The Use of Carbon Nanotubes in Textile Printing

Izabella Krucińska, Ewa Skrzetuska, Wiesława Urbaniak-Domagała

Department of Fibre Physics and Textile Metrology, Center of Advanced Technologies of Human Friendly Textiles, Technical University of Lodz, Lodz, Poland

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ABSTRACT: The characteristic properties of carbon nanotubes (CNTs), particularly their heat conduction, electrical conductivity, high modulus of elasticity, high strength, and resistance to chemicals, have resulted in widespread application of CNTs in nanotechnologies. In this study, CNTs were used to impart specific functionality to textiles by printing techniques. To this aim, modified commercial aqueous dispersions of multiwalled CNTs from Nanocyl® were used for preparing special compositions as paste for printing by conventional techniques (screen printing) and as inks for ink-jet printing to bestow the fabric antistatic and antibacterial properties. Taking into account the importance of the dispersion level of CNT in the printing composition from the point of view of antistatic properties, the quality of the CNT dispersion was assessed on the basis of particle size distribution by means of a DLS PSS Nicomp device. Printings were done on two types of woven fabrics: 100% cotton and 30/70% cotton/polyester blend. The CNTs used in printing were found to impart antistatic and antibacterial properties to the printed fabrics. These imparted properties were resistant to repeated washing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 483–490, 2011

Key words: additives; nanotechnology; dispersions; crosslinking; surfaces

INTRODUCTION

For a long time, printing has been used as a technique for decorating textiles with ornamental patterns. Textile printing methods have recently been developed to provide textiles with additional specific functions,[1] as by imparting sensor properties,[2,3] electrical conductivity,[4–7] organic transistor capabilities,[8] rubbery conductor properties,[8] or antibacterial properties.[9] This functionality can be accomplished by depositing a functionalized substance, in the form of aqueous nanoink dispersion, with the use of digital or conventional printing methods.

Carbon nanotubes (CNTs), discovered in 1991, are constructed from carbon supermolecular structures in the form of cylinders from coiled grafene—a single-atom graphite layer. The grafene layers can roll into cylindrical mono- or multiwalled hollow objects. Single-walled nanotubes have a 1.2- to 2.0-nm diameter; their length can be a million-fold greater. In contrast, multiwalled nanotubes have a diameter over 25 nm; their length is ~ 1 μm or more.

Since CNTs were discovered in 1991 by Sumio Iijima from NEC Fundamental Research Laboratories at Tsukuba in Japan, more and more applications have been developed not only in electric circuits and sensors but also in optics and microbiology.[2–7,10–12]

Nanotubes are one-dimensional quantum conduits with extreme tensile strength, unique electric properties, and excellent heat conductivity. As a consequence of these properties, nanotubes have widespread application in nanotechnology, electronics, optics, and other fields.[13,14]

CNTs are one of the most durable materials known. The tensile strength of multilayer nanotubes is 63 GPa, much higher than that of hardened steel (1.2 GPa). CNTs have a low density, only 1.3–1.4 g/cm^3.[15–17]

The high tensile strength paired with the low density makes using CNTs highly desirable.

Researchers at the University of Tokyo have moved a step closer to displays and simple computers that can be worn on a sleeve or wrapped around a couch. Furthermore, they have opened up the possibility of printing such devices, which would reduce the cost to the consumer.

Takao Someya, an electrical-engineering professor, and his colleagues make a stretchable display by connecting organic light-emitting diodes and organic transistors with a new rubbery conductor. The researchers can spread the display over a curved surface without affecting performance. The display can also be folded in half or crumpled without sustaining damage.[8]

The electrical properties of nanotubes have been exploited by Kordas et al.[1] to create conductive print on film and paper by means of an ink-jet printing

Correspondence to: E. Skrzetuska (ewa.skrzetuska@p.lodz.pl).
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TABLE I
Characteristic of Woven Fabrics

Type of substrate	Percent composition (%)	Weave	Surface mass (g/m^2)	Thickness (mm)	Seeming density (kg/m^3)
Cotton	100	Twill	206.3	0.51	382.0
Cotton/PET	30/70	Twill	205.5	0.52	387.7

technique. In that study, the ink consisted of an aqueous dispersion of nanotubes without bonding agents.

