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Hydrophobization of the Man-Made Cellulosic Fibers by Incorporating Plant-Derived Hydrophobic Compounds

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needs greener alternatives to the existing hydrophobization approaches—which are essentially based on nonrenewable and expensive hydrophobizing agents and adversely impact the environment. Herein, we report the production of novel hydrophobic cellulose based fibers produced by incorporating naturederived hydrophobic additives—betulin (BE) and betulinic acid (BA) using the Ioncell technology. The incorporation process is simple and does not require any additional step during dry-jet wet spinning. Spinning dopes containing up to 10 wt % BE and BA were spinnable and the spun fibers (10BE and 10BA) maintained their mechanical properties. Compared to BE, BA-incorporated fiber showed homogeneous surface morphology suggesting the



increased compatibility of BA with cellulose. Consequently, in contrast to BE-incorporated fibers, BA-incorporated fibers demonstrated higher yarn spinnability. Both 10BE and 10BA fibers showed hydrophobicity (water contact angle $>90^{\circ}$) in the produced nonwovens and yarns. In summary, we developed a system for hydrophobizing man-made cellulose fiber via a simple eco-friendly and cost-effective way, which has potential for scalability and industrial applications.

KEYWORDS: Hydrophobization, Man-made cellulose fibers, Ionic liquid, Betulin, Betulinic acid, Ioncell technology, Dry-jet wet spinning

INTRODUCTION

The phenomenon of "fast fashion" has promoted the use of low-cost synthetic fibers, which is one reason for the enormous expansion of global textile production by 50% during 2000-2015.¹ The production and use of synthetic fibers has several adverse effects on the environment such as microplastic accumulation and increasing carbon footprint.² Cellulose fibers produced from sustainable natural resources represent an environmentally friendly and economical alternative to synthetic fibers. Although cotton is the most popular natural cellulose fiber in textile industries, it has an ecological footprint close to synthetic fibers due to an unsustainable consumption of water and pesticides.³ As an alternative to cotton fiber, the demand for man-made cellulose fibers such as viscose and lyocell fibers are increasing. However, the viscose process has the disadvantage of requiring harmful chemicals that can potentially poison work forces and the environment.⁴ On the other hand, lyocell-process-based fibers are considered environmentally friendly textile fibers, as the process uses eco-friendly solvents, that can be recovered and recirculated.⁵ Ioncell fibers are lyocell type fibers produced via dry-jet wet spinning using a nontoxic and environmentally benign solvent, 1,5-diazabicyclo [4.3.0] non-5-ene acetate ([DBNH]OAc), a nonimidazolium-based ionic liquid.⁶ Ioncell fibers exhibit

outstanding fiber properties that are superior to cotton, viscose, and NMMO type lyocell fibers. $^{7-9}$

Similar to cotton fibers and other natural fibers, man-made cellulose fibers are hydrophilic because the hydroxyl groups in the anhydroglucose units (AGU) of the cellulose molecules in fibers or films are exposed to the surface.^{10,11} Cellulose molecules are stacked together by hydrophobic interactions and van der Waals forces, and molecular sheets are formed which have a hydrophobic interior and hydrophilic periphery and surface.¹² Rendering cellulose fibers hydrophobic is one of the key challenges for man-made cellulose fibers. Due to this hydrophilic behavior, synthetic fibers are favored for the production of hydrophobic textiles. Several different techniques were used to introduce water repellency in cellulose-based textile finishing, which involves the use of fluorine-based^{13–15} or silane-based compounds.^{16,17} However, these fluorocarbons or silane-based compounds are not environ-

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Figure 1. Structure of betulin (left) and betulinic acid (right).

mentally benign due to their toxicity or harmful effect toward the environment.^{18,19} As an example, the long-chain fluorocarbons raised serious health concern of animals and humans due to their bioaccumulation and biomagnification behavior.^{18,20} As a result, short-chain fluorocarbons—due to their reduced bio accumulative behavior—were considered as a surrogate for long-chain fluorocarbons. However, short-chain fluorocarbons were found to be similarly persistent as longchain fluorocarbons and the long-term effects of these shortchain fluorocarbons are still unknown.¹⁸ These limitations stipulate the need for discovery and applications of the ecofriendly hydrophobizing agents.

In nature, plant surfaces are modified with natural hydrophobic agents that are secreted in the plant cuticle.²¹ These hydrophobic agents such as triterpenes, waxes, and glycolipid (e.g., suberin, cutin) facilitate the water repellency of the plant surface and removal of the particulate deposition such as dust or spores.²² Moreover, during the pulping process, debarking produces birch bark enriched with triterpenes,²³ which are mostly incinerated to generate thermal energy.^{24,25} The extraction of such natural triterpenes to produce value-added products is a better utilization route than their combustion. Betulin (BE) (Figure 1) is one of those triterpenes which constitutes up to 25% of the bark in white birch trees.²⁶ Another pentacyclic triterpene is betulinic acid (BA) (Figure 1) that belongs to the lupane family.

