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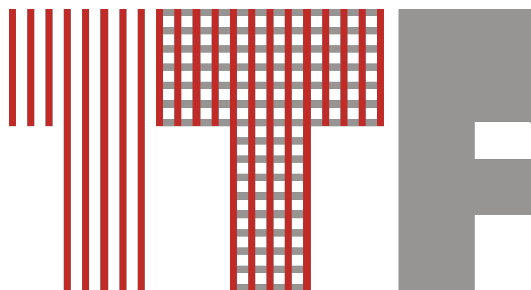
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Enzymatic Modification of Polyamide for Improving the Conductivity of Water-Based Multilayer Nanocoatings

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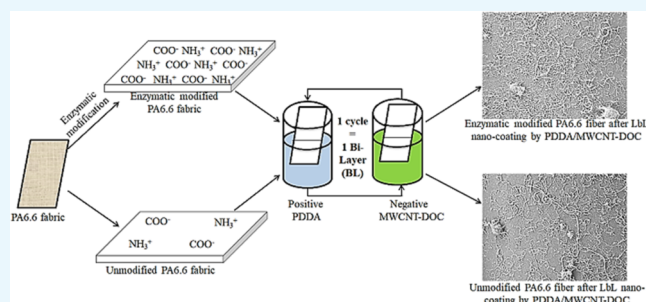
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ABSTRACT: Enzymatic modification, using a protease from *Bacillus licheniformis* (Subtilisin A), was carried out on polyamide 6.6 (PA6.6) fabric to make it more amenable to water-based nanocoatings used to impart electrical conductivity. The modified PA6.6 fibers exhibit a smoother surface, increased hydrophilicity due to more carboxyl and amino groups, and larger ζ -potential relative to unmodified polyamide. With its improved hydrophilicity and surface functionality, the modified textile is better able to accept a water-based nanocoating, composed of multiwalled carbon nanotubes (MWCNT) stabilized by sodium deoxycholate (DOC) and poly(diallyldimethylammonium chloride) (PDDA), deposited via layer-by-layer assembly. Relative to unmodified fabric, the enzymatically modified fibers exhibit lower sheet resistance as a function of PDDA/MWCNT-DOC bilayers deposited. This relatively green technique could be used to impart a variety of useful functionalities to otherwise difficult-to-treat synthetic fibers like polyamide.



INTRODUCTION

Polyamide 6.6 represents one of the most widely used synthetic materials due to its low cost, lightweight, high strength, and very good abrasion, chemical, and creep resistance.^{1,2} These properties allow polyamide to be used in numerous applications, such as seat belts, carpet, upholstery, and clothing,^{1,3} where impact resistance and strength are required. Like most polymers, PA6.6 is electrically insulating and frequently results in accumulation of potentially harmful static charge.⁴ Electrically conductive textiles can be used as electromagnetic interference shielding, antistatic flooring and ceiling materials, radar cross-section reducing protective fabrics for stealth technology, and wearable electrodes for continuous health monitoring.^{5–7}

Carbon nanotubes (CNTs) are among the most frequently exploited nanoparticles for imparting electrical conductivity. Several techniques are known for preparing CNT thin films, such as spray coating, dip coating, spin coating, vacuum filtration, electrophoretic deposition, sputter deposition, chemical vapor deposition, and layer-by-layer (LbL) assembly.^{8–13} LbL assembly is a highly tailorable nanocoating technique, involving alternate exposure of a substrate to

oppositely charged polyelectrolyte solutions or suspensions, giving rise to a multilayer thin film.¹⁴ This simple, inexpensive, and environmentally benign technique, which is carried out at atmospheric pressure and room temperature, uses dilute aqueous solutions. The variety of the different ingredients that can be used for this technique, such as polyelectrolytes, inorganic particles, organic nanomaterials, and renewable macromolecules, makes it possible to create nanocoatings with impressive functionality.^{15,16} LbL assembly has been used to impart a variety of properties, including antimicrobial^{17,18} and antifouling,¹⁹ flame retardant,²⁰ anticorrosion,²¹ gas barrier,²² drug delivery,²³ and electrical conductivity,^{9–13,24–27} on various substrates. Several studies of LbL modification of polyamide fibers have been conducted to impart flame retardancy^{28–32} and sensor activity³³ and to improve the durability of a polyamide reverse osmosis membrane.³⁴

Although LbL assembly is a very simple and promising technique, effective deposition on nylon fibers remains a

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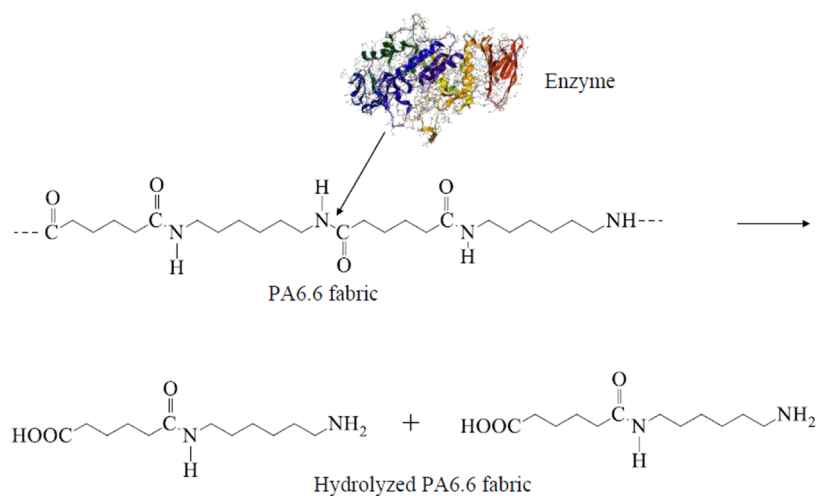


Figure 1. Enzymatic hydrolysis of PA6.6 by protease enzyme.