No data are currently available concerning the toxicological effects of nanotubes on surfaces. Thus, the authors designed aqueous dispersions using auxiliary agents. The auxiliary agents used were compounds of aliphatic urethane acrylate, photoinitiator, dodecylbenzenesulfonic acid (DBSA), and sodium lauryl sulfate (SLS). For conventional printing (screen printing), the inks were thickened by adding the crosslinking mixture. This approach provided a means of durably combining nanotubes with the textile substrate.

Notably, current CNTs do not demonstrate antimicrobial properties, but the additional substances carried out to CNT water dispersion as DBSA and SLS show, according to references,[18,19] these kinds of properties.

The goal of this study was to prepare CNT-based multifunctional inks to impart functional antistatic and antibacterial properties to printed textiles. The design goals were further specified as follows:

1. The ink should have antibacterial properties and proper electrical resistivity.
2. The ink should print onto two types of woven fabrics: 100% cotton and 30/70% cotton/polyester blend.
3. The ink should be based upon aqueous nanotube dispersions with auxiliary agents.
4. The ink should be usable in both conventional (screen printing) and modern (jet-printing) techniques.
5. The antistatic and antimicrobial properties of the printed textile should be sustained despite repeated washing.

The developed and tested nanotube inks were found to satisfy these design goals.

MATERIALS AND METHODS

Materials

The aqueous dispersion of CNTs under the trade name AquaCyl (AQ0101) from Nanocyl was used. This dispersion contains 0.5–1.5% MWCNT of the Nanocyl®7000 series. AquaCyl AQ0101 has 57 mN/m surface tension, 36 cP viscosity, and pH 7. These parameters were determined at a temperature of 25°C. The dispersion additionally contained 0.1–3% dispersing agent.

Additional chemicals were added: Ebecryl 2002 (aliphatic urethane acrylate from Cytec, water compatible, UV curable system); Esacure DP250 (water dispersion of photoinitiators from Lamberti SPA); DBSA ($C_{12}H_{25}C_6H_4SO_3H$) solution 70 wt % in isopropanol (analytically pure from Sigma Aldrich); and SLS ($CH_3(CH_2)_{11}OSO_3Na$, analytically pure from Sigma Aldrich).

Printing was carried out on two types of woven fabrics: 100% cotton and 30%/70% cotton/polyester blend (Table I).

Ink preparation and printing procedures

Based on the antibacterial properties of sulfur,[20,21] two substances were selected: DBSA and SLS. Ink was prepared by addition of 10% (by volume) of DBSA or SLS into AquaCyl. To remove any agglomerates that formed, the ink was filtered under vacuum with a membrane filter whose pore size was 0.45 μm.

The obtained disperse was used to print woven fabrics by a conventional technique (screen printing) with the use of printing pastes and by the digital method (jet printing) at the Technical University of Lodz.

The prepared inks, in combination with a compound of photoinitiator and aliphatic urethane acrylate, were deposited on cotton and cotton/polyester woven fabrics. The dispersions were combined with the crosslinking compound based upon the expected form of printing.

The crosslinking mixture was prepared with 10% Ebecryl 2002 and 0.7% Esacure DP 250 in water (in the case of ink) or AquaCyl (in the case of paste). The mixture was processed for 30 min with a magnetic agitator.

For the ink, the crosslinking mixture was prepared, filtered, and applied (jet printed) onto the woven fabric surface.

For the paste, the crosslinking mixture was prepared, AquaCyl was added, and the final mixture was applied (screen printed) onto the woven fabric after mixing for 30 min by magnetic agitation.

The experimental fabric was rectangular (A4 format). The entire surface (area: 0.05 m^2) was printed.