BA can be either extracted form plane bark²³ or chemically synthesized (with high yield) from BE using green chemistry approaches.²⁷ Toxicological study of the betulin and betulinic acid in animals (such as rats and dogs for betulin's toxicity; mice and rats for betulinic acid's toxicity) revealed that both compounds are nontoxic.^{28,29} These pentacyclic triterpenes are known to have a wide range of pharmaceutical activities such as antivirus, anti-inflammatory, anticancer, and other properties.^{25,30} Makarov et al. produced BE-cellulose composite fibers using the NMMO-based lyocell process to introduce antifungal properties into the fibers.³¹ BE was previously also used to hydrophobize cellulosic textiles,¹⁰ but BA has not been used before for hydrophobic textile production. Huang et al. demonstrated the approach of hydrophobizing cotton textiles using BE via physically adhered BE coatings as well as covalently attaching BE to the cellulose.^{10,32} Recently, a waterrepellent textile was produced via postmodification of the textile using natural wax.³³ These postmodifications of the textiles require additional procedures, time, and costs.

As an alternative to postmodification for textile hydrophobization, we investigated the applicability of the incorporation technique for introducing natural additives such as betulin and betulinic acid during the dissolution process. Additive incorporation refers to codissolution of additives and cellulose without any further process step. This study is based on two hypotheses: (i) The incorporation of natural additives produces homogeneous bicomponent fibers, rendering the single fibers hydrophobic. (ii) These nature-derived additives show good compatibility with the cellulose matrix.

In order to investigate the development of hydrophobicity of the different biobased additives, betulin and betulinic acid were incorporated into cellulose films and the additive amount was optimized. The optimized amount (10 wt %) of both BE and BA additives were incorporated into the cellulose solution and the spinnabilities of both additive-incorporated dopes were assessed. Furthermore, the effect of additive incorporation was addressed based on the mechanical properties, water contact angle measurements and surface properties analysis using X-ray photoelectron spectroscopy, SEM imaging, and Raman mapping. We also spun the additive-incorporated fibers into yarn and investigated the yarn spinnability compared to the additive-free fibers.

EXPERIMENTAL SECTION

Raw Material. Birch prehydrolyzed Kraft pulp was obtained from Stora Enso, Enocell, Finland (intrinsic viscosity 482 mL/g; M_w 161 kDa and M_n 49.3 kDa and polydispersity index 3.3; hemicellulose content \sim 7%). White postconsumer cotton in the form of hospital bed sheets was provided by the Uusimaa Hospital Laundry (Uudenmaan Sairaalapesula Oy, Finland), which was pretreated by the E-EG-P-A sequence (Alkaline extraction-Endoglucanase enzymatic treatment-Hydrogen Peroxide treatment-Acid washing). The intrinsic viscosity of the final treated cotton was 417 mL/g. Both pulp and postconsumer cotton were ground using a Wiley Mill containing a 1 mm sieve. The ionic liquid (IL) [DBNH][OAc] was synthesized using an equimolar amount of acetic acid (glacial, 100%, CAS number 64-19-7, Merk, Germany) and 1,5-diazabicyclo [4.3.0] non-5-ene (DBN, 99%, Fluorochem, CAS number 3001-72-7): betulin (Mw 456.7; CAS number 473-98-3) technical grade (93%) and pure betulin was purchased form Innomost Oy. Betulinic acid $(M_w$ 442.7; CAS number 472-15-1) was obtained from Acros Organics.

Suberin and Cutin was provided by the Department of Chemistry, University of Aveiro. Suberin was isolated from cork particles of 40– 60 mesh supplied by Amorim & Irmãos, S.A. (Santa Maria de Lamas, Portugal). Suberin extracts were obtained by alkaline methanolysis with 2% sodium methoxide according to previously published procedure.³⁵ The analysis of suberin composition by GC–MS was carried out as TMS derivatives³⁵ (Supporting Information, SI, Figure S7; Table S7).

However, cutin was extracted from the white grape skin. The grape skins from mixed pomaces of different white grape varieties were supplied by wine cooperative from the Douro region (Portugal). The grape skins were separated from stalks and seeds and extracted by water (solid-to-liquid ratio of 10) at 100 °C for 1 h.³⁶ The skins were washed with water and dried at 40 °C for 12h. The cutin was isolated from the dried grape skins by extraction with dichloromethane for 6 h in Soxhlet.³⁷ The analysis of extract was carried out by GC–MS as TMS derivatives³⁷ (SI Figure S8; Table S8).

Dissolution of Cellulose and Additives. [DBNH][OAc] was first melted at 80 °C, then IL was added to a kneader which was preheated at 80 °C. In the case of the additive incorporated dope, first the additive was added to IL and stirred (30 min for betulinic acid, 120 min for betulin) at 80 °C with 30 rpm. Compared to BE, BA showed higher solubility in ionic liquid. A previous study reported that the presence of a hydrophilic carboxylic group in the BA increases the solubility of BA in the solvent DMSO compared to BE.³⁸

Once the additive was dissolved in the IL, the cellulose pulp was added and blended for another 90 min at 80 °C with 30 rpm at reduced pressure (10–30 mbar). The cellulose + BE or BA concentration of the dope was adjusted to 13 wt %. The solutions were filtered through a hydraulic press filter device (metal filter mesh with $5-6 \mu m$ absolute fineness, Gebr. Kufferath AG, Germany) at 80 °C to remove undissolved substrate, which would lead to unstable spinning. The prepared dope was finally shaped into the dimensions of the spinning cylinder and solidified upon cooling overnight.