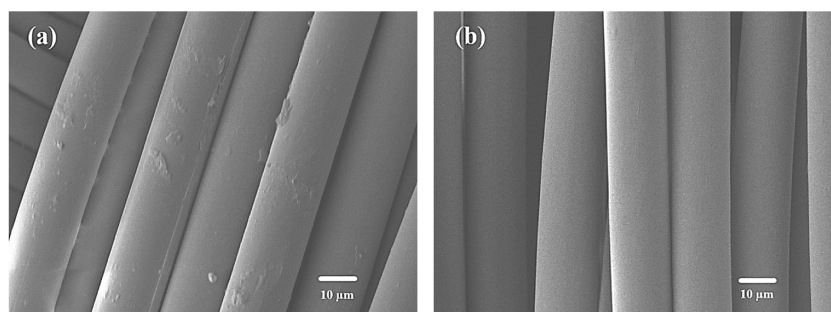


Figure 2. SEM images of (a) unmodified and (b) enzymatically modified PA6.6 fibers.

challenge. The major problem is poor interfacial adhesion between the substrate and the polyelectrolyte solutions/suspensions, which depends on the charge of the polyelectrolytes, pH and ionic strength of the solution, as well as the hydrophilicity and surface charge of the substrate.¹⁵ Polyamide fibers are relatively hydrophobic because they have insufficient functional groups on their surfaces.^{35–38} Several processes have been reported to functionalize nylon by chemical and physical methods.^{3,39} Harsh chemical methods include alkaline or acid hydrolysis, can have a negative environmental impact, and cause damage to the fabric structure.⁴⁰ UV radiation and plasma activation are “clean” methods,^{41,42} but functionalization is uneven and often accompanied by surface damage. Moreover, these techniques require complex machinery that is very expensive. Enzymatic modification of the polyamide surface is another chemical (biochemical) treatment performed under mild, environmentally benign conditions.³⁹ Enzyme treatment saves water, energy, and chemicals, and uses processing equipment currently available in the textile industry.⁴³ Proteases,^{35–38} amidases,⁴⁴ and cutinases^{39,45,46} have been successfully used to hydrolyze polyamide fibers.

In the present study, a previously reported enzymatic modification was employed to improve the hydrophilicity (wettability) of PA6.6 fabric.³⁸ By introducing additional surface carboxyl and amino groups, polyamide fibers achieved conductivity with fewer deposited bilayers (BLs) than unmodified polyamide. Although enzymatic modification of PA6.6 is well known, it has never been combined with layer-by-layer (LbL) deposition to impart functionality to textiles. Enzymatically modified PA6.6 exhibits increased wettability

and higher ζ -potential relative to unmodified fabric. Layer-by-layer deposition of poly(diallyldimethylammonium chloride) (PDDA)- and sodium deoxycholate (DOC)-stabilized multi-walled carbon nanotubes (MWCNT) results in electrically conductive fibers. The enzymatically modified fabric exhibits a more uniform nanocoating and higher conductivity with fewer layers deposited, relative to the unmodified fabric. This type of natural modification of synthetic fibers could be used as a means to more effectively deposit water-based treatments for greater functionality.

RESULTS AND DISCUSSION

Enzymatic Modification of Fabric. Enzymatic modification of the PA6.6 fabric was carried out using protease that acts under mild working conditions: 60 °C, pH 6.8, and a 60 min treatment time.^{38,45,46} During this treatment, the hydrophobic surface of PA6.6 should be hydrolyzed through hydrolytic cleaving of the peptide bonds, producing carboxyl and amino groups, as shown in Figure 1. Successful enzymatic modification is imperative for producing conductive polyamide fabric with fewer nanotube-based bilayers deposited. The effectiveness of this process is confirmed through changes in polyamide surface morphology, fabric wettability, and surface charge.

Scanning electron microscopy (SEM) images of PA6.6 fibers before and after enzymatic modification are shown in Figure 2. Unmodified fibers show some residual polymer, as well as impurities, probably remaining from the extrusion process (Figure 2a). After enzymatic modification, residual polymer and impurities are removed, making the surface of the fibers

smoother, without any irregularities. The smooth and clean surface of these modified PA6.6 fibers is one confirmation that the enzymatic treatment is effective.

The hydrophilicity of the enzymatically modified PA6.6 fabric was evaluated by determining the time it takes for a drop of Triton X-100 nonionic surfactant solution to be completely absorbed into the fabric, as well as by analyzing the shape of the water drop 3 min after the drop touches the surface of the fabric. The results in Figure 3 indicate that the unmodified

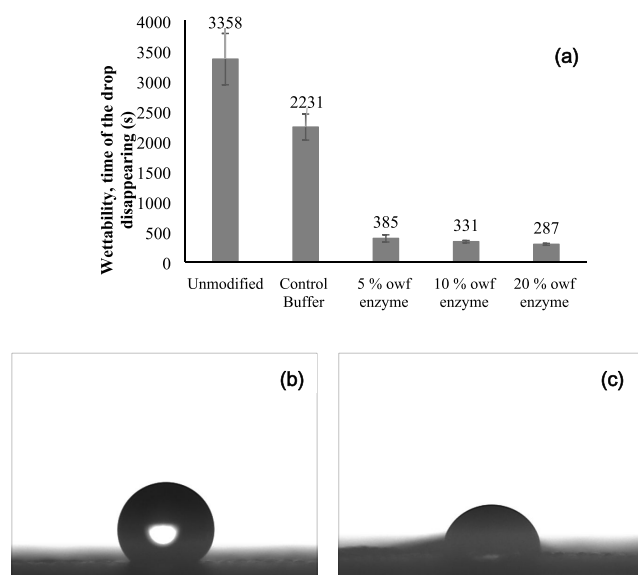


Figure 3. (a) Wettability determined by the drop absorption time using $1 \text{ cm}^3/\text{dm}^3$ Triton X-100 solution. Images of the water drop 3 min after being deposited on (b) unmodified PA6.6 fabric and (c) enzymatically modified PA6.6 fabric.

fabric needs an average time of 3358 s to completely absorb the drops, while the modified PA6.6 fabric exhibits improved wettability and thus lower drop absorption time. During the observation of the drops wetting the unmodified PA6.6 fabric, it appeared that the drops actually evaporated rather than being absorbed into the fabric.

