due to higher solid content in the coating solutions with nanoparticles and enhanced adhesion.

FTIR Analysis

FTIR curves of TPU and nanocomposites are shown in Figure 4. The peak at 1200 cm^{-1} shows the cyanide in the TPU polymer overlapping aliphatic amine peak. The peak around 1500 cm^{-1} appears as a result of carbon-carbon stretching in the ring or in the fillers. The peaks in 1700 cm^{-1} confirm the presence of ester group (C=O stretch) in the polymer. An additional peak is seen all samples except pure TPU in the range of 2330 cm^{-1}. The peak indicates the presence of carbon dioxide (CO_2) in the compound. The other two peaks at the range of 2900 and 3300 cm^{-1} is due to the bonding of hydrogen with carbon and nitrogen. As the samples were air dried at room temperature, a small amount of solvent ODCB was present in the samples. For this, the IR peak around 750-800 cm^{-1} may be attributed to the presence of alkyl halide (carbon chloride bond) or the stretching of carbon hydrogen bond (aromatic benzene ring) due to ODCB. In a nut shell, the FTIR results confirm the presence of the polymer, the filler and traces of solvent.

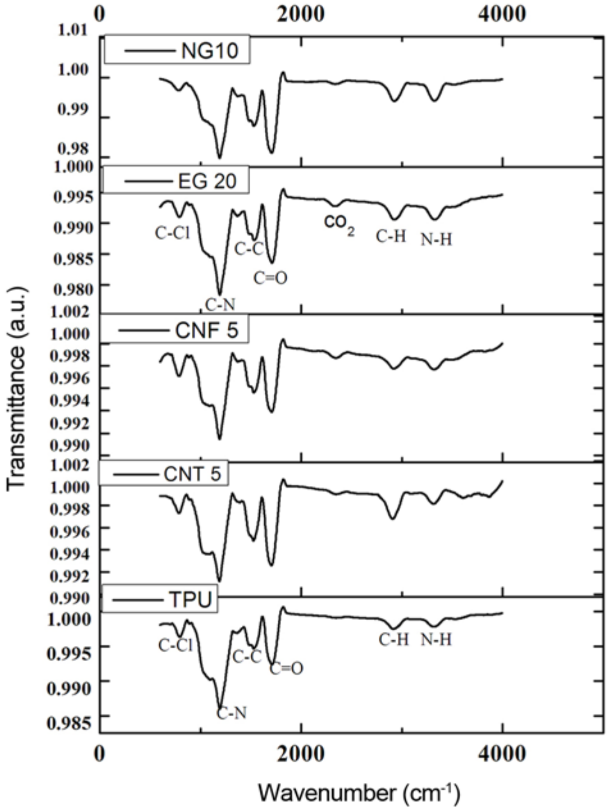

Figure 4. FTIR curves of pure TPU and nanocomposites.

Conductivity of Nanocomposite Coated Fibers

The resistance was measured at test lengths from 0.5 cm to 5.0 cm. Figure 5 shows the resistance of nanocomposite coated fibers per unit length. For both the cotton and silk fibers, NG based coatings show very high resistance as compared to other coated samples. The conducting network formation inside the polymer matrix is poor in case of NG based coating as it has low aspect ratio than other nanofillers. Among all nanofillers, CNT and CNF show very good result at filler loading of 2 wt% (for CNT) and 5 wt%, 10 wt% (for CNF). Considering the resistance of pure cotton and silk (in the order of 10^9 ohm or more), the improvement in electrical conductivity of the nanocomposite coated fibers is quite significant. 10 wt% CNF dispersed nanocomposite coated fiber shows a resistance of less than 100 kΩ per cm for both