Preparation of Additive-Incorporated Cellulose Film. The total concentration of the solute (cellulose or cellulose-additive) 5.6 wt % was used for all the films. The additives were dissolved in the IL prior to addition and dissolution of cellulose. Films were prepared using a spin-casting process according a standard laboratory procedure.³⁹ Film casting was done using a K-rod coater (K202 control coater). The thickness of the films was adjusted with the rod of 500 μ m diameter maintaining speed of 6. After pouring the cellulose or cellulose-additive solution, both the rod and the substrate (glass plate 20 × 20 cm²) were heated to 80 °C. After that, the films were casted in a solution state. The solution state casted films were placed in the oven for 10 min to ensure removal of possible defects. Then, the films were coagulated in a deionized water bath overnight. During the coagulation period, the water was changed several times to wash away the IL. Finally, the films were fixed in flat metal plated using tape and dried in 50% RH at 23 °C for 24 h.

Rheological Measurement. Rheological properties of the dopes were analyzed using an Anton Paar MCR 301 rheometer containing 25 mm parallel plate geometry (gap size 1 mm). The shear rate range was 0.01 and 100 s⁻¹. Dynamic frequency sweeps were performed with a strain of 0.5% within the angular frequency range of 0.1–100 s⁻¹ at various temperatures from 60 to 90 °C, the complex viscosity, storage, and loss moduli were recorded during measurements. The zero shear viscosity was calculated using cross model assuming the Cox–Merz rule was valid.⁴⁰

Spinning. Multifilaments were spun with a customized laboratory piston spinning system (Fourné Polymer Technik, Germany). The solidified spinning dope was heated to 80 °C in the spinning cylinder to form a highly viscous fluid. The molten solution was then extruded through a 200-hole spinneret with a capillary diameter of 100 μ m and a capillary length to diameter ratio (L/D) of 0.2. After the fluid filaments had passed an air gap of 10 mm, they were coagulated in a water bath (8–12 °C) in which they were guided by Teflon rollers to the godet couple. The extrusion velocity ([L]/[t]) was set to 3.5 m min⁻¹. The spun fibers were washed with hot water (80 °C) and airdried. After that the spun fibers were analyzed using different characterization techniques (SI Table S2)

Carbohydrate Analysis and Soxhlet Extraction to Measure Additive Content of the Spun Fibers. Carbohydrate analysis was performed according to the NREL/TP-510-42618 standard and the samples were analyzed using an ion chromatograph (ICS-3000 HPAEC-PAD) with a Dionex CarboPac PA20 column (Thermo Fisher Scientific, U.S.A.). The results were calculated according to procedures published by Janson.⁴¹ The amount of additive was calculated as percent on the dry sample.

Additives were Soxhlet extracted for 6 h from the additiveincorporated fibers (1-2 g) using methanol (250 mL) as a solvent. After that, the solvent was evaporated and weight (g) of the extracted additives was reported. The extraction was repeated twice for each sample. The percentage of additive was calculated using the initial mass of the fiber and the mass of the extracted additive which can be described as follows:

amount of additive (%) =
$$\frac{\text{amount of extracted additive } (g) \times 100}{\text{Initial amount of fiber } (g)}$$
 (1)

Fiber Testing. The tensile properties of the spun fibers (n = 20) in conditioned and wet state were determined by an automatic single-fiber tester Favigraph (Textechno H. Stein GmbH & Co, Germany) based on the ISO 5079 standard (20 mm gauge length, 0.6 cN/tex pretension, 20 mm/min test speed, fiber count 20). Samples were conditioned overnight ($20 \pm 2 \degree C$, $65 \pm 2\%$ relative humidity) before the analyses. The slope of the average stress strain curve was used to calculate the elastic modulus of the spun fibers according to ASTM standard D2256/D2256Mf.

Yarn Testing. Mechanical properties of the spun yarns (tenacity (cN/tex) and elongation at break (%)) was measured by a MTS 400 tensile tester equipped with a 50 N load cell having a gauge length of 250 mm and a test speed of 250 mm/min. The yarn was conditioned overnight (20 ± 2 °C, $65 \pm 2\%$ relative humidity) and its average linear density (tex = g/1000m) value was calculated from a 5 m hank of yarn prior to the measurement. Strength realization was calculated as follows:

$$SR(\%) = (mean yarn tenacity/mean fiber tenacity) \times 100\%$$
 (2)

where SR is the strength realization.

Birefringence. Birefringence of fibers was measured using a polarized light microscope (Zeiss Axio Scope, Zeiss AG, Germany). First, the linear density of the fibers was measured using the Favigraph tester, then the fibers were placed under tension between two pieces of double-sided tape on a microscope slide. The optical retardation was determined in three different places along the fiber. Birefringence (Δn) was calculated using the optical retardation of polarized light divided by the diameter. Total orientation (f_t) was obtained via dividing Δn by the maximum value of birefringence (0.062) for cellulose.⁴²

X-ray Diffraction (XRD). X-ray diffraction data were collected in a transmission mode setting of CuK α X-ray instrument SmartLab (RIGAKU) operated at 45 kVand 200 mA. Cellulose fibers were cut into tiny powders by scissors. The powder samples were then pressed into disks using a pellet press instrument with a constant force for 30 s. Powder diffraction data were collected in a continuous mode from 5° to 60° 2 θ by $\theta/2\theta$ scan setting.

