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Article

VAR Fabric Modification: Inducing Antibacterial Properties, Altering Wettability/Water Repellence, and Understanding Reactivity at the Molecular Level

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ABSTRACT: The present work focuses on the surface coating of VAR technical fibers, consisting of 64% viscose (cellulose), 24% Kevlar, 10% other types of polyamides, and 2% antistatic polymers. Kevlar is an aramid material exhibiting excellent mechanical properties, while cellulose is a natural linear polymer composed of repeating β-D-glucose units, having several applications in the materials industry. Herein, we synthesized novel, tailor-designed organic molecules possessing functional groups able to anchor on VAR fabrics and cellulose materials, thus altering their properties on demand. To this end, we utilized methyl-α-D-glucopyranose as a model compound, both to optimize the reaction conditions, before applying them to the material and to understand the chemical behavior of the material at the molecular level. The efficient coating of the VAR fabric with the tailor-made compounds was then implemented. Thorough characterization studies using Raman and IR spectroscopies as well as SEM imaging and thermogravimetric analysis were also carried out. The wettability and water repellency and antibacterial properties of the modified VAR fabrics were also investigated in detail. To the best of our knowledge, such an approach has not been previously explored, among other factors regarding the understanding of the anchoring mechanism at the molecular level. The proposed modification protocol holds the potential to improve the properties of various cellulose-based materials beyond VAR fabrics.

INTRODUCTION

The technical fabric sector occupies an increasingly large share of the production of textile materials. Among other, the automotive industry, as well as the healthcare, the constructions, and the agricultural sectors use technical fabrics, taking advantage of their performance and functional properties.[1] Moreover, technical fabrics are used in body armor of military and law enforcement personnel for protection from ballistic and edged weapons, protecting the wearer from shrapnel, knife, and low velocity guns.[2] To achieve this goal, layers/plates of plain woven fabrics with aramid or ultrahigh-molecular-weight polyethylene fibers are used, enclosed in a carrier. The carrier is usually a waistcoat or tabard-style garment, providing protection to the critical organs of the torso.

VAR is a technical fabric that is used as an efficient carrier for atomic shielding. This material has a special composition of viscose (made from natural sources of regenerated cellulose), para-aramid (Kevlar), and polyamide fibers, which are combined to provide exceptional properties of flame resistance, waterproofing, and air permeability.[3−6] Materials in this category create high-performance fibers, particularly when combined with other polymers, such as aramids, through their modification.[7] They form relatively durable fibers due to their chemical structure and crystallinity.

Cellulose is an organic raw material with applications in the drug industry, textiles, advanced materials, and more.[8−14] It is a sustainable, low-cost, and renewable resource possessing interesting physical properties and chemical reactivity. Cellulose is a linear polymer composed of repeating β-D-glucose units.[15,16] Cellulose fibers tend to be more durable when exposed to moisture as they become harder and more rigid. However, these fibers lose their durability and are eventually destroyed in the presence of acids. Due to the ampleness of hydroxyl groups on anhydroglucose units, they can efficiently form hydrogen bonds with aramids, making the incorporation of cellulose a straightforward process.

Hydrophobic fabrics have gained significant attention, because a hydrophobic surface can prevent the material from getting dirty, due to its contact with liquids, also extending the lifespan of the material by mitigating degradation caused by water.[17−19] Long-carbon-chain organic molecules have been widely employed in Material Science to introduce hydrophobicity. For example, surface functionalization of graphene oxide (GO) using alkylamines of varying chain lengths results in the formation of superhydrophobic surfaces, with the higher chain lengths performing better.[20,21] Long-carbon-chain

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amines are also known to induce antibacterial properties, when used in the form of their quaternary ammonium salts.[22] Likewise, 2,3-epoxypropyltrimethylammonium chloride (EPTAC) is known for its applications in the material science field, e.g., toward achieving "surface cationization", a chemical treatment that increases the materials' affinity with anionic dyes,[23] improves their water repellency,[24] and more. Along these lines, we recently published two protocols for the anchoring of 3-allyl-5,5-dimethylhydantoin (ADMH), 3-(acrylamidopropyl)trimethylammonium chloride (APTAC), and 2,4-dihydroxybenzophenone on different types of fabrics, thus improving their water repellency, antibacterial properties, and UV protection.[25,26]

In our present work, we synthesized two novel, tailor-made organic compounds and also used a third, commercially available one that can impart very useful characteristics to VAR and other cellulose-based materials, such as antibacterial properties and water repellency. We initially used methyl-α-D-glucopyranose as the model compound to optimize the reaction conditions that would later be implemented into the fabrics as well as to better understand the behavior of these materials at the molecular level. To the best of our knowledge, such a mechanistic study at the molecular level has not been reported in the literature. Next, we successfully anchored these compounds to the VAR fabrics. We studied the success of our coating protocol using Raman and IR spectroscopies, SEM imaging, and thermogravimetric analysis. Changes in the wettability of the material and the acquisition of antibacterial properties were also comprehensively assessed for the first time with VAR in such a thorough manner.

EXPERIMENTAL SECTION

Materials (Fabrics, Organic Compounds, Etc.). All chemicals were analytical-grade reagents obtained from commercial sources and used without any further purification.