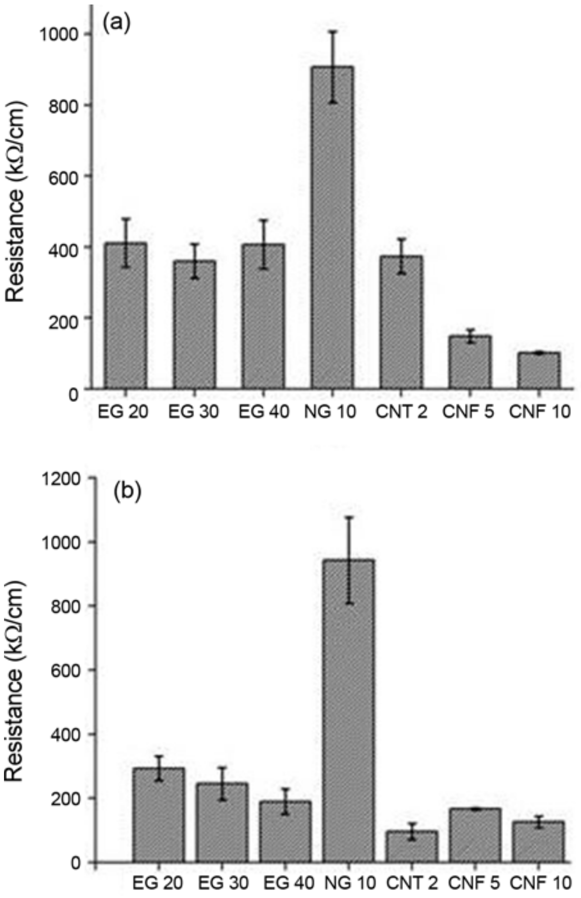

Figure 5. Resistance with various fillers; (a) cotton and (b) silk.

Table 3. Conductivity (with S. E.) of cotton and silk coated yarn

Sl. No	Sample name	Conductivity cotton (S/m)	Conductivity silk (S/m)
1.	EG 20	0.6±0.09	3.7±0.5
2.	EG 30	0.8±0.10	6.4±0.6
3.	EG 40	0.6±0.10	8.3±0.6
4.	NG 10	0.2±0.02	0.9±0.1
5.	CNT 2	0.4±0.05	11.0±0.4
6.	CNF 5	1.2±0.14	6.3±0.1
7.	CNF 10	2.0±0.07	12.5±0.6

cotton and silk. For silk, CNT gives lowest resistance value because of high add-on as compared to CNF (Table 2). The liquid exfoliated graphite (EG) does not show much improvement among different weight fractions in case of cotton. However, for silk it shows steady decrease in resistance with particle loading.

The diameters as well as the cross-sections of the coated yarns are different among all samples; hence the conductivity (S/m) value reflects more normalized data for comparison between the samples. Again, bulk conductivity measurement is more realistic than the surface one as the coating polymer penetrates inside the air gaps of the multi-filaments. Table 3 shows the bulk conductivities of the coated fibers. Results indicate that nanocomposite coated silk filaments have more conductivity than coated cotton. For cotton, electrical conductivities of less than 1 S/m were observed for all nanocomposite coatings except CNF based coatings. The large