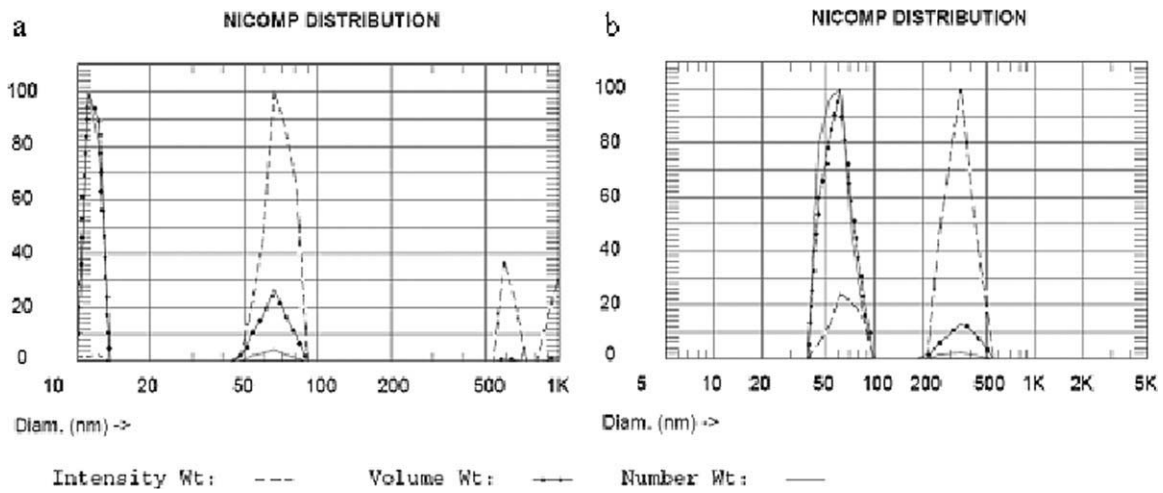

Figure 1 AquaCyl particle size distribution (a) before filtration and (b) after filtration.

Each fabric sample was covered by a constant amount of applied ink, about 15 mL.

Next, the printed inks were crosslinked according to conditions determined in pilot studies. Optimization of the crosslinking process was achieved by total tying crosslinking mixture. Most important was to avoid destroying the fabrics, as can happen under application of UV radiation. The obtained prints were crosslinked by means of UV-C 335 radiation with a 2100-W UV lamp (Philips) with a working length of 195 mm. The lamp was placed 15 cm above the sample, and the sample was irradiated for 5.4 s. The radiation dose was 3.5 J.

Dispersion measurements

The quality of the obtained dispersion was tested by measurement of light scattering using a DLS PS Nicomp device. Volumetric distribution of the size of the functionalizing substance was assumed as the basic parameter. The physical properties of dispersion, such as surface tension and viscosity, were also tested.

Viscosity was measured using the Ubbhelohde viscosimeter with constant $K = 0.1075$.

The surface tension was tested with the Radian DCA 322-Thermo Scientific Fisher tensiometer, with static and dynamic measurements of the surface tension taken by means of the "ring Du Nouy'a method" in stable liquid temperature, according to the EN 14370:2005 standard.

Quality and functionality assessment of printings

The assessment of obtained textile prints was performed using a JSM-5200LV electron scanning microscope from JEOL, a detector of secondary electrons and a reflecting optical microscope from PZO.

The electrical properties of the printed fabrics were estimated using measures of surface resistance. The samples were tested before printing by the direct electrometric method using a 610C electrometer (Keithley) and a 4218 DC supply device (RFT) with voltage range 0–3000 V and a high stability and low noise factor. The electrode system with the test sample was placed on a Faraday's electrostatic

TABLE II
Characteristics of AquaCyl Particle Size Distribution

	AquaCyl					
	Before filtration			After filtration		
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
Intensity weighting						
Mean diam. (nm)	11.3	69.1	617.0	66.4	344.4	0.0
Percent (%)	1.6	71.7	26.7	19.4	80.6	0.0
Volume weighting						
Mean diam. (nm)	11.7	66.1	619.0	60.1	353.8	0.0
Percent (%)	78.3	21.0	0.7	88.6	11.4	0.0
Number weighting						
Mean diam. (nm)	11.6	65.1	617.0	58.0	340.8	0.0
Percent (%)	95.6	4.3	0.1	97.8	2.2	0.0