For the purpose of our study, we used inherently heat and flame-resistant VAR fabrics engineered for professional clothes, provided by Siamidis SA, Oinofyta, Greece, with a weight of 185 g m^{-2}, 2/1 plane, fabric count of 24 wrap treads/10 cm and 24 weft threads/10 cm, consisting of viscose fibers, para-aramid, polyamide, and antistatic fibers with the following composition: 64% viscose/24% para-aramid (Kevlar)/10% polyamide/2% antistatic fibers.

The *E. coli* strain used was DH5α purchased from Invitrogen. The medium used for growing and maintaining the bacterial liquid cultures was a Luria−Bertani (LB) growth medium [1.0% Tryptone (Panreac), 0.5% yeast extract (Merck), 1.0% sodium chloride (Panreac), and pH adjusted to 7.3 ± 0.1 with 5.0 N NaOH (Merck)]. The unicellular cyanobacterium *Synechococcus* sp. PCC7942 was obtained from the Collection Nationale de Cultures de Microorganismes CNCM, Institut Pasteur, Paris, France, grown in a BG11 medium.

Methods: VAR Coating. *Synthesis of Methlyl-6-O-tosyl-α-D-glucopyranoside (1).*[27] Methyl α-D-glucopyranoside (5.15 mmol, 1 equiv) was added in dry pyridine, stirred, and cooled to −20 °C, followed by tosyl chloride (6.44 mmol, 1.25 equiv) addition in four portions. During each addition, the temperature was lowered to −30 °C. The mixture was stirred at −20 °C for 24h. Afterward, 7 mL of methanol was added in portions and the cooling bath was removed. Most of the pyridine was removed under vacuum. The monotosylated product was isolated via column chromatography (DCM:MeOH 8:2). Yield = 70%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 4.54 (d, *J* = 3.7 Hz, 1H), 4.30 (dd, *J* = 10.7, 1.9 Hz, 1H), 4.15 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.63 (m, 1H), 3.52 (q, *J* = 10.1, 9.7 Hz, 1H), 3.17 (t, *J* = 9.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD): δ 145.07, 133.08, 129.59, 127.70, 99.83, 73.55, 71.86, 69.95, 69.65, 69.60, 54.27, 20.17.

Synthesis of N-(3-(2-(2-(3-Aminopropoxy)ethoxy)ethoxy)-propyl)pentan-1-amine (2).[28] To a solution of 4,7,10-trioxa-1,13-diaminotridecane (24.1 mmol, 10 equiv) at 0 °C was added 1-bromodecane (2.41 mmol, 1 equiv) under Ar. The mixture was stirred at 0 °C for 1 h and then at room temperature for 16 h. Next, the reaction mixture was partitioned between ethyl acetate (EtOAc), brine, aqueous $NaHCO_3$, and H_2O. The aqueous phase was extracted with EtOAc, and the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product was isolated via column chromatography as a pale-yellow oil (DCM:MeOH 8:2). Yield = 67%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.60−3.39 (m, 12H), 3.25 (d, *J* = 12.2 Hz, 3H), 2.77 (m, 2H), 2.65 (m, 2H), 2.55 (m, 2H), 1.77−1.67 (m, 4H), 1.49−1.37 (m, 2H), 1.25−1.13 (m, 14H), 0.86−0.71 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 77.38, 49.99, 47.21, 39.44, 31.78, 30.01, 29.92, 29.50, 29.47, 29.47, 29.21, 27.30, 22.56, 14.00; HRMS (ESI-TOF) *m*/*z* ([M + H]$^+$) ($C_{20}H_{45}N_2O_3$) calcd 361.3430 found 361.3472.

Synthesis of N-(3-(2-(2-(3-Aminopropoxy)ethoxy)ethoxy)-propyl)pentanamide (3).[29] 4,7,10-Trioxa-1,13-diaminotridecane (10.48 mmol, 4 equiv) was mixed with pyridine (2.62 mmol, 5 equiv) in 5 mL of dry *N*,*N*-dimethylformamide (DMF) for 10 min at room temperature under Ar. After transferring the reaction mixture to an ice bath, decanoyl chloride (2.62 mmol, 1 equiv) was added dropwise. This mixture was then stirred at room temperature for 19 h. After filtration and washing with H_2O, the filtrate was extracted with EtOAc. The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The product was isolated as a yellow oil. Yield = 37%. ^{1}H NMR (CH_3OD, 400 MHz): δ 3.64−3.50 (m, 12H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.76 (m, *J* = 6.5, 2.8 Hz, 4H), 1.60 (t, *J* = 7.2 Hz, 2H), 1.30 (dd, *J* = 6.9, 3.4 Hz, 14H), 0.90 (t, *J* = 6.6 Hz, 4H); ^{13}C NMR (CH_3OD, 50 MHz): δ 174.73, 70.17, 69.88, 69.83, 69.82, 69.07, 68.52, 38.80, 36.38, 35.82, 31.67, 29.25, 29.10, 29.04, 28.96, 25.70, 22.37, 13.14; HRMS (ESI-TOF) *m*/*z* ([M + H]$^+$) ($C_{20}H_{43}N_2O_3$) calcd 375.3223 found 375.3200.