The influence of the enzyme concentration on the wettability of the enzymatically modified PA6.6 is also illustrated in Figure 3. With increasing enzyme concentration, fabric wettability increases. Modified PA6.6 fabric with 5% overweight of the fabric (owf) enzyme exhibits an 8.7-fold increase in wettability, while those modified with 10 and 20% (owf) display 10.1- and 11.7-fold wettability increases, respectively, compared to the unmodified fabric. Although the 20% (owf) enzyme-treated textile achieves the highest wettability, the 10% (owf) concentration is used for further investigation, due to high cost and diminishing benefit from higher concentration. The treatment with the enzyme concentration of 5% (owf) imparts similar wettability to the fabric compared to that of 10% (owf), but the standard deviation of the average value is much higher. The images of the water drop taken 3 min after touching the surface of the fabric reveal higher water-absorbing ability of the modified PA6.6 fabric, compared to the unmodified one, as shown in Figure 3b,c. These tests further confirm the successful modification of PA6.6 due to the greater hydrophilicity shown here from the presence of amino and carboxyl groups.

The scheme of enzymatic modification (Figure 1) indicates that the enzymes hydrolyze molecules of PA6.6, producing carboxyl and amino groups. Dyeing the fabric is a good method for determining the presence of these functional groups.^{38,47} Methylene blue is a positively charged basic dye for determining the presence of carboxyl groups, while acid orange 7 is a negatively charged acid dye for assessing the presence of amino groups. The intensity of the dyeing is a good indicator of the amount of functionality existing on the surface.^{38,45,50,51} The images and the *K/S* values of unmodified and modified PA6.6 fabric, dyed with methylene blue and acid orange 7 (Table 1), clearly show differences between unmodified and modified samples. The modified fabric exhibits more intense color and higher *K/S* values after dyeing with both dyes. The same trend of higher *K/S* values of enzyme-modified relative to unmodified polyamide was reported previously when protease, acylase, and cutinase were used for successful modification of polyamide fibers.^{36,38,45} These

Table 1. Amount of Carboxyl and Amino Groups on PA6.6 Fabric Determined by Dyeing

Sample	Pictures of the dyed samples		K/S	
	MB	AO7	MB	AO7
Unmodified PA6.6			1.68	4.50
Enzymatic modified PA6.6			2.74	7.98

results indicate that, upon enzymatic modification, new carboxyl and amino groups were introduced.

ζ -Potential and isoelectric point (IEP) are also good indicators of functionality existing on the surface of PA6.6, as shown in Figure 4. These results reveal that, upon enzymatic

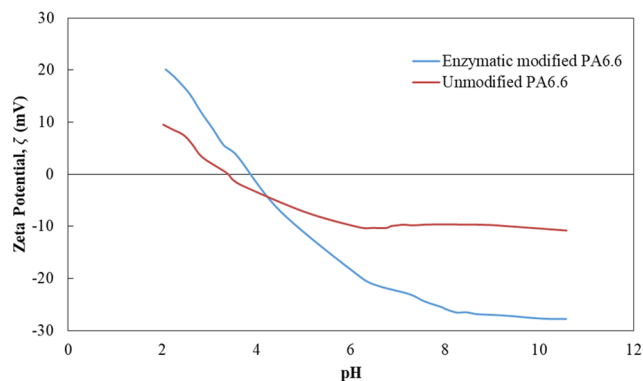


Figure 4. ζ -Potential of unmodified and enzymatically modified PA6.6 fabric.

treatment, new carboxyl and amino groups are introduced. Enzymatically modified fabric has almost twice the positive and 2.5 \times the negative surface charge relative to the unmodified fabric. This increase of the positive ζ -potential and the decrease of the negative ζ -potential are due to the introduction of carboxyl and amino groups during the enzymatic treatment. Indeed, this confirms the presence of the carboxyl, responsible for the negative charge, and the amino, responsible for the positive charge of the fabric surface, on PA6.6 fabric. The curve patterns of ζ -potential as a function of pH of the unmodified and enzymatically modified polyamide are similar to those of nylon modified by the acylase enzyme.³⁶ The isoelectric points of the unmodified and enzymatically modified fabric are at pH 3.45 and 3.6, respectively. Enzymatically modified PA6.6 has a greater IEP as a result of more positive amino groups created during the enzymatic hydrolysis.

Deposition of Conductive Nanocoating on Fabric. A multilayer nanocoating composed of PDPA and MWNT-DOC^{9–11} was used to impart electrical conductivity to PA6.6 fabric. The layer-by-layer deposition of the coating is shown schematically in Figure 5a. Figure 5b shows sheet resistance of the fabric. The unmodified and modified samples have almost the same sheet resistance values after being coated with two and three PDPA/MWNT-DOC bilayers. With 4 BL deposited, the unmodified PA6.6 fabric has almost the same value of sheet resistance as those coated with two and three bilayers, while the enzymatically modified fabric exhibits a substantially decreased sheet resistance (i.e., higher conductivity). After coating with 5 to 7 BL, the sheet resistance of both fabrics continues to decrease, but the enzymatically modified PA6.6 exhibits progressively lower sheet resistance than the unmodified sample. These results suggest that the percolation threshold of the enzymatically modified system is at or above 4 BL, while that of the unmodified fabric is at or above 5 BL.