The scattering profile was corrected by subtracting air scattering and inelastic contribution. The amorphous cellulose contribution $(I_{\rm bkg})$ was subtracted from the remaining elastic scattering profile using a smoothing procedure as described previously.⁴³

The background corrected profiles were fitted with lattice planes of cellulose II and additional peaks for Betulin and Betulinic acid. For cellulose II crystal, pseudo-Voigt functions was used for $(1\overline{10})$, (002), (110), and (020) diffraction peaks of cellulose II (SI Figure S3). For the Betulin composite, two peaks were added at 12.9 and 14.7 2θ . For the Betulinic acid composite, 7 peaks were added at 9.3, 10.1, 11.8, 12.6, 14.3, 15.4, 16.1, 23.6, and 24.5 2θ (SI Figure S3). The software *lmfit* was used for the fitting. Scherrer equation was used to estimate the crystal widths (CW_{hkl}) as follows:

$$CW_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta}$$
(3)

where K = 0.90 is the shape factor, λ is the X-ray wavelength, β_{hkl} is the full width of half-maximum (fwhm) of the diffraction peak in radians and θ is the diffraction angle of the peak. Estimated amorphous contribution and area under Crystallin peaks of Betuline and Betulinic acid ($S_{additive}$) were used to estimate the crystallinity index (CI) of cellulose material using a range from 8° to 55° 2 θ :

$$CI = 100 \times \frac{\int I(2\theta) d2\theta - \int I_{bkg}(2\theta) d2\theta - S_{additive}}{\int I(2\theta) d2\theta - S_{additive}}$$
(4)

Contact Angle Measurement. Contact angles were measured via a Contact Angle Meter CAM 200 (Aalto University). A 10 μ L water (Milli-Q) droplet was placed onto the material surface. The static contact angle was measured for up to 60 s, of which the first 20 s were considered as the time to reach an equilibrium state.⁴⁴ Hence, the average contact angle was calculated from the data obtained from the remaining 40 s using the Young–Laplace equation.⁴⁴ A final average was calculated from three parallel measurements.

X-ray Photoelectron Spectroscopy (XPS). For the evaluation of the fiber surface composition within the topmost atomic layers, XPS experiments were performed with an AXIS Ultra electron spectrometer (Kratos Analytical, Manchester, U.K.) at low power setting of 100 W and under neutralization. Small fiber bundles were attached onto the sample holder so that they hung partially outside the holder, in order to avoid background signal from the holder. Samples were pre-evacuated overnight to secure stable ultrahigh vacuum conditions during the experiment. Furthermore, a clean reference sample of 100% cellulose filter paper was added to each sample batch to monitor the contamination levels.⁴⁵

Each measurement location was optimized manually. Data acquisition times were extended due to the quite small analysis areas of fibril surfaces. Both low resolution wide scans and high-resolution C 1s and O 1s regions were recorded on multiple locations. Elemental compositions were determined from wide scans, and the carbon chemistry was evaluated from C 1s regional scans, using CasaXPS software and C 1s component fit tailored for celluloses.⁴⁰ According to the analysis of the reference sample spectra recorded, all experiments reported here were performed under clean and stable ultrahigh vacuum conditions.

SEM Imaging. For the cross-section samples, fibers were cryofractured and placed in the cross-section sample holders. The fiber samples or films were placed on top of a carbon tape attached to the sample holder. Before imaging, the samples were sputtered with Au/ Pt for 90 s at 20 mA. After that, scanning electron microscope images were taken using a Zeiss Sigma VP connected to a secondary electron detector with an acceleration voltage of 1.2–1.5 keV.

Raman Mapping. The samples were analyzed with an alpha 300 RA confocal Raman microscope (Witec GmbH, Germany, www. witec.de) at ambient conditions. The Raman spectra were obtained by using a 532 nm frequency doubled Nd:YAG laser (used at 30 mW) and a $100 \times$ immersion oil objective (numerical aperture (NA) = 1.25, coverslip correction 0.17 mm). The Raman system was equipped with a DU970 N-BV EMCCD camera behind a 600 lines/mm grating. The excitation laser was polarized horizontally. The fibers were fixated on objective slides and covered with a glass coverslip (0.17 mm thickness) to avoid fiber movement. The size of each image was $20 \times$ 50 μ m² with 80 points per line and 200 lines per image. An integration time of 0.3 s was applied. Raman images were created using the WITec Suite 5.1 software WiTec GmbH, Germany, www. witec.de) by integration over selected wavenumber regions, with the background being set to zero at four wavenumbers below and above the respective range. Average spectra of the fibers were collected from the Raman images. Raman spectra of betulin and betulinic acid were collected using a $20 \times$ air objective (NA = 0.4) with an integration time of 0.5 s and 20 accumulations. Absorption bands with wavenumbers outside the range of 250-3650 cm⁻¹ were removed and a baseline correction was performed by fitting a fifth order polynomial over selected wavenumber areas.

Yarn Spinning. Fibers were opened (Trash Analyzer 281C, Mesdan Lab, Mesdan S.p.A., Italy) separately and conditioned ($20 \pm$

2 °C, 65 \pm 2% RH) overnight to reduce electrostatic charges during the yarn spinning. The opened fibers were carded (Carding Machine 337A, Mesdan Lab, Mesdan S.p.A., Italy) to obtain a fiber web which was formed into a sliver. It was further elongated with a draw frame (Stiro Roving Lab 3371, Mesdan Lab, Mesdan S.p.A., Italy) and formed into a false-twist Roving. The yarn was spun with a ring spinning machine (Ring Lab 82BA, SER.MA.TES srl, Italy): yarn twist direction: *Z*; twists per meter: 500 for the reference yarn, 400 for the BE yarn, and 450 for the BA yarn. The carded fiber web (nonwoven fabric) prior to the sliver formation was used for the contact angle measurements.