Synthesis of Methyl-6-butylamino-α-D-glucopyranoside (4).[30] Methyl-6-*O*-tosyl-α-D-glucopyranoside (0.46 mmol, 1 equiv) was dissolved in acetonitrile. After 10 min, butylamine was added, and the mixture was stirred under reflux for 16 h. Afterward, the solvent was evaporated under reduced pressure. The product was collected via column chromatography as a yellow oil (dichloromethane:CH_3OH 8:2). Yield = 42%. ^{1}H NMR (400 MHz, CD_3OD): δ 4.68 (d, *J* = 3.7 Hz, 1H), 3.72−3.59 (m, 2H), 3.43 (overlapping with solvent, 1H), 3.40 (dd, *J* = 9.7, 3.9 Hz, 1H), 3.36 (s, 1H), 3.14 (t, *J* = 9.3 Hz, 1H), 3.00 (dd, *J* = 12.4, 3.2 Hz, 1H), 2.74−2.59 (m, 3H), 1.53 (m, 2H), 1.38 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD): δ 99.93, 73.51, 73.05, 72.14, 69.46, 54.48, 50.77, 48.99, 31.19, 20.13, 13.00; HRMS (ESI-TOF) *m*/*z* ([M + H]$^+$) ($C_{11}H_{24}NO_5$) calcd 250.1654 found 250.1717.

Anchoring of Compounds 2 (Leading to VAR3) and 3 (Leading to VAR2) onto VAR Fabrics. To a solution of DMF

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(40 mL) and Et_3N (1 mL, 7 mmol), a piece of VAR fabric (8 cm diameter) was added. Tosyl chloride (1.8 g, 9.4 mmol) was added at 0 °C, and the mixture was stirred for 4 h at 0 °C. After transferring the fabric to another bath of fresh 40 mL of DMF, compound **2** was added and the mixture was stirred at 80 °C for 8 h. Finally, the fabric was washed with H_2O and dried at 60 °C for 20 h in the oven. The same experimental procedure was followed for the binding of compound **3** to the VAR fabric.

Anchoring of EPTAC onto VAR Fabrics (Leading to VAR1). EPTAC (1 mL) was dissolved in 50 mL of DMF at room temperature. A piece of VAR fabric (8 cm diameter) was immersed in this bath under stirring. After 10 min, the temperature was increased to 60 °C. Then, NaOH (0.8 g, 20 mmol) was added in portions, and the mixture was agitated for 10 min. The fabric sample was then removed from the bath, rinsed several times with H_2O, and acidified with 1% acetic acid (1 mL). Next, the fabric was washed with H_2O again and dried at room temperature.

Characterization Methods of Modified Fabrics. Infrared (IR) spectra were obtained on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies).

Raman measurements were recorded with a Renishaw confocal spectrometer upon excitation at 514 nm at 10% of 0.265 mW power and with xL50 length. The corresponding data were obtained and analyzed with Renishaw Wire and Origin software. Thermogravimetric analyses were acquired using a TGA Q500 V20.2 Build 27 instrument by TA in a nitrogen (purity >99.999%) inert atmosphere.

Scanning electron microscopy (SEM) secondary electron images were acquired utilizing an FEI Quanta Inspect microscope operating at 10 kV accelerating voltage.

Wettability. The wettability of the VAR fabric samples was determined by the water contact angle (WCA) test to investigate the hydrophilicity or hydrophobicity of the fabric. The measurements were done using a custom-made experimental setup, with distilled water in the static mode of the sessile droplet method, on both intact and treated samples. Using a 2.0MP500x USB digital microscope, images were taken of a 5 μL water droplet on the surface of each substrate within 30 s of droplet deposition. Droplet profiles were analyzed by using standard MATLAB functions. Briefly, images were first converted to gray scale. For the calculations of the WCA, the intersection between the apparent vertical symmetry axis of the droplet and the solid/liquid interface was chosen as the origin of the coordinates. The edge profiles weretreated in polar coordinates (r) since polynomial functions can be fitted satisfactorily to the smoothly varying $r(\theta)$ with θ. The WCA values were converted back to Cartesian coordinates, resulting from the derivatives at the contacts of the left and right sides of the droplet with the surface. The value of the WCA for the specific sessile drop was obtained as the average of the right and left contact angles, the deviation of which was less than 2°. Four sessile droplets were placed on each sample, measuring 20 × 10 cm, and the final WCA value was obtained from the average of the four measurements. The WCAs were measured at room temperature.

Antibacterial Activity. The antibacterial protection of the modified VAR fabric was determined using two methods. The ISO 20645 method was used for qualitative determination,[31] with the Gram-negative Bacterium *E. coli* DH5α. The bacterial strain used was inoculated into LB nutrient broth and grown overnight at 37 °C with constant agitation at 220 rpm. One milliliter of a 1−5 × 10^8 CFU/mL working culture was added, with vigorous shaking to evenly distribute the bacteria, to 150 mL of agar. The bacterial culture was used to inoculate the upper agar layer, consisting of 5 ± 0.1 mL of LB nutrient with 7.5 g/L agar (precooled to 45 ± 1 °C), in which 25 ± 5 mm diameter test specimens were placed. The bottom layer consists of a culture medium free of bacteria. Using sterile forceps, the samples were pressed on the nutrient medium until the texture of the fabric was uniformly imprinted. Petri dishes were incubated for 18−24 h at 37 °C. The level of antibacterial activity is assessed by examining the extent of bacterial growth in the contact zone between the agar and specimen and, if present, the extent of the inhibition zone around the specimen.