The percolation threshold is a characteristic for inhomogeneous conductors, such as polymer composites containing electrically conductive filler (e.g., carbon nanotubes). The conductive composites begin to transition from insulator to conductor as more conductive filler is added to the insulating

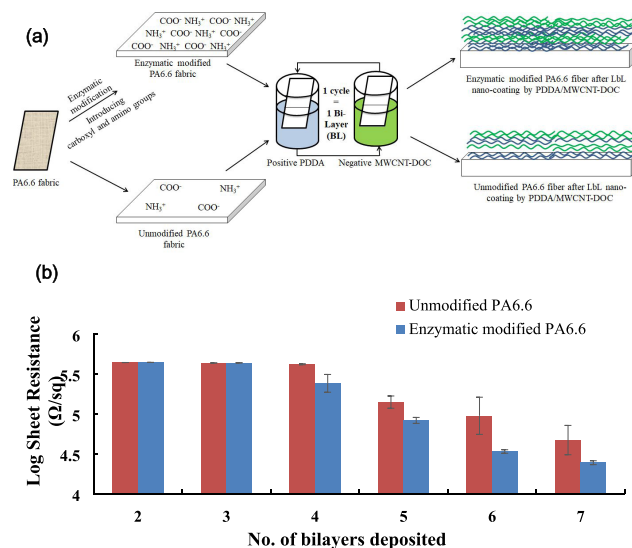


Figure 5. (a) Schematic procedure for deposition of a conductive coating on unmodified and enzymatically modified PA6.6 fabric using the PDPA/MWNT-DOC multilayer system. (b) Sheet resistance as a function of the number of PDPA/MWNT-DOC bilayers deposited.

polymer matrix. This critical concentration of conductive filler where interconnected network is formed is known as the percolation threshold.^{48,49} PDPA/MWNT-DOC bilayers form a version of this type of nanocomposite (i.e., conductive MWNT within insulating PDPA). As compared to previously reported studies, the sheet resistance values for the present enzymatically modified nylon are an order of magnitude greater, but these studies either used more hydrophilic textile (e.g., polyester/cotton blend) or a different type of carbon nanotubes (e.g., single-walled carbon nanotubes).^{50,51} It is well established that more hydrophobic textiles are more difficult to coat, which typically leads to worse deposition and higher sheet resistance values.^{52–54} Furthermore, altering the type of carbon nanotube in these LbL-deposited coatings has been shown to improve sheet resistance.¹¹ While these LbL coatings yield higher sheet resistances than other studies, it is believed that changing the carbon nanotube type would make the sheet resistances competitive with these other studies.

Images of the conductive fabric, coated with two PDPA/MWNT-DOC bilayers, are shown in Figure 6. Although nanotubes are present on the surface of both types of fabric, the enzymatically modified sample has substantially greater amount of MWNT. The lower-magnification micrographs indicate that a conductive network that contains more PDPA than MWNT is formed on the surface of the unmodified fabric (Figure 6c). This nanocoating is observed as a continuous film on the surface of the fabric, with interconnecting fibers and PDPA. The conductive network of the enzymatically modified sample covers each fiber more individually than that observed on the unmodified PA6.6 (Figure 6d). The fabric coated with four bilayers is similar to the two-bilayer coating for the unmodified PA6.6 fabric (Figure 6e). The conductive network of the enzymatically modified fabric exhibits greater MWNT content and intertube bridges (Figure 6f), but this 4 BL coating still conformally covers each individual fiber.

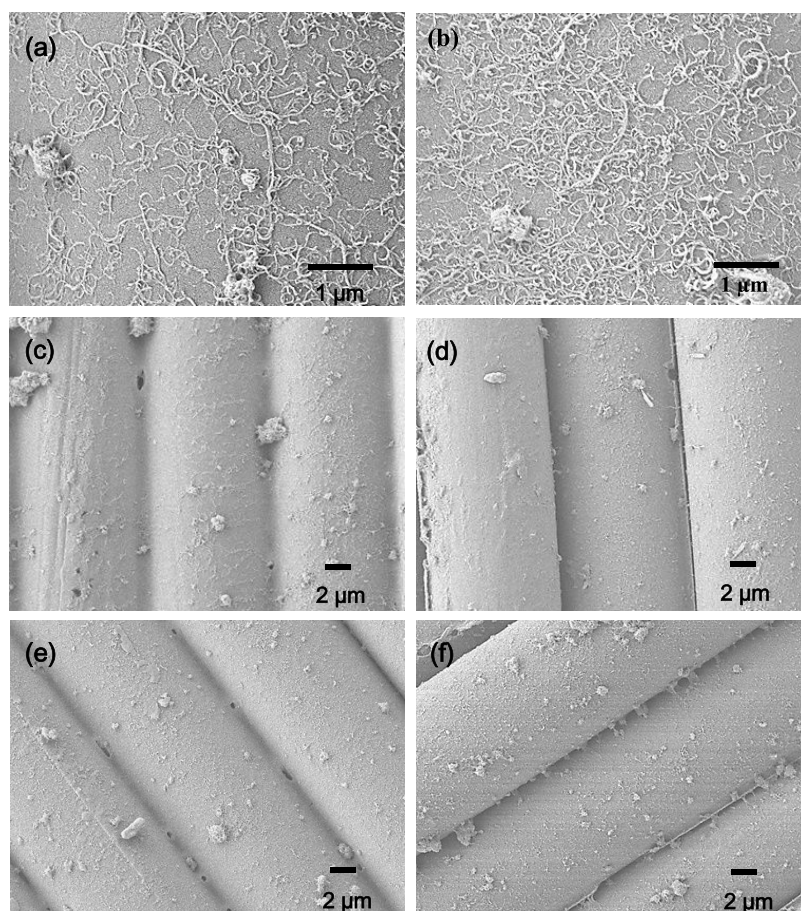


Figure 6. SEM images of (a), (c) unmodified and (b), (d) enzymatically modified PA6.6 fabric coated with two bilayers of PDDA/MWCNT-DOC. SEM images of (e) unmodified and (f) enzymatically modified PA6.6 fabrics after deposition of a 4 BL nanocoating.