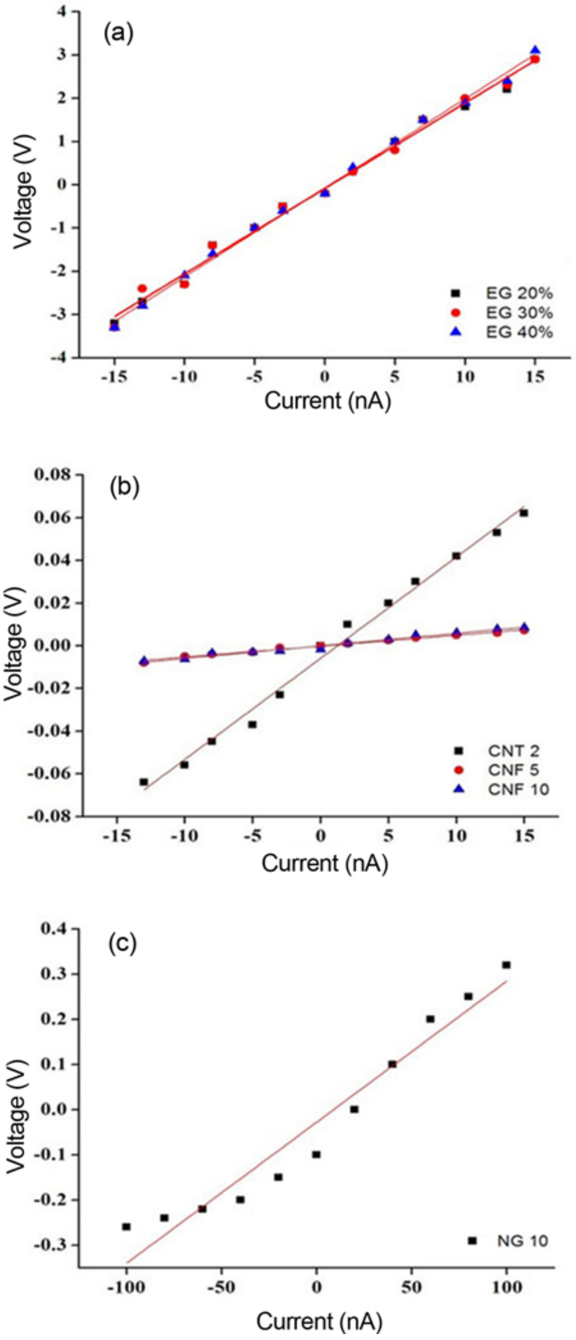

Figure 6. Current-voltage (IV) curve of nanocomposite coated cotton (a) coated with EG 20, EG 30 and EG 40, (b) coated with CNT 2, CNT 5 and CNF 10, and (c) coated with NG 10.

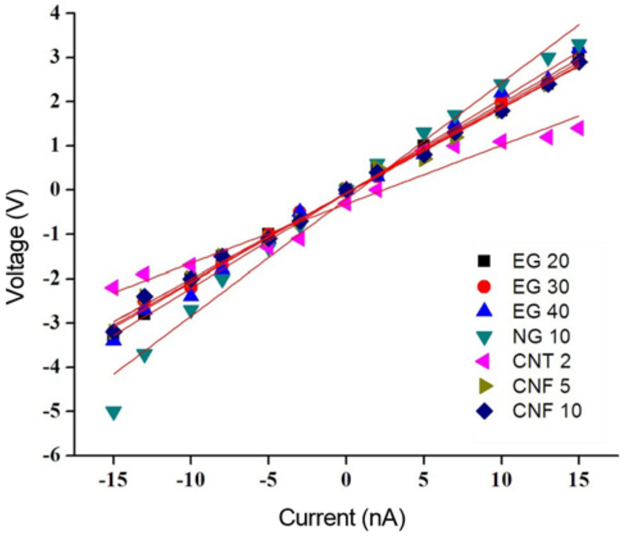

Figure 7. Current-voltage (IV) curve of nanocomposite coated silk fibers.

amount of voids in the cotton yarn resulted in loss in continuity for nanocomposite conducting coatings. For silk, the structure is more compact and thus the coating continuity is maintained. The add-on is also somewhat higher in case of silk which also has contributed in the enhanced electrical conductivity. All silk based nanocomposite coated fibers show good conductivity up to 12.5 S/m except NG based coating which can be attributed to its low aspect ratio. Both 2 wt% CNT and 10 wt% CNF coated silk fibers show conductivity of more than 10 S/m. The conductivity of liquid exfoliated graphite based silk coatings was also very high which signifies its potential for nanocomposite coating on silk. However, the higher variations in electrical conductivity for coated silk fibers emphasize the need of more process control.

Current-voltage (IV) Curve for Nanocomposite Coated Fibers

Figure 6 shows current-voltage (IV) characteristics of the nanocomposite coated cotton. NG based coating shows large deviation from linearity. Except that, other nanocomposite coatings show linear change of voltage with current which is important for successful applications as sensor or transmitter.

Figure 7 shows IV characteristics of nanocomposite coated silk fibers where EG and CNF shows linear nature. Though CNT has highest conductivity, it does not show linearity. Hence, CNF and EG coatings are more promising for such applications.