An *in situ* antimicrobial susceptibility test method, based on *in vivo* measurements of cyanobacteria chlorophyll α (Chl α) fluorescence, was used to quantify the antibacterial protection.[32,33] In summary, the unicellular cyanobacterium *Synechococcus* sp. PCC7942 (Collection Nationale de Cultures de Microorganismes CNCM, Institut Pasteur, Paris, France) was cultured in the BG11 medium[34] under white fluorescent light (100 $\mu E \cdot m^{-2} \cdot s^{-1}$), in an orbital incubator (Galenkamp INR-400) at 31 °C and aeration with 5% v/v CO_2 in air.[35] To determine the antibacterial protection of the fabrics, an appropriate amount of PCC7942 cells was harvested from the culture suspensions by centrifugation (5000 rpm, 5 min) and resuspended in buffered BG11, so that the concentration of Chl α was at 52.0 $\mu g \cdot mL^{-1}$. Chl α concentration was determined in DMF extracts of cell pellets according to Moran 1982.[36] A drop of the cyanobacteria sample, 0.05 mL in volume, is transferred to each fabric sample, creating a spot up to 3.0 mm in diameter. Growth or growth inhibition of cyanobacteria in VAR samples was monitored by measuring Chl α fluorescence (F_0) every 2 h for 10 days, using a PEA fluorometer (PEA, Hansatech Instruments LTD, Norfolk, UK), after first adjusting the samples to darkness for 15 min with an appropriate clip. F_0 was the first reliable Chl α fluorescence measurement at 20 μs. According to eq 1 and the Mi index, the normalized fluorescence changes of the cyanobacteria in each sample are calculated,

$$M_l = \frac{F_{0_i} - F_{0_0}}{F_{0_0}} \times 100 \quad (1)$$

where F_{0_0} is the value of Chl α fluorescence of cyanobacterium at zero contact time and F_{0_i} is the value of Chl α fluorescence of cyanobacterium after 1, 2, ..,i days.

The material's antibacterial action is represented by the Bacterial Protection Index (BPI) Π_7, given by the eq 2:

$$\Pi_{10} = \frac{M_{U_{10}} - M_{T_{10}}}{M_{U_{10}}} \times 100 \quad (2)$$

where $M_{U_{10}}$ is the change in cyanobacterial Chl α_{F0} value on the untreated sample after 10 days of incubation and $M_{T_{10}}$ is the change in the cyanobacterial Chl α_{F0} value on the treated sample after 10 days of incubation.[37]

Throughout the measurements, the samples are kept in an incubator under white fluorescent light (100 $\mu E\ m^{-2}\ s^{-1}$) at 31 °C. All experiments were performed in three replicates using different cyanobacterial cell cultures.

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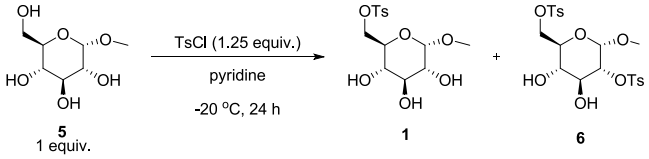
RESULTS AND DISCUSSION

VAR fabric largely consists of cellulose and, to a lesser extent, Kevlar aramid fibers. Aiming at the optimization of the VAR coating experiments, as well as to better understand the chemical behavior of the fibers at the molecular level, we synthesized and studied a model compound with a chemical structure analogous to that of cellulose. Along these lines, we designed a sugar bearing a functionalized primary hydroxyl group through which the anchoring of the desired compounds can take place. We started with the selective tosylation of the primary hydroxyl group of methyl-α-D-glucopyranose, using tosyl chloride (Scheme 1).[27] The tosyl moiety is an excellent leaving group that can be replaced by a variety of nucleophiles, such as amines, alkoxides, azides, etc. Using this modification strategy, one can attach compounds possessing antibacterial, water repellent, and other desired properties to the VAR fabric and, more general, to all types of cellulose materials.[27]

Scheme 1. Tosylation of Methyl-α-D-glucopyranose 5



Our first tosylation experiments were carried out using temperatures in the range −5 to 0 °C. However, under these conditions, the sugar bearing two tosyl groups was obtained as the main product. For this reason, the reaction was then carried out at −20 °C, whereupon the yield of the desired product **1** was significantly improved (39% after purification with column chromatography).[27] Compound **1** was then used in the model studies of the binding of molecules inducing characteristic properties to the cellulose/aramid fiber, VAR.