CONCLUSIONS

Enzymatic modification is demonstrated as a straightforward process for achieving good hydrophilicity of PA6.6 fibers that is responsible for more effective deposition of a conductive multilayer nanocoating. Successful modification of PA6.6 is demonstrated by its smoother surface, increased hydrophilicity, more carboxyl and amino groups, and more positive charge above pH 3.6 (and more negative charge below pH 3.6) than the unmodified fabric. This greater hydrophilicity and surface charge improve the ability of the modified PA6.6 textile to accept a water-based, functional nanocoating. Layer-by-layer deposition of PDDA/MWCNT-DOC bilayers reduced sheet resistance of modified fabric at a greater rate than the unmodified PA6.6. The conductive network on the surface of the modified fabric had a better morphology from that on the unmodified sample. The nanocoating covers each enzymatically modified fiber conformally, with more MWCNT present that creates interfiber bridges. This mild and environmentally friendly treatment could likely be used to impart functionality to a variety of hydrophobic synthetic fibers.

EXPERIMENTAL SECTION

Substrate and Materials. PA6.6 plain-weave 80 g/m² fabric, supplied by Seattle Fabric (Seattle, WA), was used as the substrate for modification. Protease from *Bacillus licheniformis*, Subtilisin A (EC number 3.4.21.62), sodium phosphate buffer [Na₂HPO₄ (disodium phosphate), NaH₂PO₄ (sodium dihydrogen phosphate)], Triton X-100 (nonionic surfactant),

Na₂CO₃, methylene blue (C.I. 52015 cationic dye), acid orange 7 (C.I. 15510 anionic acid dye), poly-(diallyldimethylammonium chloride) (*M_w*, 100–200 kg/mol, 20 wt % aqueous solution), and sodium deoxycholate (≥97%) were purchased from Sigma-Aldrich (Milwaukee, WI). Multi-walled carbon nanotubes were obtained from Bayer Material Science (12–15 nm outer diameter and 4 nm inner diameter and 1+ μm length; C ≥ 95 wt %; Leverkusen, Germany). The enzyme has 2.4 U/g activity. One unit hydrolyzes casein to produce a color equivalent to 1.0 mmol (181 μg) of tyrosine per minute at pH 7.5 at 37 °C (color by the Folin–Ciocalteu reagent). All solutions were prepared with 18.2 MΩ deionized (DI) water. The conductive recipe consisted of a positively charged, aqueous solution of 0.25 wt % PDDA, and a negatively charged dispersion of 0.05 wt % MWCNT stabilized with 2.0 wt % DOC.^{10,11} Prior to use, the anionic solution was sonicated at 20 W for 30 min and slowly stirred for 0.5 h, while the cationic solution was rolled for a minimum of 12 h to ensure full dissolution.⁹ All of the solutions were used without altering their pH.

Enzymatic Modification of PA6.6 Fabric. The PA6.6 fabric was first washed in a bath of 2 cm³/dm³ Triton X-100 and 2 g/dm³ Na₂CO₃ with a 30:1 liquor ratio (LR), at 50 °C for 60 min, to remove all impurities.⁴⁵ After that, the fabric was rinsed twice with distilled water at 50 °C for 15 min. Enzymatic modification was done in a bath with 30:1 LR at pH 6.8 (0.1 M phosphate buffer), using 5, 10, and 20%, on weight of the fabric (owf), protease enzyme at 60 °C for 60 min,

according to a previously described procedure.^{38,45,55,56} The products of enzymatic hydrolysis were removed by treating the fabric with 2 cm³/dm³ Triton X-100 and 2 g/dm³ Na₂CO₃ at 50 °C for 60 min.³⁵ The modified fabric was rinsed twice with distilled water at 50 °C for 15 min, rinsed in running cold tap water for 5 min, and dried in open air.

Layer-by-Layer Deposition. Multilayered nanocoatings were deposited using a home-built automated dipping system.⁵⁷ The PA.6.6 fabric was first immersed into a 0.25 wt % solution of PDDA for 5 min. The fabric was then submerged in DI water for 1 min. The same dipping and rinsing procedure was carried out with 0.05 wt % MWCNT in 2 wt % solution of DOC. This cycle marks one bilayer deposited. The immersion times were reduced to 1 min for the subsequent deposition cycles, which were repeated until the desired number of bilayers were deposited.

Characterization of Enzymatically Modified Fabric. Images of the fabric were collected using a JEOL (Akishima, Tokyo, Japan) JSM-7500 field emission scanning electron microscope. Prior to imaging, a 5 nm Pt/Pd coating was applied to the surface of the nylon fibers to minimize charging. Fabric wettability (hydrophilicity) was determined by measuring the time it takes for a drop of 1 cm³/dm³ Triton X-100 solution to be completely absorbed into the fabric, according to the procedure described in the AATCC 79-2000 standard. The presented results are mean values of 10 measurements. Surface wettability was evaluated using a CAM 200 optical contact angle and surface tension meter (KSV Instruments, Ltd., Monroe, CT). This goniometer is equipped with an autodispenser, a video camera, and drop-shape analysis software. A drop of water (5 μL) was pictured 3 min after deposition onto the fabric surface.