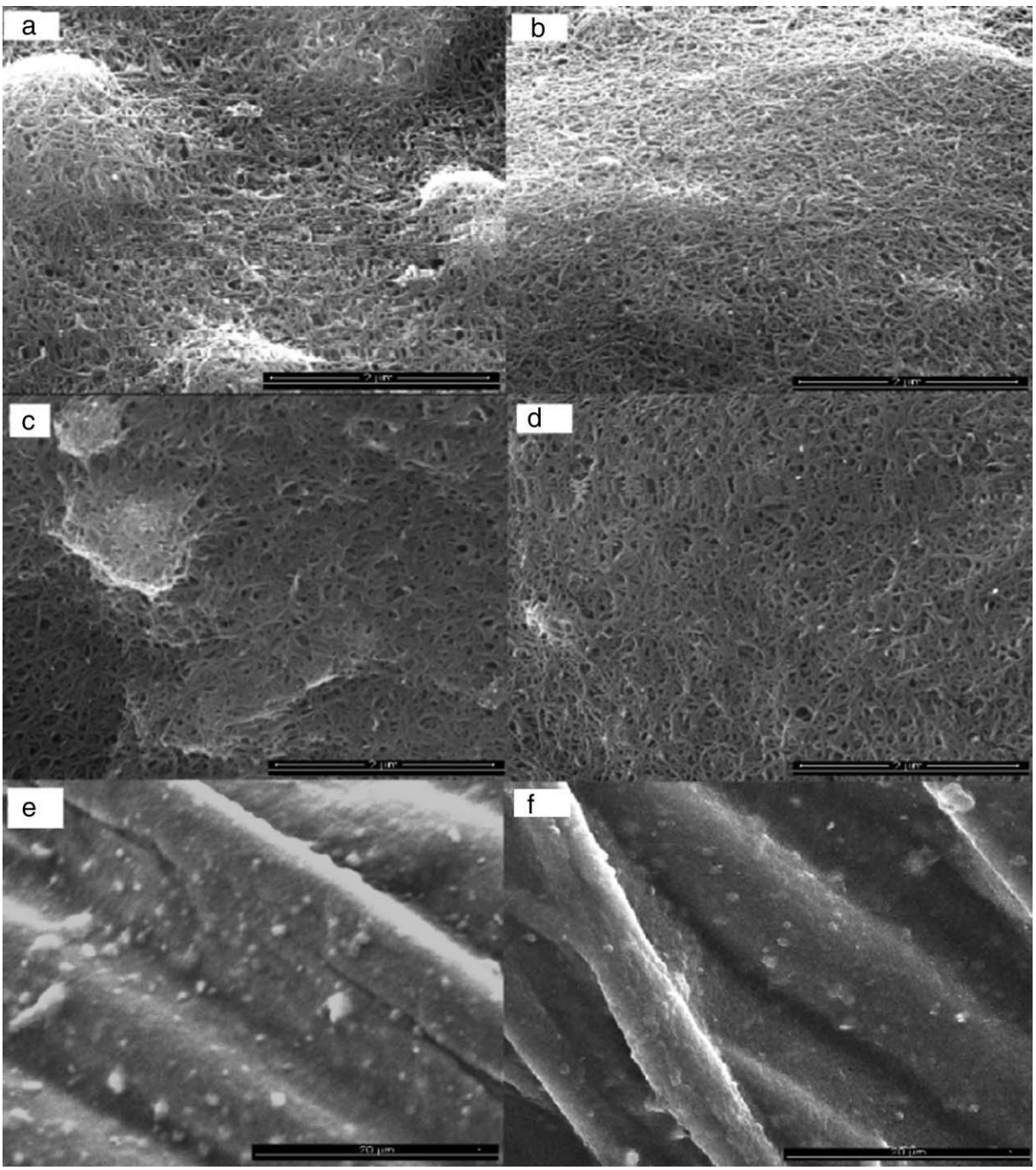

Figure 2 MWCNT deposited on textile substrates (a, c, e) before and (b, d, f) after filtration.

screen. The printed samples were tested by the direct method using an M-4660A multimeter (Metex) and a 5121 DC supply unit (Unitra) with a voltage range up to 40 V. The electrical properties of the printed fabrics were tested according to standard EN 1149-1 : 2006. Samples were conditioned and tested under constant conditions: $T = 23°C$ and RH = 25%.