Washing Fastness Test of Nonwoven and Knitted Fabrics. Washing fastness test of the BE and BA coated nonwoven and knitted fabrics were performed according to the ISO 105-C06:2010 standard. The sample were covered with 4×10 cm² multifiber fabric (type DW) and sewed. After that, these prepared samples were placed in a stainless-steel container which contained 10 stainless steel balls and 150 mL of detergent (AATCC 1993 Standard Reference Detergent WOB) solution (detergent/water = 1 g/250 mL). The container was then placed into a customized washing machine (Linitest, Heraeus GmbH, Germany) adjusting the washing parameters (40 °C, 30 min). After the washing cycles, the samples were rinsed thoroughly with deionized water and dried in air.

RESULTS AND DISCUSSION

Rheology and Fiber Spinning. Filament formation in the dry-jet wet spinning process depends on the stretch ability of the cellulose solution and its response to the deformation force inside capillary spinneret holes as well as in the air gap.⁴⁷ The stretch ability of the cellulose solution is connected to the rheological properties. The presence of additives affected the rheology of the dope which can be observed from the changes in zero shear viscosities and complex moduli (Figure 2, SI Table S1).



Figure 2. Comparison of complex viscosities and the dynamic moduli of the standard dope and additive containing dope as a function of shear rate at their spinning temperature 80 °C.

Compared to additive free dope, the additive containing dopes (both 10BA and 10BE dopes) have higher complex viscosities, although the cellulose concentration was 11.8 wt % instead of 13 wt % (Figure 2; SI Table S1). The interaction between additives and cellulose/hemicellulose might create a carbohydrate-additive matrix which restricts the movement of the cellulose chain resulting in higher complex viscosities. An earlier study explained the similar phenomena in the case of the cellulose–lignin blend.⁵ In addition, the carbohydrate-additive network might prolong the relaxation time of the

solution and as a result additive incorporated dopes' crossover points (COP) shifted to lower frequencies (Figure 2; SI Table S1). Although the complex viscosity increased with the addition of additives, the dynamic modulus decreased. The dynamic modulus increases with higher cellulose concentration and higher molecular mass due to increasing entanglements of the cellulose chain.⁸ In case of additive incorporated cellulose solution, the actual cellulose concentration was lower than that in the standard dope, which resulted in a decrease of the dynamic modulus at COP and the elastic properties of the fluid.

Previous studies defined the optimum spinning window for cellulose solution in [DBNH][OAc] of having η_0 of 20 000–30 000 Pa·s and a COP of 2000–5000 Pa at an angular frequency of ca. 1 s^{-1.5,8} The spinning stability is defined by the maximum draw ratio: DR < 2 (nonspinnable), 2–4 (poor), 8–14 (good), and >14 (excellent). Although the viscosities were outside the optimum value, all spinning trials of the additive incorporated dopes were stable with maximum DR of 18 (10 wt % BE-incorporated dope) and DR 15 (10 wt % BA-incorporated dope). Additionally, the spinning was continuous for more than 15–20 min at the target DR (DR 12/titer~1.3 dtex), indicating that the spinnability was excellent for both BE- and BA-incorporated dopes.

According to the results of the Soxhlet extraction, the actual amount of additives retained in the spun 10BE and 10BA fibers was close to the theoretical content (Figure 3). This data



Figure 3. Theoretical and measured percentages (using Soxhlet Extraction and gravimetric measurement) of additives into additive incorporated fibers (10BE and 10BA)

reflects a minor loss of additives in the spin-bath. During initial trials to optimize the additive amount, betulin was incorporated with different percentages (3, 5, 8, and 10 wt %) into

postconsumer cotton fibers. Betulin loss was also minor for those betulin incorporated cotton fibers (SI Table S3; Figure S1)

Mechanical Properties of Fibers and Structure Analysis. The linear density of all the fibers remained similar at a given draw ratio, as the same solute concentration was used. However, 10BE and 10BA fibers showed minor reduction of tenacity and elongation compared to the standard fiber (Table 2). The mechanical properties of the fiber depend on the degree of orientation. Indeed, the total orientation was decreased for both 10BE and 10BA fibers. Previous studies reported that presence of additives interfere with the highly ordered structure formed by the cellulose chains.⁵ Additives create discontinuities in the cellulose structure such as voids which affect the fiber structure.⁴⁸ Moreover, additive particles interfere with the effective alignment of the cellulose molecules along the molecular axis (orientation) at a given draw ratio during the fiber formation process.⁴⁹ Along with the total orientation, the crystallinity was also reduced for both 10BE and 10BA fibers, which may also have contributed to the lower mechanical properties (Table 2). Furthermore, reduced orientation of the cellulose molecules during the spinning process alters the crystals shape or structure of cellulose II. The BE-incorporated (3, 5, 8, and 10 wt %) postconsumer cotton fibers (used for optimizing additive amounts) also showed the reduction in mechanical properties and the fiber orientations with the increased additive incorporation (SI Table S4; Figure S2).

Compared to additive-free fibers, both 10BE and 10BA fibers have a reduced crystal size with a concomitant reduction in total orientation (Table 2). Interestingly, 10BA fibers simultaneously have a smaller crystallite size (31.3 Å) and a higher total orientation (0.698) compared to the crystallite size (33.3 Å) and total orientation (0.626) of 10BE fibers (Table 2), possibly reflecting a stronger association of BA with cellulose to disorganize the crystal structure of the cellulose II.