The fabric was dyed with methylene blue and acid orange 7 for determining carboxyl and amino groups present. Methylene blue dyeing was done in a bath, with LR 100:1, 0.02 g/dm³ methylene blue in Britton–Robinson buffer (pH 7.1–7.4) at 30 °C for 30 min, in an Incubating Mini Shaker (VWR, Radnor, PA) at 150 rpm. Acid orange 7 dyeing was done in a bath with LR 100:1, 0.02 g/dm³ acid orange 7, pH 3 (adjusted by 1 M HCl) at 30 °C for 30 min in the VWR Incubating Mini Shaker at 150 rpm. The stained fabrics were washed in a bath with LR 100:1, 1 cm³/dm³ Triton X-100, at room temperature for 10 min and then rinsed in running cold tap water for 10 min and air-dried. The color strength (*K/S*) of the stained samples was measured with a reflection spectrophotometer (X-Rite Color i7 spectrophotometer, Grand Rapids, MI), using illuminant D₆₅ with a 10° standard observer. The *K/S* was calculated from the reflectance values using the Kubelka–Munk equation

$$K/S = \frac{(1 - R)^2}{2R}$$

where *R* is the reflectance, *K* is the absorption coefficient, and *S* is the light scattering coefficient. The presented results are the mean values of five measurements. Images of the dyed PA6.6 fabrics are provided for visualization of the qualitative differences between the unmodified and enzymatically modified samples. A Brookhaven-Paar (Brookhaven, NY) electrokinetic analyzer was used to determine the ζ-potential and isoelectric point (IEP) of the fabric in a 0.001 M potassium chloride solution.⁵⁸ A range of pH values of the electrolyte solution was investigated up to a maximum of pH

11, achieved with 0.1 M sodium hydroxide, and then reduced (ca. 1 pH unit) with 0.1 M hydrochloric acid.

Characterization of Nanocoated Conductive Fabric. To assess the electrical properties of the coated fabric, sheet resistance was measured using a Signatone Pro4 Four-Point Probe (Gilroy, CA), with 0.4 mm probe tip diameter and 1.0 mm tip spacing, connected to a E3644A DC power supply (Agilent Technologies Inc., Santa Clara, CA), with an operating voltage of 10 V and a 2400 Keithley Multimeter (Cleveland, OH).¹¹ Voltage and current values were collected by LabVIEW (National Instruments Inc., Austin, TX), using an SCB-68 Shield I/O Connector Block. The reported sheet resistance is the average of five measurements.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PA6.6, polyamide 6.6 fabric; LbL, layer-by-layer; MWCNT, multiwall carbon nanotubes; DOC, sodium deoxycholate; PDDA, poly(diallyldimethylammonium chloride); CNT, carbon nanotubes; SEM, scanning electron microscopy; MB, methylene blue; AO7, acid orange 7

REFERENCES

- (1) Richards, A. F. Nylon Fibres. In *Synthetic Fibres: Nylon, Polyester, Acrylic, Polyolefin*; McIntyre, J. E., Ed.; Woodhead Publishing: Cambridge, 2005.
- (2) Vasiljević, J.; Colovic, M.; Jerman, I.; Simončić, B. Recent advances in production of flame retardant polyamide 6 filament yarns. *Tekstilec* **2018**, *61*, 136–148.
- (3) Jia, X.; Herrera-Alonso, M.; McCarthy, T. J. Nylon surface modification. Part 1. Targeting the amide groups for selective introduction of reactive functionalities. *Polymer* **2006**, *47*, 4916–4924.
- (4) Xie, C.; Han, H.; Hu, H.; Zhao, J.; Zhao, Y.; Li, C. Endurable conductivity of nylon fibers by interfacial grafting and aniline polymerization. *Mater. Lett.* **2018**, *218*, 213–216.
- (5) Oh, K. W.; Kim, S. H.; Kim, E. A. Improved surface characteristics and the conductivity of polyaniline–nylon 6 fabrics by plasma treatment. *J. Appl. Polym. Sci.* **2001**, *81*, 684–694.
- (6) Hallfors, N. G.; Alhawari, M.; Abi Jaoude, M.; Kifle, Y.; Saleh, H.; Liao, K.; Ismail, M.; Isakovic, A. F. Graphene oxide: nylon ecg sensors for wearable iot healthcare-nanomaterial and soc interface. *Analog Integr. Circuits Signal Process.* **2018**, *96*, 253–260.
- (7) Zhao, Y.; Cao, Y.; Liu, J.; Zhan, Z.; Li, X.; Li, W. J. Single-wall carbon nanotube-coated cotton yarn for electrocardiography transmission. *Micromachines* **2018**, *9*, 132–141.
- (8) Fu, L.; Yu, A. M. Carbon nanotubes based thin films: fabrication, characterization and application. *Rev. Adv. Mater. Sci.* **2014**, *36*, 40–61.
- (9) Mateos, A. J.; Cain, A. A.; Grunlan, J. C. Large-scale continuous immersion system for layer-by-layer deposition of flame retardant and