The antibacterial activity of printed fabrics was tested on plates with agar culture, according to standard EN ISO 20645:2006. The bacteria were evaluated within the zone of agar-sample contact to

TABLE III
Physical Properties of Inks

Ink composition	Surface tension (mN/m)	Specific viscosity (mPa)
Aquacyl	57.6	14.2
AquaCyl after filtration	42.6	7.8
AquaCyl after filtration, with DBSA added	33.8	6.2
AquaCyl after filtration, with SLS added	34.6	8.4

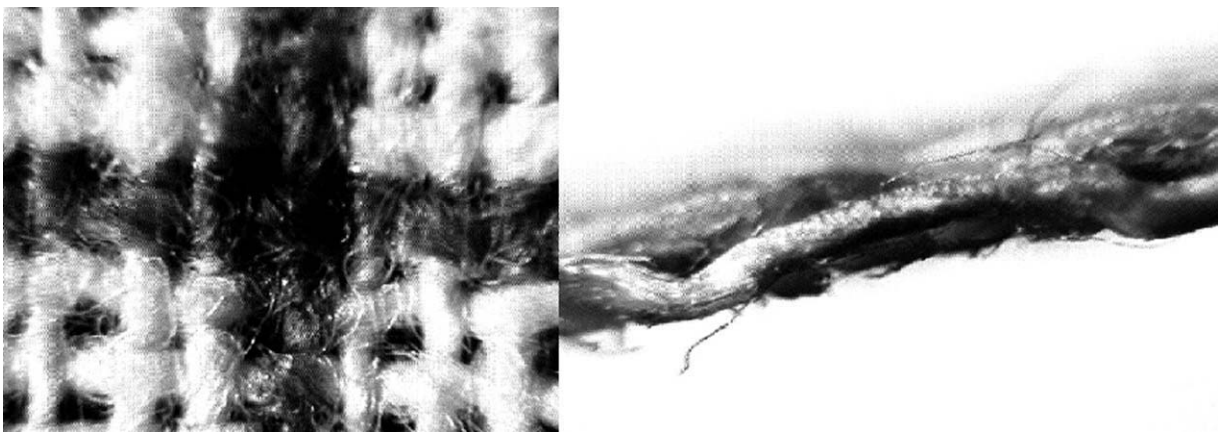

Figure 3 Electroconductive path of AquaCyl on a cotton fabric with a plain weave.

determine the growth retardation zones around samples. The retardation zone width, i.e., the zone without bacteria near the working sample edge, was calculated using the following formula:

$$H = \frac{D - d}{2},$$

where H is the retardation zone width in mm, D is the total diameter of the working sample and retardation zone width in mm, and d is the diameter of the working sample in mm. Next, the samples were placed in a microscope with 20× magnification and lower lighting to assess the bacterial growth within the contact zone on the back side of sample.

The durability of electric resistivity and antibacterial effects was assessed after repeated washing (25 cycles). The washing process was carried out according to standard ISO 105-C06:1996/Apr 1, 1999.