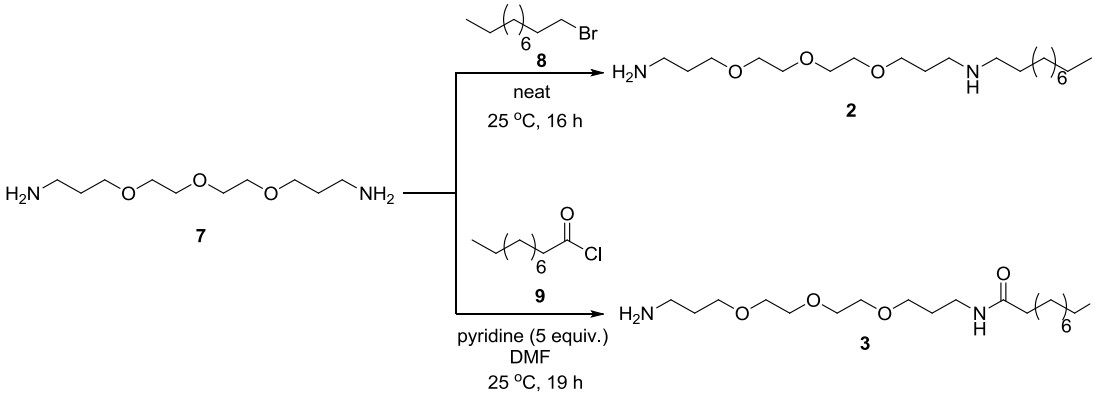
Long-carbon-chain organic molecules can be used as water repellent agents due to their lipophilic character.[38] Therefore, we chose to synthesize two long, linear molecules having a free primary amine suitable for anchoring on the VAR/cellulose material we wanted to modify. The first compound results in from the substitution reaction of bromodecane with 4,7,10-trioxa-1,13-diaminotridecane (Scheme 2).[28] Upon using triethylamine as the base and DMF as the solvent, the desired product is obtained in a very low yield. Alternatively, use of an excess amount of bromodecane, in the absence of solvent, leads to **2** in 67% isolated yield. Next, we tried reacting one of the amine moieties of compound **7** with decanoic acid using hydroxybenzotriazole (HOBt) and *N*,*N*′-diisopropylcarbodiimide (DIC); however, both the disubstituted and monosubstituted products were obtained, making their separation/purification highly demanding.[39] The desired compound was alternatively synthesized from the condensation of decanoyl chloride with 4,7,10-trioxa-1,13-diaminotridecane.[40] Decanoyl chloride results from the reaction of decanoic acid with thionyl chloride ($SOCl_2$). For the condensation reaction, we used pyridine in DMF as the solvent (Scheme 2), obtaining the desired product **3** in a 37% isolated yield.[29]

Prior to anchoring the compounds inducing the required properties to VAR, we optimized the modification reaction conditions using the reaction of compound **1** (simulating cellulose) with the simple linear amine butylamine (Scheme 3).[30] Different solvents, such as ethanol, acetonitrile, or DMF were used, with acetonitrile providing the best results. Product **10**, having an amine attached to the former primary alcohol's carbon atom, was thus isolated in 42% yield. It must be noted that the relatively low isolated yields of compounds **1** and **10** do not signify a problematic surface functionalization of the material to be modified. This is due to the fact that the possible tosylation (and/or the consecutive amination) of other free alcohol moieties does not impose any problem at all in the case of the surface functionalization. Furthermore, column chromatographic purification, a procedure not applied to the surface functionalized material, decreased the isolated yields of compounds **1** and **10**.

Scheme 3. Synthesis of Compound 10

Having the optimum anchoring conditions in hand, we started studying the coating of VAR fabrics, using tailor-made compounds inducing the desired properties to the material. Attachment of compounds **2** or **3** to cellulose takes place through the tosylated hydroxyl groups of cellulose, as in the case of model compound **1**. Then, through an S_N2 substitution reaction, the desired amine (**2** or **3**) is attached to the cellulose (Scheme 4).[41,42]

Scheme 2. Synthesis of Compounds 2 and 3



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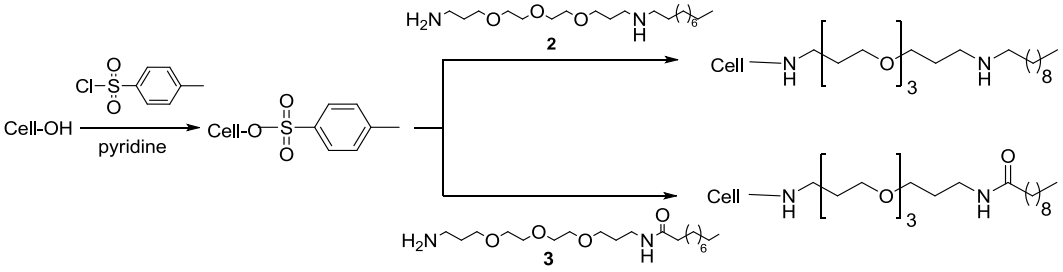
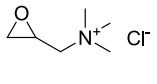
Scheme 4. Chemical Modification of Cellulose Fabric (VAR) using Compounds 2 and 3 through an S_N2 Substitution Reaction



Another modification strategy studied herein is that with 2,3-epoxy-propyltrimethylammonium chloride (EPTAC, Figure 1), a quaternary ammonium salt known in the literature for



EPTAC

Figure 1. 2,3-Epoxy-propyltrimethylammonium chloride (EPTAC).

its antibacterial properties.[43] The attachment of EPTAC on VAR can take place after deprotonation of either the amide groups of its Kevlar component or/and the alcohol groups of its cellulose component with a base (NaOH), followed by a nucleophilic attack of the Kevlar- or cellulose-based anions on EPTAC's epoxide, resulting in the epoxide's opening.[44] Following this modification of VAR, its surface acquires trimethylammonium moieties that induce antibacterial properties.