Yarn Spinning. The produced staple fibers were prepared for yarn spinning by washing with water, air drying, and opening with a fiber opener. No spin-finish treatment was used before yarn spinning because the spin-finish treatment contains a surfactant which removed the additives up to 34% for 10BE and 30% for 10BA (SI Figure S6), thereby, reducing the hydrophobic properties of the final yarns.

The lack of spin finish agent in the fibers caused some heterogeneity in the sliver, which resulted in a higher standard deviation of yarn linear densities and tensile properties (Table 3). In addition, due to the variation of linear densities the tex and twist per meter values of each yarn sample are different (Table 3).

Yarn tensile properties depend on the fiber properties and the yarn structure.⁵¹ The main fiber properties impacting the mechanical properties of yarn are fiber strength and cohesion property. The yarn twist, and thus the twist angle, causes the

Table 2. Mechanical Properties of the Standard, 10BE, and 10BA Fibers and Their Birefringence Properties along with Crystallinity and Crystal Sizes

		tenacity (cN/tex)	elongation (%)	birefringence			
fiber sample	titer (dtex)	cond.	cond.	Δn	f_t	crystallinity(%)	crystal width(Å)
standard	1.30 ± 0.16	46.83 ± 2.02	12.52 ± 1.49	0.044 ± 0.010	0.704 ± 0.16	35.5	34.8
10BE	1.36 ± 0.16	43.43 ± 3.92	11.72 ± 1.71	0.039 ± 0.003	0.626 ± 0.06	31.1	33.3
10BA	1.31 ± 0.04	42.35 ± 2.92	10.86 ± 1.26	0.043 ± 0.005	0.698 ± 0.08	29.4	31.3

 Table 3. Mechanical Properties of the Yarn Produced from

 Reference Fiber, BA and BE Incorporated Cellulose Fibers

sample	linear density (tex)	tenacity (cN/tex)	elongation (%)
standard yarn	40.24 ± 6.27	22.85 ± 3.81	7.48 ± 0.05
10BA yarn	59.66 ± 0.50	20.65 ± 5.11	7.41 ± 0.87
10BE yarn	46.80 ± 1.44	17.79 ± 6.43	7.51 ± 0.52

yarn tensile properties to increase to an optimum level before it starts to decrease due to the higher packing of the yarn. Furthermore, the twist angle (or twist density) depends on the twist per meter and the linear density of the yarn, and it can be expressed as twist multiple (TM).⁵² The calculated yarn twist multiples (*expressed in English cotton count* N_e) were 3.3, 2.9, and 3.6 for reference, BE and BA yarn, respectively.

The strength realization in the yarn can be expressed as the ratio (in %) of the mean yarn tenacity to the mean fiber tenacity.⁵³ In this study, the calculated strength realization for the standard, 10BE, and 10BA yarns were 49%, 42%, and 49%, respectively. The lower strength realization of the BE yarn may result from the lowest TM value (TM = 2.9). The yarn spinning of the BE yarn was challenging because of the fiber stickiness. However, the TM value of the BA yarn is the highest (TM = 3.6), reflecting the increase of the fiber inclination compared to the reference yarn (TM = 3.3). The strength realization of 10BA yarn was the same as that of the standard yarn and the yarn spinnability of the 10BA yarn was better than that of the 10BE yarn. Interestingly, the elongation at break values of each yarn samples was rather similar.

In order to compare tenacity, we prepared yarn from commercial viscose (Danufil 1.3 dtex, 40 mm) and lyocell (Tencel 1.3 dtex, 38 mm) having TM of 3.3 and reported their yarn mechanical properties (Table S4). Tenacity of viscose yarn (Table S4) is clearly lower compared to other yarns due to the lower fiber tenacity (19.2 cN/tex). The strength realization values of viscose and Tencel yarns were 70% and 60% which were higher than the other yarns in this study. The main reason for the higher strength realization values of viscose and Tencel yarns was the spin finish treatment which improved the yarn spinnability and the cohesion between fibers. However, the tensile properties of BE and BA yarns are higher than the viscose yarn and only slightly lower than Tencel yarn despite of the lack of spin finish treatment of 10BE and 10BA yarns.

The tensile properties of lyocell-type yarns were studied extensively. For example, in the study of Soltani and Sohari the tenacities of conventional ring-spun yarns were 12-13 cN/tex

with comparable gauge length and testing speed settings as in our study.⁵⁴ While Kilic and Okur have obtained higher tenacity values (ca. 25 cN/tex) for 20 tex ring-spun yarn,⁵⁵ Chattopadhyay et al. have reported a slightly lower value (ca. 23 cN/tex) for 30 tex ring-spun yarn.⁵⁶ Due to the lack of spin finish treatment, also the standard yarn showed slightly lower tenacity compared to commercial lyocell yarns.

Water Contact Angle Measurement. The wettability of the surfaces (film, nonwoven fabric, and yarn) was measured by static water contact angle (WCA) measurements. Initially, the additive amount for the spun fibers were optimized with cellulose films. It was hypothesized that if the additives would hydrophobize the film surface, it will also introduce hydrophobicity in the staple fibers. In addition, film preparation requires smaller amount of materials which can be beneficial for the optimization process. The WCA of BE incorporated films was compared with the reference film. BE incorporated film showed gradual increase in contact angle with the increasing percentage (3, 6, and 10 wt %) of BE (Figure 4) and hydrophobicity (WCA~85°) was achieved with 10 wt % of BE incorporation.