Impedance Analysis of Nanocomposite Coated Fibers

The impedance of different coated fibers was measured at different test lengths up to 5 cm and at different frequencies (100 Hz, 120 Hz and 1 kHz). The results as per cm length were plotted in Figure 8. The impedance was decreased with frequency for all samples. The dielectric core of coated fibers resulted in such frequency dependence. However, CNT and CNF coated nanocomposite fibers showed very low impedance due to their higher electrical conductivities. NG based nanocomposite coated fibers were found to have highest impedance due to its low aspect ratio as compared to other nanofillers used.

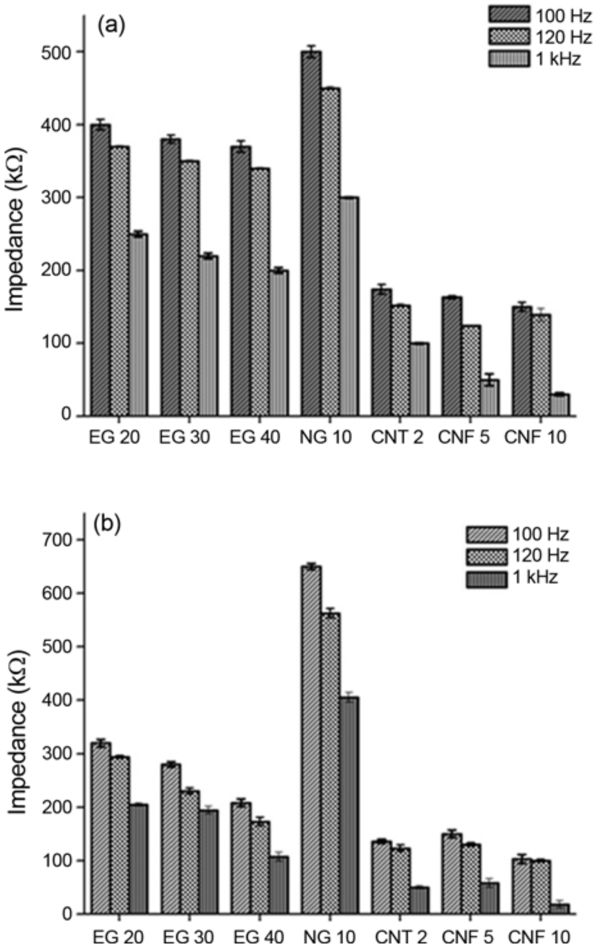

Figure 8. Impedance per cm length of nanocomposite coated; (a) cotton and (b) silk fibers.

Conclusion

Carbon based nanofillers have successfully dispersed in TPU polymer matrix for nanocomposite coating on cotton yarn and silk filaments. Results show that CNF and CNT have strong potential to impart stable conductivity on such fibers. The improvements were quite significant. The resistance goes down to less than 100 kΩ for both cotton and silk fibers when they were coated with 10 wt% CNF. The electrical conductivity of 10 wt% CNF based nanocomposite coated cotton yarn showed 2 S/m; while for silk filament it reached more than 12 S/m. Very good conductivity of 11 S/m was also observed for 2 wt% CNT dispersed nanocomposite coated silk fiber. The large void fraction in coated cotton yarn (~12 %) is attributed for such difference in electrical conductivity. Hence, continuous filament fibers are more suitable to develop such nanocomposite coated fibers than staple yarns.

Both the resistance and impedance tests were carried out at different test lengths up to 5 cm and converted into per cm value. The variations in test results were not very high, hence, it can be concluded that the conducting network formation by the nanofillers are continuous and uniformity in electrical conductivity is achieved through this coatings. This conclusion is more justified for CNT and CNF based nanocomposite coatings. Liquid exfoliated graphite shows more potential as a nanocomposite coating on silk fiber; rather than on cotton yarn. The exfoliation and coating process may need to be improved in future. The silk filaments are smooth and hence maintaining the uniformity over a large length is a processing challenge. The uniform adhesion of nanocomposite coating on such substrates would be a subject of future research.

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