Chemical Characterization/Morphology of the VAR Surface. VAR fabrics, consisting of both Kevlar and cellulose fibers, present IR spectra with a plethora of strong absorption bands, such as at 1641 cm^{-1} attributed to the carbonyl amide stretching, at 1390 and 1525 cm^{-1} due to the C−N stretching, N−H vibrational modes at 3300 cm^{-1}, at 1371, 1479, and 2918 cm^{-1} due to C−H stretching, as well as at 1371 cm^{-1} owned to the H−O−C bending of the polysaccharide rings of cellulose (Figure 2a).[45,46] The absorption band at 898 cm^{-1} is characteristic of β-glycosidic linkage between glucose units, while the band at 1061 cm^{-1} is assigned to the vibration of C−O in the pyranose ring existing in the cellulose chain backbone.[47] The intense modes described above cover the expected N−H vibration modes for **VAR1** and **VAR3** materials. The same goes for the amide bond in the IR spectrum of **VAR2**, overlapping with the band at around 1641 cm^{-1} in the IR spectrum of VAR.

Raman spectra for the parent VAR fabric and modified materials, recorded upon excitation at 514 nm, are shown in Figure 2b. The Raman spectra of all materials are dominant with a band attributed to VAR fabrics, with the most prominent modes at 1614 and 1649 cm^{-1} deriving from the stretching vibrational mode of the C−C phenyl ring and the C═O unit.[48]

The thermal stability of the modified fabrics was evaluated by thermogravimetric analysis (TGA) recorded under a nitrogen atmosphere. Intact VAR was found to be thermally stable up to 200 °C, exhibiting a 54% mass loss up to 585 °C. On the other hand, **VAR1** shows a higher mass loss of 64% up to 585 °C, while **VAR2** and **VAR3** lose almost 80% of their mass at the same temperature region (Figure 2c). The higher mass losses for all three VAR-modified materials validate

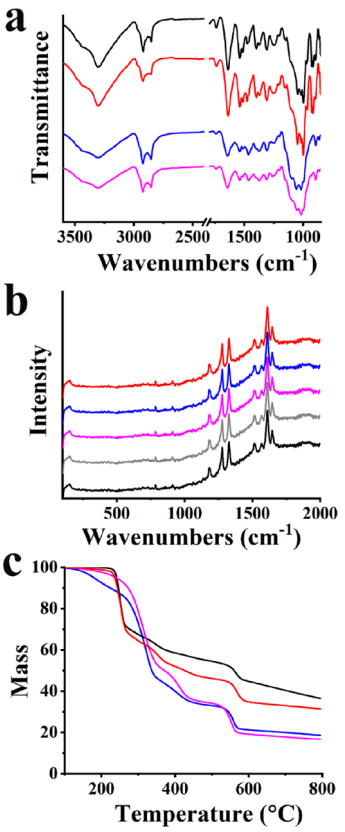


Figure 2. (a) IR spectra, (b) Raman spectra (514 nm), and (c) TGA graphs for **VAR1** (red), **VAR2** (pink), **VAR3** (blue), and intact VAR fabric (black).

successful functionalization and grafting of the organic components onto the fabric. The similarity in mass loss observed in **VAR2** and **VAR3** up to 585 °C can be attributed to the similar molecular weight of the attached organic molecules, which notably surpasses that of EPTAC in **VAR1**. All three VAR-modified materials displayed substantial mass losses up to 800 °C, 81%, 83%, and 69% for **VAR3**, **VAR2**, and **VAR1**, respectively, in contrast to the 64% mass loss observed in the intact VAR fabric. This observation indicates that the covalent modification process induces additional thermal degradation of the polymer chains present in the VAR fabric.

Scanning Electron Microscopy. Our study of both intact and modified VAR fabrics included a thorough examination of their surface morphology using scanning electron microscopy (SEM). The SEM images depicted in Figure 3 reveal that untreated VAR fabrics possess a smooth texture with minimal impurities. In contrast, the modified VAR variants (**VAR1**, **VAR2**, and **VAR3**) display a well-coated surface. The coating of the fiber surface is a notable outcome of the modification