Similar to the observed hydrophobicity in the films, the same trend in WCA was observed for BE-incorporated postconsumer cotton fibers (3,5,8,10 wt %) which were processed into a nonwoven fabric (Figure 4). On the basis of the hydrophobicity data obtained from films and nonwovens made of BE-incorporated postconsumer cotton fibers, both BE and BA (optimized 10 wt % amount) were incorporated into pulp and spun into staple fibers, which were further studied to investigate the wettability and surface properties. Nonwoven fabrics and yarns made of 10BE and 10BA fibers showed similar hydrophobic behavior. The average WCA of 10BA- and 10BE-incorporated nonwovens were $100^{\circ} \pm 1.2^{\circ}$ and $101^{\circ} \pm 1.9^{\circ}$, respectively (Figure 5). The average WCA of 10BA yarn $(98^{\circ} \pm 0.6^{\circ})$ was similar to the average WCA of 10BE yarn $(100^{\circ} \pm 0.7^{\circ})$ (Figure 5).

Previously, cotton fabric was coated with BE using impregnation of fabric into betulin-ethanol solution and compress molding of the fabric with betulin based films. The study reported the average contact angles were $147^{\circ}-153^{\circ}$ for impregnation technique and $104^{\circ}-123^{\circ}$ for the compress molding.¹⁰ Although the BE- or BA-modified fibers produced from incorporation technique have lower average contact angle, the advantage of this process is that it does not require any additional step during production, or the fibers or fabrics are exposed to any additional solvents.



Figure 4. CA increased with the increasing amount of the BE percentages both in (a) films and (b) nonwoven fabrics made of betulin-incorporated postconsumer cotton.

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Figure 5. Average contact angles of 10BE and 10BA nonwovens and yarns.

Apart from betulin and betulinic acid, suberin and cutin were also incorporated (10 wt %) into the cellulose films and cellulose fibers. Both the films and fibers did not show noticeable hydrophobic properties (SI Table S6). Cutin incorporated fibers retained the Cutin after spinning, however most of the suberin was lost into the spin bath (SI Table S6).

Surface Properties Analysis. XPS analysis was performed to investigate the changes in surface properties of the hydrophobic 10BE and 10BA fibers. The amount of nonpolar C-C carbon in the 10BA and 10BE fibers was higher compared to standard fiber (Table 4). However, the difference

Table 4. CA Average and XPS Results Obtained from Reference Fiber, BE, and BA Incorporated Fibers

	wide scan atomic %						
sample	C 1s	O 1s	N 1s	CC	СО		
standard	77.2	19.7	0.4	55.4	32.5		
10BE	91.1	8.9	0	73.3	19.9		
10BA	80.8	18.4	0	61.0	26.7		

might not be significant in C-C carbon considering the overlapping carbonaceous layer formation during measurement. According to XPS data, the reference fiber also showed a strong C-C component in C 1s (i.e., carbon atoms without oxygen neighbor which is absent in cellulose) (SI Figure S4). XPS experiments are performed in ultrahigh vacuum, i.e., under extremely dry conditions. Previous studies showed that eliminating water from the cellulosic materials during the pump-down is critical for the measured XPS surface composition.⁵⁷ Hence, most of the nonpolar C-C carbon would be expected to originate from a carbonaceous passivation layer formed on the fiber surfaces during the pump-down, in order to lower the surface energy of hydrophilic cellulose in the absence of water.⁴⁵ This justifies XPS as a suitable test for qualitative confirmation of change in the surface properties for additive incorporated fibers. The nonpolar C-C did not increase for cutin or suberinincorporated fibers and the C-C was even lower for suberin incorporated fibers compared to the standard fibers (SI TableS6)—which is in line with the nonhydrophobic behavior of both cutin and suberin incorporated fibers.

The surface properties of the films and fibers along with and without additive incorporations and the fiber cross sections are presented in Figure 6. While the standard cellulose film displayed a homogeneous porous structure, the film with BE incorporated showed a heterogeneous surface structure caused by the aggregation of BE particles. Compared to the 10BE film, the 10BA demonstrated a considerably more homogeneous structure. A similar behavior was observed for the fiber surfaces for standard, 10BE and 10BA fiber. The standard fiber showed a smoother surface, while the 10BE fiber showed heterogeneous structure with BE particle aggregation. In addition, microdomains of betulin were observed in the cross section of 10BE fibers (Figure 6).

The surface heterogeneity of 10BE fiber might arise due to the phase separation between betulin crystals and cellulose during coagulation and cocrystallization. Previous studies on cotton fabrics coated with betulin by impregnation and compress molding also reported that the distribution of betulin in the betulin coated fabric was inhomogeneous.¹⁰ Compared to 10BE, 10BA showed more homogeneous coating behavior and minor phase separation. This reflects the higher compatibility of the BA with cellulose compared to BE. In addition, BA-incorporated fibers showed smoother surface compared to the BE-modified fibers. The presence of the hydrophilic -COOH group in betulinic acid enhances its compatibility with cellulose. From the SEM image of the fiber cross sections, it was evident that the presence of additives or noncellulosic contents create less ordered fibrillar structures and voids. The standard fiber showed a more ordered fibrillar structure without any voids (Figure 6).

In order to further investigate the coating behavior of the additives, the Raman images of both 10BE and 10BA fibers were compared with the standard fiber. Raman images were created by integration of the CH/CH₂ stretching band at $2770-3020 \text{ cm}^{-1}$ (Figure 7a) and the C=C stretching band at $1618-1670 \text{ cm}^{-1}$ (Figure 7b) to observe the distributions of the additives onto the fiber surface.