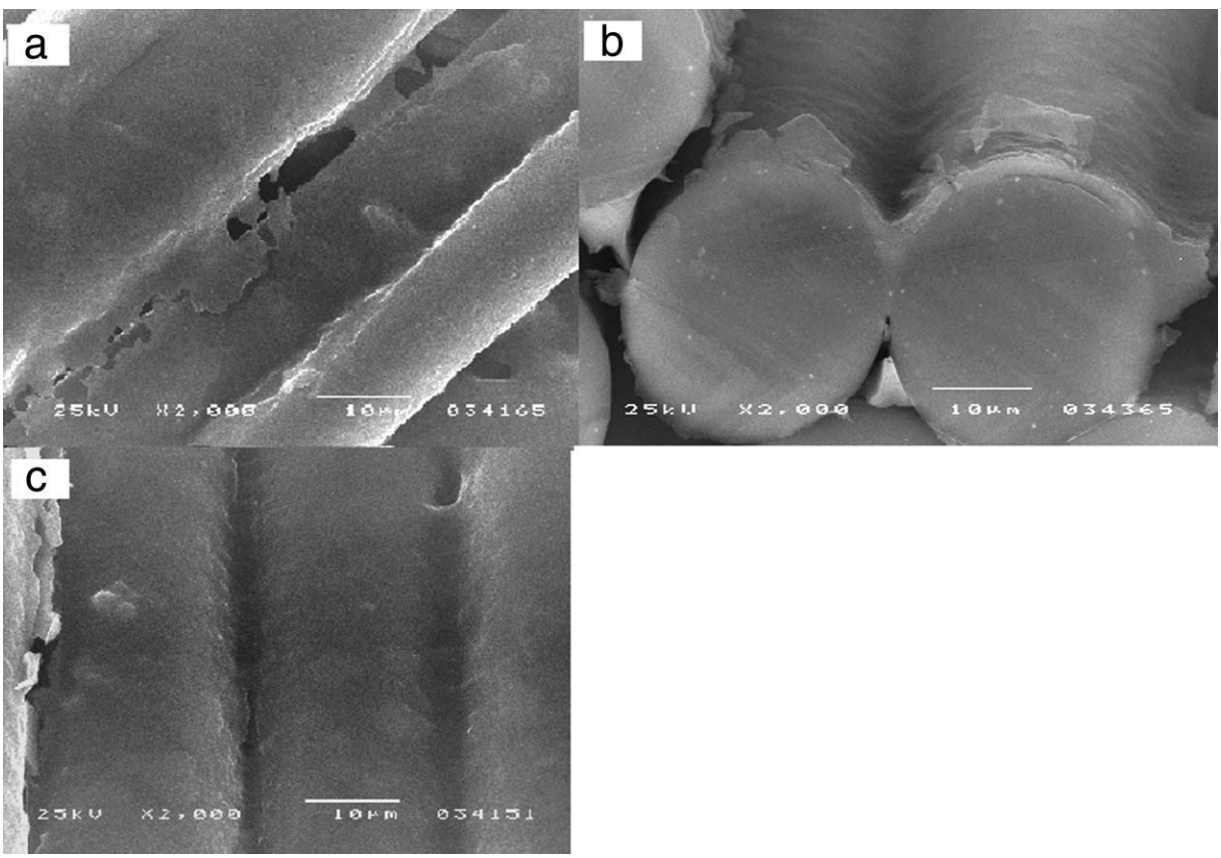

Figure 4 SEM pictures of the AquaCyl deposited with the addition of: (a) crosslinking compound, (b) crosslinking compound and DBSA, and (c) crosslinking compound and SLS.

TABLE IV
Test Results of Surface Electrical Resistivity of the Printed Fabrics

Ink composition	Fabric type	Surface electrical resistivity (Ω) (RH = 25%, t = 23°C)	
		Before washing	After repeated washing
AquaCyl	Cotton/PET	280	17103
AquaCyl	Cotton	200	16818
Aquacyl + crosslinking compound	Cotton/PET	800	856
Aquacyl + crosslinking compound	Cotton	682	712
Aquacyl + crosslinking compound + DBSA	Cotton/PET	1818	1890
Aquacyl + crosslinking compound + DBSA	Cotton	1666	1689
Aquacyl + crosslinking compound + SLS	Cotton/PET	181	321
Aquacyl + crosslinking compound + SLS	Cotton	160	263

RESULTS AND DISCUSSION

Test results of functional inks

Particle size distribution of inks

The usefulness of the AquaCyl dispersion and the modified AquaCyl for jet printing was assessed based upon their distribution of particle size, surface tension, and viscosity.

The filtration of the AquaCyl aqueous dispersion eliminated agglomerates larger than 500 nm. This size elimination has been established for inks to be suitable for trouble-free use in jet printing.

Figure 1(a) and Table II show the test results of the MWCNT particle size distribution in the aqueous dispersion before filtration. These results indicate a susceptibility of AquaCyl to agglomeration; average agglomerate size ranged from 66 to 620 nm. In the ink prepared for jet printing, this fraction of agglomerates was removed. Figure 1(b) shows a diagram of particle size distribution in the filtered aqueous dispersion of AquaCyl.

The diagram has a characteristic Gaussian-like distribution with a median line. After filtration, the remaining agglomerates had an average size reduced to 350 nm, and thus the accepted size constraint was satisfied. After introduction of modifying additions (DBSA or SLS) to the dispersion of AquaCyl, the distribution of particle sizes was similar to that of commercial AquaCyl, and thus the inks required filtration.