- conductive nanocoatings on fabric. *Ind. Eng. Chem. Res.* **2014**, *53*, 6409–6416.
- (10) Park, Y. T.; Ham, A. Y.; Grunlan, J. C. Heating and acid doping thin film carbon nanotube assemblies for high transparency and low sheet resistance. *J. Mater. Chem.* **2011**, *21*, 363–368.
- (11) Park, Y. T.; Ham, A. Y.; Grunlan, J. C. High electrical conductivity and transparency in deoxycholate-stabilized carbon nanotube thin films. *J. Phys. Chem. C* **2010**, *114*, 6325–6333.
- (12) Blackburn, J. L.; Ferguson, A. J.; Cho, C.; Grunlan, J. C. Carbon-nanotube-based thermoelectric materials and devices. *Adv. Mater.* **2018**, *30*, No. 1704386.
- (13) Culebras, M.; Cho, C.; Krecker, M.; Smith, R.; Song, Y.; Gomez, C. M.; Cantarero, A.; Grunlan, J. C. High thermoelectric power factor organic thin films through combination of nanotube multilayer assembly and electrochemical polymerization. *ACS Appl. Mater. Interfaces* **2017**, *9*, 6306–6313.
- (14) Decher, G. Fuzzy nanoassemblies: toward layered polymeric multicomposites. *Science* **1997**, *277*, 1232–1237.
- (15) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: suitable materials, structure and properties. *Macromol. Rapid Commun.* **2000**, *21*, 319–348.
- (16) Hammond, P. T. Form and function in multilayer assembly: new application at a nanoscale. *Adv. Mater.* **2004**, *16*, 1271–1293.
- (17) Zhu, X.; Loh, X. J. Layer-by-layer assemblies for antibacterial applications. *Biomater. Sci.* **2015**, *3*, 1505–1518.
- (18) Azlin-Hasim, S.; Cruz-Romero, M. C.; Cummins, E.; Kerry, J. P.; Morris, M. A. The potential use of a layer-by-layer strategy to develop LDPE antimicrobial films coated with silver nanoparticles for packaging applications. *J. Colloid Interface Sci.* **2016**, *461*, 239–248.
- (19) Smith, R. J.; Moule, M. G.; Sule, P.; Smith, T.; Cirillo, J. D.; Grunlan, J. C. Polyelectrolyte multilayer nanocoating dramatically reduces bacterial adhesion to polyester fabric. *ACS Biomater. Sci. Eng.* **2017**, *3*, 1845–1852.
- (20) Holder, K. M.; Smith, R. J.; Grunlan, J. C. A review of flame retardant nanocoatings prepared using layer-by-layer assembly of polyelectrolytes. *J. Mater. Sci.* **2017**, *52*, 12923–12959.
- (21) Schindelholz, E. J.; Spoerke, E. D.; Nguyen, H.-D.; Grunlan, J. C.; Qin, S.; Bufford, D. C. Extraordinary corrosion protection from polymer–clay nanobrick wall thin films. *ACS Appl. Mater. Interfaces* **2018**, *10*, 21799–21803.
- (22) Song, Y.; Geringer, J.; Qin, S.; Grunlan, J. C. High oxygen barrier thin film from aqueous polymer/clay slurry. *Ind. Eng. Chem. Res.* **2018**, *57*, 6904–6909.
- (23) Kim, B. S.; Park, S. W.; Hammond, P. T. Hydrogen-bonding layer-by-layer-assembled biodegradable polymeric micelles as drug delivery vehicles from surfaces. *ACS Nano* **2008**, *2*, 386–392.
- (24) Lee, S. W.; Kim, B.-S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. Layer-by-layer assembly of all carbon nanotube ultrathin films for electrochemical applications. *J. Am. Chem. Soc.* **2009**, *131*, 671–679.
- (25) Paloniemi, H.; Lukkari, M.; Aaritalo, T.; Arega, S.; Leiro, J.; Heinonen, M.; Haapakka, K.; Lukkari, J. Layer-by-layer electrostatic self-assembly of single-wall carbon nanotube polyelectrolytes. *Langmuir* **2006**, *22*, 74–83.
- (26) Shim, B. S.; Tang, Z.; Morabito, M. P.; Agarwal, A.; Hong, H.; Kotov, N. A. Integration of conductivity, transparency, and mechanical strength into highly homogeneous layer-by-layer composites of single-walled carbon nanotubes for optoelectronics. *Chem. Mater.* **2007**, *19*, 5467–5474.
- (27) Gheith, M. K.; Pappas, T. C.; Liopo, A. V.; Sinani, V. A.; Shim, B. S.; Motamedi, M.; Wicksted, J. P.; Kotov, N. A. Stimulation of neural cells by lateral currents in conductive layer-by-layer films of single-walled carbon nanotubes. *Adv. Mater.* **2006**, *18*, 2975–2979.
- (28) Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Ruch, D. Layer-by-layer deposition of a TiO₂-filled intumescent coating and its effect on the flame retardancy of polyamide and polyester fabrics. *Colloids Surf., A* **2015**, *469*, 1–10.
- (29) Kundu, C. K.; Wang, W.; Zhou, S.; Wang, X.; Sheng, H.; Pan, Y.; Song, L.; Hu, Y. A green approach to constructing multilayered nanocoating for flame retardant treatment of polyamide 66 fabric from chitosan and sodium alginate. *Carbohydr. Polym.* **2017**, *166*, 131–138.
- (30) Apaydin, K.; Laachachi, A.; Ball, V.; Jimenez, M.; Bourbigot, S.; Toniazzo, V.; Ruch, D. Intumescent coating of (polyallylamine-polyphosphates) deposited on polyamide fabrics via layer-by-layer technique. *Polym. Degrad. Stab.* **2014**, *106*, 158–164.
- (31) Kundu, C. K.; Wang, X.; Song, L.; Hu, Y. Borate cross-linked layer-by-layer assembly of green polyelectrolytes on polyamide 66 fabrics for flame-retardant treatment. *Prog. Org. Coat.* **2018**, *121*, 173–181.
- (32) Majka, T. M.; Cokot, M.; Pielichowski, K. Studies on the thermal properties and flammability of polyamide 6 nanocomposites surface-modified via layer-by-layer deposition of chitosan and montmorillonite. *J. Therm. Anal. Calorim.* **2018**, *131*, 405–416.
- (33) Lee, Y.; Kim, J.; Hwang, H.; Jeong, S.-H. Highly stretchable and sensitive strain sensors based on single-walled carbon nanotube-coated nylon textile. *Korean J. Chem. Eng.* **2019**, *36*, 800–806.
- (34) Shao, F.; Xu, C.; Ji, W.; Dong, H.; Sun, Q.; Yu, L.; Dong, L. Layer-by-layer self-assembly TiO₂ and graphene oxide on polyamide reverse osmosis membranes with improved membrane durability. *Desalination* **2017**, *423*, 21–22.
- (35) Song, J. E.; Kim, H. R. Improvement in nylon fabrics' reactivity via enzymatic functionalization. *J. Text. Inst.* **2017**, *108*, 155–164.
- (36) Kim, H. R.; Seo, H. Y. Enzymatic hydrolysis of polyamide fabric by using acylase. *Text. Res. J.* **2013**, *83*, 1181–1189.
- (37) Song, A. R.; Kim, H. R. Effectiveness of flavourzyme treatment on polyamide fabric. *Fibers Polym.* **2013**, *14*, 2212–2220.
- (38) Kanelli, M.; Vasilakos, S.; Ladas, S.; Symianakis, E.; Christakopoulos, P.; Topakas, E. Surface modification of polyamide 6.6 fibres by enzymatic hydrolysis. *Process Biochem.* **2017**, *59*, 97–103.
- (39) Silva, C.; Cavaco-Paulo, A. M.; Fu, J. J. Enzymatic Biofinishes for Synthetic Textiles. In *Functional Finishes for Textile: Improving Comfort, Performance and Protection*; Paul, R., Ed.; Woodhead Publishing: Cambridge, 2015; pp 153–191.
- (40) Kisner, A.; Rainert, K. T.; Ferrari, F.; Nau, C. T.; Barcellos, I. O.; Pezzin, S. H.; Andraus, J. Chemical functionalization of polyamide 6.6 fabrics. *React. Funct. Polym.* **2013**, *73*, 1349–1356.
- (41) Shearer, A. E. H.; Paik, J. S.; Hoover, D. G.; Haynie, S. L.; Kelley, M. J. Potential of an antibacterial ultraviolet-irradiated nylon film. *Biotechnol. Bioeng.* **2000**, *67*, 141–146.
- (42) Yip, J.; Chan, K.; Moon Sin, K.; Shui Lau, K. Low temperature plasma-treated nylon fabrics. *J. Mater. Process. Technol.* **2002**, *123*, 5–12.
- (43) Cavaco-Paulo, A.; Gübitz, G. M. *Textile Processing with Enzymes*; Woodhead Publishing Ltd: England, 2003.
- (44) Heumann, S.; Eberl, A.; Pobeheim, H.; Liebming, S.; Fischer-Colbrie, G.; Almansa, E.; Cavaco-Paulo, A.; Gübitz, G. M. New model substrates for enzymes hydrolysing polyethyleneterephthalate and polyamide fibres. *J. Biochem. Biophys. Methods* **2006**, *69*, 89–99.
- (45) Silva, C.; Silva, C. J.; Zille, A.; Guebitz, M. G.; Cavaco-Paulo, A. Influence of mechanical agitation on cutinases and protease activity towards polyamide substrates. *Enzyme Microb. Technol.* **2007**, *40*, 1678–1685.
- (46) Silva, C.; Cavaco-Paulo, A. Monitoring biotransformations in polyamide fibres. *Biocatal. Biotransform.* **2004**, *22*, 357–360.
- (47) Jordanov, B. I.; Mangovska, B.; Simoncic, B.; Forte-Tavcer, P. Changes in the non-cellulosic components of cotton surface after mercerization and scouring. *AATCC Rev.* **2010**, *10*, 65–72.
- (48) Kirkpatrick, S. Percolation and Conduction. *Rev. Mod. Phys.* **1973**, *45*, 574–588.
- (49) Moriarty, G. P.; Whittemore, J. H.; Sun, K. A.; Rawlins, J. W.; Grunlan, J. C. Influence of Polymer Particle Size on the Percolation Threshold of Electrically Conductive Latex-Based Composites. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1547–1554.
- (50) Kowalczyk, D.; Brzeinski, S.; Makowski, T.; Fortuniak, W. Conductive hydrophobic hybrid textiles modified with carbon nanotubes. *Appl. Surf. Sci.* **2015**, *357*, 1007–1014.