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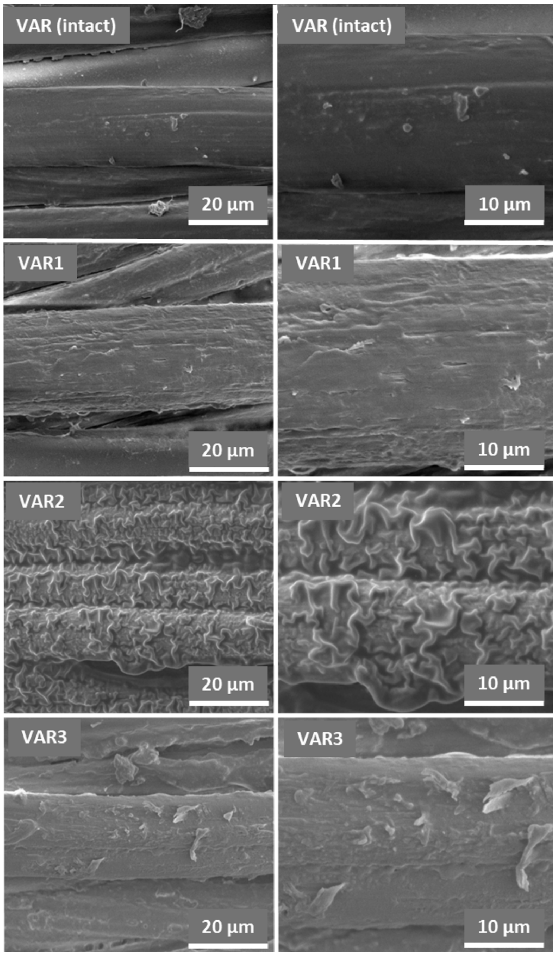


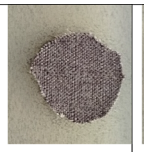
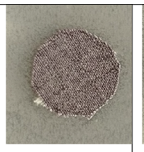
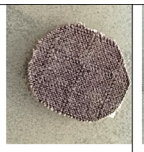
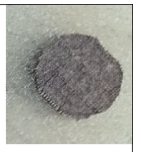
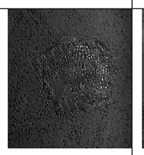
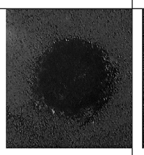
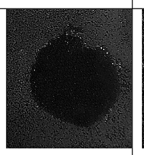
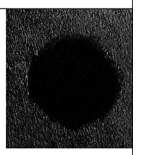
Figure 3. SEM images of intact VAR, functionalized VAR with EPTAC (**VAR1**), functionalized VAR with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentanamide (**VAR2**), and functionalized VAR with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)-ethoxy)propyl)pentan-1-amine (**VAR3**).

process applied to the VAR fabrics. Notably, the VAR fibers remain structurally intact, showing no signs of degradation. These images serve as compelling evidence of the successful modification of VAR materials, providing insight into the significant enhancement achieved in terms of the improved antibacterial activity.

Wettability. The value of the contact angle between the water droplet and surface of a material provides straightforward observation of its wettability properties. Fabrics with a water contact angle <90° (WCA) can be categorized as hydrophilic, while those with a WCA value between 90 and 150° are characterized as hydrophobic.[49] Figure 4 presents the images of sessile droplets on both intact and treated fabric surfaces. The intact sample has a WCA value of 129.7° indicating a relatively hydrophobic surface. EPTAC treatment does not appreciably change the wettability of the fabric, slightly increasing the WCA value to 131.8°. On the other hand, modification with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)-ethoxy)propyl)pentanamide or *N*-(3-(2-(2-(3-aminopropoxy)-ethoxy)ethoxy)propyl)pentan-1-amine shows a comparatively lower WCA value, 118.1° and 97.0°, respectively. However, despite this decrease in WCA, the hydrophobicity of the fabrics remains at satisfactory levels.

Antibacterial Properties. The agar plate diffusion test, with *E. coli* Gram-negative bacterial pathogens, was used for the qualitative evaluation of the antibacterial activity of the treated textiles. The nongrowth of organisms under and around the test sample is an indication of the ability of the antibacterial substance to protect against bacteria. The images with agar plates after the test are presented in Table 1.

Table 1. Antibacterial Effect of Treated VAR Fabrics[a]

				
				
Inhibition zone	Ø	Ø	Ø	Ø
Growth	heavy	none/slight	none	none
Assessment	-	good effect/ limit of efficacy	good effect	good effect
	(a) Intact VAR	(b) VAR1	(c) VAR2	(d) VAR3

[a](a) Intact VAR, (b) VAR modified with EPTAC, (c) VAR modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)-pentanamide, and (d) VAR modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentan-1-amine.

Evaluation of the images in the second row of Table 1, where the sample is not present on the plate, shows that there is a significant inhibition of bacterial growth on all three treated fabrics, with no detectable zone of inhibition. In particular, under the intact VAR fabric, there is a full growth of bacteria. A very slight growth is observed under the VAR fabric modified with EPTAC, while VAR fabric treated with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentanamide or *N*-(3-

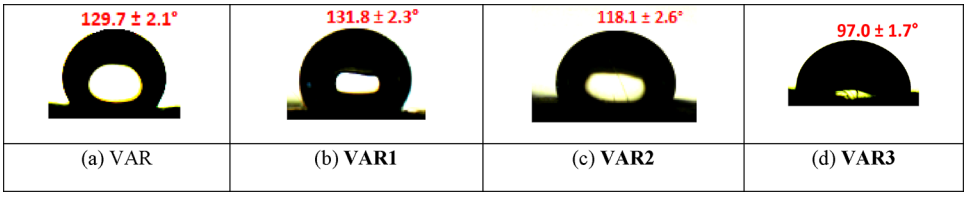


Figure 4. Wettability effect of VAR fabrics: (a) intact VAR fabric, (b) VAR1 fabric modified with EPTAC, (c) VAR2 fabric modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentanamide, and (d) VAR3 fabric modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)-propyl)pentan-1-amine.