To observe the agglomeration process, scanning electron microscopy (SEM) was used. Figure 2, a SEM image, shows MWCNTs deposited on textile substrates before and after filtration.

On the basis of these tests, filtration of dispersion was confirmed to be necessary.

Physical properties of functional inks

The physical properties of the produced inks were assessed, and the functionalities of the prints on textile fabrics were examined.

The inks were used in both conventional and modern printing techniques. For screen printing, the inks required thickening by addition of the crosslinking mixture. For jet printing, the goal was to prepare inks with appropriate properties based on literature[4,7,8] and tests of commercial ink:

- surface tension of 28.5–35 mN/m and
- specific viscosity of 4.5–15 mPa.

The test results of surface tension and specific viscosity are listed in Table III.

Based on the test results, the physical properties of the prepared inks fulfill the conditions of suitability for jet printing.

Test results of functional ink penetration into textiles

Further assessments evaluated how ink penetrated the textiles. The goal was to obtain durable prints with minimal ink penetration into the textiles to minimize ink consumption.

To observe the penetration effects, an optical microscope was used. Figure 3 shows on the textile substrate the traces of ink prepared from AquaCyl and DBSA and the compound of Ebecryl 2002 and Esacure DP 250.

The presented top view and cross section of the fabric illustrate the ink path, showing a width of about 3 mm. The ink remained on the substrate surface with no penetration into the fabric structure. This indicates proper physical properties of the dispersion and fulfillment of the target goals.

To confirm the optical observations and to quantify the behavior of the inks on the fabric substrates, the obtained prints were also observed under an electron microscope. This examination also assessed the effect of the type of additive (DBSA or SLS) on the quality of the prints obtained. Figure 4 shows the electron microscope pictures of AquaCyl, which

TABLE V
Results of Microbiological Tests on Printed Fabrics

Ink composition	Fabric type	Bacteria retardation zone (mm)			
		E. coli (Gram−)		*B. subtilis* (Gram+)	
		Before washing	After repeated washing	Before washing	After repeated washing
AquaCyl	Cotton/PET	0.0	0.0	0.0	0.0
AquaCyl	Cotton	0.0	0.0	0.0	0.0
Aquacyl + crosslinking compound	Cotton/PET	0.0	0.0	0.0	0.0
Aquacyl + crosslinking compound	Cotton	0.0	0.0	0.0	0.0
Aquacyl + crosslinking compound + DBSA	Cotton/PET	0.5	0.0	6.5	5.0
Aquacyl + crosslinking compound + DBSA	Cotton	0.5	0.5	7.0	4.5
Aquacyl + crosslinking compound + SLS	Cotton/PET	0.0	0.0	4.0	3.0
Aquacyl + crosslinking compound + SLS	Cotton	0.0	0.0	3.5	3.0

contained the compound of aliphatic urethane acrylate and photoinitiator. The first sample contains AquaCyl and the crosslinking compound [Fig. 4(a)]; DBSA was added to the second sample [Fig. 4(b)], and SLS was added to the third sample [Fig. 4(c)].

Based on the above SEM pictures, the influence of the additive on the behavior of nanotubes in the composition is uncertain. A membrane formed on the fiber surface as a continuous field; this opens the possibility of quickly increasing the percolation threshold of charge carrier conduction in the electric field if an appropriate density of the ink deposited on the substrate is ensured.

Test results of textile functionality

The goal was to prepare multifunctional inks with antibacterial properties and good electrical resistivity at a level up to 1×10^5 Ω, with these new properties being durable despite repeated washing. Assumptions were made protective clothing electrostatic properties according to standard EN 1149-5:2008. Tables IV and V contain the test results of textile functionality obtained by means of jet printing, on cotton and cotton/PET fabrics, before and after washing process.

The differences in results of investigated properties between cotton and cotton/PET fabrics show that they are dependent on the fibers kind in fabrics. On cotton the ink flow away is bigger than on the cotton/PET fabrics. On cotton the wetting angle of inks investigated is smaller than on the cotton/PET fabrics.