(51) Zhang, W.; Johnson, L.; Silva, S. R. P.; Lei, M. K. The effect of plasma modification on the sheet resistance of nylon fabrics coated with carbon nanotubes. *Appl. Surf. Sci.* **2012**, *258*, 8209–8213.

(52) El-Bendary, M. A.; Abo El-Ola, S. M.; Moharam, M. E. Enzymatic surface hydrolysis of polyamide fabric by protease enzyme and its production. *Indian J. Fibre Text. Res.* **2012**, *37*, 273–279.

(53) Jimenez, M.; Guin, T.; Bellayer, S.; Dupretz, R.; Bourbigot, S.; Grunlan, J. C. Microintumescent mechanism of flame-retardant water-based chitosan-ammonium polyphosphate multilayer nanocoating on cotton fabric. *J. Appl. Polym. Sci.* **2016**, *133*, No. 43783.

(54) Leistner, M.; Abu-Odeh, A. A.; Rhomer, S. C.; Grunlan, J. C. Water-based chitosan/melamine polyphosphate multilayer nanocoating that extinguishes fire on polyester-cotton fabric. *Carbohydr. Polym.* **2015**, *130*, 227–232.

(55) Silva, C.; Silva, C. J.; Zille, A.; Guebitz, M. G.; Cavaco-Paulo, A. Laccase immobilization on enzymatically functionalized polyamide 6,6 fibres. *Enzyme Microb. Technol.* **2007**, *41*, 867–875.

(56) O'Neill, A.; Araujo, R.; Casal, M.; Guebitz, M. G.; Cavaco-Paulo, A. Effect of the agitation on the adsorption and hydrolytic efficiency of cutinases on polyethylene terephthalate fibres. *Enzyme Microb. Technol.* **2007**, *40*, 1801–1805.

(57) Jang, W.-S.; Grunlan, J. C. Robotic dipping system for layer-by-layer assembly of multifunctional thin films. *Rev. Sci. Instrum.* **2005**, *76*, No. 103904.

(58) Grancaric, A. M.; Tarbuk, A.; Pusic, T. Electrokinetic properties of textile fabrics. *Color. Technol.* **2005**, *121*, 221–227.