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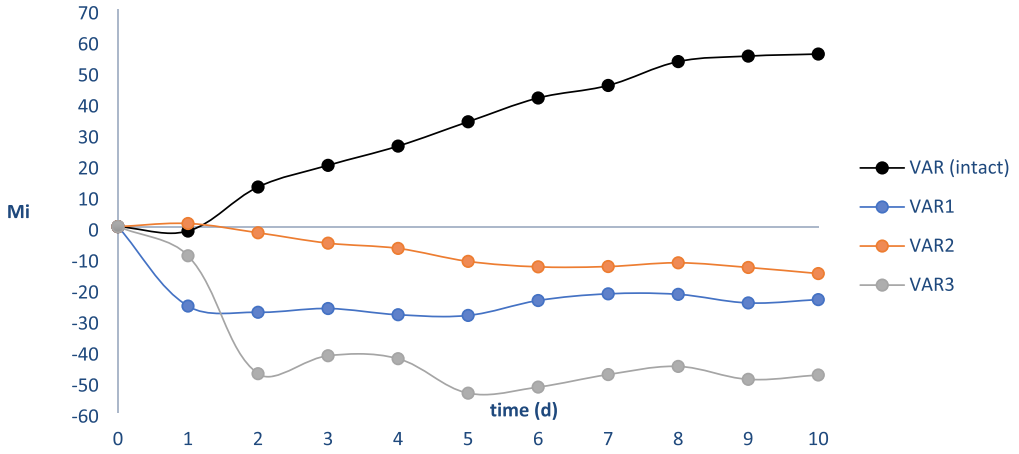

Figure 5. $M_t$evolution curves of cyanobacteria on VAR samples: (black) intact VAR fabric, (blue) **VAR1** fabric modified with EPTAC, (orange) **VAR2** fabric modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentanamide, and (gray) **VAR3** fabric modified with *N*-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentan-1-amine.

(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)pentan-1-amine strongly inhibits the growth of bacteria under them.

An increase in Chl *α* fluorescence (F_0) intensity corresponds to the ability of cyanobacterial cells to proliferate, while a decrease in Chl *α* fluorescence (F_0) intensity means that cyanobacterial cell cannot proliferate; thus, the Chl *α* degradation has begun, and the cells are dying. Along these lines, negative or lower values on comparable surfaces are interpreted as enhanced antibacterial behavior. Figure 5 shows the changes in the bacterial population of the samples, as reflected in the changes in the M_t values. The untreated sample shows an increase in M_t values until the 10th day, when the growth cycle of the cyanobacterial cells in the VAR fabric is completed, while all modified VAR fabrics show a decrease in M_t values, suggesting that the substances utilized to modify the material not only inhibit the proliferation but also decrease their viability.

Table 2 shows the values of the bacterial protection index (Π_{10}), which are all over 100 (Π_{10}: **VAR1** 142.3, **VAR2** 127.2, and **VAR3** 186.0), showing the excellent level of antibacterial protection that the substances used provide to the modified fabrics.

Table 2. Π_{10} (Bacterial Protection Index) Values for the Examined VAR Samples: VAR1 Modified with EPTAC, VAR2 Modified with *N*-(3-(2-(2-(3-Aminopropoxy)ethoxy)ethoxy)propyl)pentanamide, and VAR3 Modified with *N*-(3-(2-(2-(3-Aminopropoxy)ethoxy)ethoxy)propyl)pentan-1-amine

parameter	VAR1	VAR2	VAR3
Π_{10}	142.3	127.2	186.0

CONCLUSIONS

In summary, herein, we disclose a thorough study of the binding mechanisms through which VAR fabrics can be modified using a model compound simulating cellulose materials. Moreover, we describe the synthesis of new organic molecules with antibacterial and water repellent properties and successfully employ them to extensively modify VAR fabrics for the first time. We utilize IR and Raman spectroscopies, thermogravimetric analysis, and SEM imaging as well as contact angle and antibacterial properties measurements to determine the effect that the binding of these compounds has on the properties of the VAR materials. Our results suggest that the water repellency of the VAR fabric samples slightly increases upon their modification using EPTAC. When long-carbon-chain compounds are used, water repellency decreases, albeit it remains at satisfactory levels. Interestingly, all three compounds endow excellent antibacterial properties to the VAR fabrics. Using our modification strategy, one can attach compounds possessing antibacterial, water repellent, and other desired properties not only to VAR fabrics but also to all types of cellulose-containing materials. Technical fabrics increasingly attract the attention of the corresponding industry; therefore, it is of ultimate importance to continue studying and modifying them to discover new useful applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c05552.

Experimental procedures; compounds characterization data; and copies of ^{1}H, ^{13}C NMR, and HRMS spectra. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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