The commercial form of AquaCyl without the additives used by the authors showed no antibacterial properties. Antistatic properties of commercial AquaCyl deteriorated considerably in the washing process.

The inks simultaneously gave textiles both electrostatic and antibacterial properties. Based on the microbiological testing, the inks developed show larger zones of growth retardation for Gram-positive bacteria. In the case of Gram-negative bacteria, inhibition zones were very small. Nonetheless, the lack of increase of the bacteria verifies that the tested woven fabrics had good antibacterial properties.

The results obtained were reproducible, and the imparted properties were resistant to repeated washing.

CONCLUSIONS

A commercial dispersion of CNTs under the trade name AquaCyl was modified and used for printing to impart antistatic and antibacterial properties to the printed textiles. The functionality effects obtained were satisfactorily resistant to repeated washing.

Assessments of particle size distribution of the AquaCyl dispersion indicate that CNTs are susceptible to agglomerate formation. The dispersion contains fractions of agglomerates with sizes of about 12, 66, 617 nm and above 1 μm; therefore, the dispersion was filtered to eliminate agglomerates larger than 500 nm. The use of filtration makes the AquaCyl dispersion usable in jet-printing techniques.

Additives (DBSA, SLS) into the aqueous dispersion exerted a beneficial influence on the inks' antistatic and antibacterial properties. The crosslinking compounds (Ebecryl 2002 and Esacure DP 250) directly increased the dispersion viscosity. By depositing the aqueous dispersion and the crosslinking compound, the desired printing form—paste or ink—was obtained.

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References

1. Kordas, K.; Mustonen, T.; Toth, G.; Jantunen, H.; Lajunen, M.; Soldano, C.; Talapatra, S.; Kar, S.; Vajtai, R.; Ajayan, P. M. Small 2006, 8/9, 1021.
2. Wei, J.; Sun, J. L.; Zhu, J. L.; Wang, K.; Wang, Z.; Luo, J.; Wu, D.; Cao, A. Small 2006, 8/9, 988.

3. Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J. Science 2000, 287, 622.
4. Mościcki, A.; Pietraszuk, B.; Gwiaździński, P. Arcis Micropackaging Days Conference, Gardanne, 2007.
5. Patent PL, 198898 B1, EP 2140742 (A1)/2010, Transparent substrate provided with electroconductive strips.
6. Brunet, O.; Patrice, P.; Elbaz, D.; Binnagot, F., Leriche, Ch.; Calvas, B. In 3rd International IEEE Conference on Polymers and Adhesives in Microelectronic, Montreux, 2003; p 231.
7. Moscicki, A.; Felba, J.; Gwiaździński, P.; Puchalski, M. Conference Polytronic, Tokyo, 2007.
8. Patel, P. Technol Rev 2009, 5, 69.
9. General Catalogue (v.5.03)—Depliant AntiMicrobial 8, Europolveri, http://www.europolveri.it/downloads/ERP_Antimicrobial8UKb.pdf
10. Trans, S. J.; Verschueren, A. R. M.; Dekker, C. Nature 1998, 393, 49.
11. Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. Science 2001, 294, 1317.
12. Wei, J.; Sun, J.; Zhu, J.; Wang, K.; Wang, Z.; Luo, J.; Wu, D.; Cao, A. Small 2006, 8/9, 988.
13. Przygocki, W.; Wlochowicz, A. Fullerene and Carbon Nanotube. Property and Application; WNT: Warsaw, 2004.
14. Huczko, A. Carbon Nanotube—Black Diamond XXI Century; BEL: Warsaw, 2004.
15. Colins, P.; Avouris, P. Sci Am 2000, 6, 283.
16. Huhtala, M.; Kurnonen, A.; Kaski, K. Comput Phys Commun 2002, 1, 146.
17. Min-Feng, Y. Science 2000, 287, 637.
18. Patent WO/2004/060303, Methods and reagents for the enhancement of virus transduction in the bladder epithelium.
19. Patent WO/2005/007101, Compositions and methods for the enhanced up take of therapeutic agents through the bladder epithelium.
20. Julia, T.; Gunther, A. J Exp Med 1947, 85, 531.
21. Gupta, A. K.; Nicol, K. J Drugs Dermatol 2004, 8/9, 73.