The CH/CH₂ stretching band consists of several overlapping bands and was observed for cellulose, BA and BE (SI Figure S5). However, the small band around 1642 cm⁻¹ can be assigned to the double bond (C=C) only present in both BE and BA (SI Figure S5). The band with its maximum at ca. 1642 cm⁻¹ stretches from ca. 1618 to ca. 1670 cm⁻¹. A very



Incorporation of hydrophobic compounds

Figure 6. SEM image of the film surface, fiber cross-section, and surface of the standard Ioncell, Betulin, and Betulinic acid incorporated Ioncell fibers. Scale bar 5 μ m.



Figure 7. Raman images based on band integration from 2770 to 3020 $\rm cm^{-1}$ (a) and from 1618 to 1670 $\rm cm^{-1}$ (b).

faint intensity of this band in the standard fiber can be attributed to noise (Figure 7b). In line with the SEM images, Raman visualization also demonstrated the more heterogeneous distribution of BE on the fibers compared to BA (Figure 7b). The intensity of the C=C stretching band was much lower for the BA fibers. Presumably, the thin top layer of BA resulted in a larger contribution of the Raman signal from the subjacent fiber, particularly if the focal plane during the Raman mapping was not exactly at the BA layer. The Raman spectra of BE and BA also contained a number of other Raman bands in the wavenumber range of $250-1500 \text{ cm}^{-1}$, but they overlapped with Raman bands in the standard fiber (SI Figure S5).

Demonstration Products and Washing Fastness. Nonwoven and knitted/handloomed fabrics were prepared from the BE and BA-modified fibers and yarns (Figure 8). Hydrophobicity of the staple fibers were transferred to the final fabric.

The durability of the coating of BE- and BA-modified fibers was studied using wash-fastness test. Both nonwoven and yarnmade fabrics lost the hydrophobic properties after washing with detergent although the hot water (90 °C) washing did not the affect the hydrophobicity. Hence this BE- and BA-modified hydrophobic fibers, produced via incorporation technique, have the potential for the industrial production of nonwoven fabric. Huang et al. reported that the durable textile coating was developed via covalently attaching the betulin to cellulose. However, the fiber lost the mechanical properties significantly due to harsh chemical reaction conditions,³² which is not feasible for industrial applications. Further research is required to introduce covalent bonding between the cellulose and BE or BA using the reactions that will not significantly affect the mechanical properties of the fibers.

CONCLUSIONS

Reducing the hydrophilic properties of cellulose based textile fibers in an ecofriendly way is one of the major challenges in the textile industries. Considering the adverse impacts on the environment, textile industries warrant sustainable yet simple hydrophobization technique to reduce the use of harmful chemicals and complex processes. In this work, we have presented an eco-friendly and simple hydrophobization method for man-made cellulose fibers. During this study, man-made cellulose fibers were hydrophobized using 10 wt %

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c) Nonwoven from 10BA staple fibers

d) Knitted textile from 10BA varn

Figure 8. Demonstration samples: (a) Nonwoven from 10BE modified staple fibers; (b) hand loom textile from 10BE modified continuous filament; (c) nonwoven from 10BA modified staple fibers; and (d) knitted textile from 10BA yarn.

betulin (BE) and betulinic acid (BA) via incorporation during the dissolution step of the spinning process. Compared to BE, BA showed better solubility in the ionic liquid. Both additive incorporated (10BE and 10BA) dopes showed excellent spinnability at a moderate temperature. The additive contents in the spun fibers were close to the theoretical value which reflects insignificant additive loss during spinning. In contrast to the standard fiber, the mechanical properties of 10BE and 10BA fibers decreased slightly-possibly due to the decreased orientation and crystallinity. In addition, yarn-spinnability of 10BA fibers was better compared to 10BE fibers. While, the average WCAs of the nonwoven made from 10BE and 10BA were 101° and 100°, respectively-WCAs of 10BE and 10BA yarns were 98° and 100° , respectively. In contrast to BE, BA showed increased compatibility with cellulose-as evident from the scanning electron microscopic images (both in films and textiles) and Raman images (fibers).

In this study, we utilized the plant-derived sustainable raw materials as hydrophobizing additives through simple incorporation technique—a major advantage over the current hydrophobization techniques. The obtained hydrophobic fibers maintained their mechanical properties and showed efficient yarn spinnability—suggesting that the hydrophobic property could be transferred to the yarn. In addition, these hydrophobic fibers can be useful for nontextile applications such as in hygiene or medical products, packaging, sportswear, and agricultural products.

As previously mentioned, the hydrophobicity of the fiber or nonwoven was compromised during spin finish treatment or standard washing with detergent—possibly due to the lack of covalent linkages between the additive and the cellulose. This should be further investigated to develop a durable coating via the introduction of covalent linkages between cellulose and the additives. The presence of double bonds (both in BA and BE) and active functional group like -COOH (present in BA) could potentially be harnessed for further modifications such as covalent binding of the functional groups to the cellulose.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c00695.

Rheology data, fiber characterization techniques, betulin incorporation into postconsumer cotton, mechanical properties of the commercial viscose and Tencel yarns, X-ray diffraction analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, spin finish treatment of the staple fibers, suberin and cutin incorporation, and compositional analysis of suberin and cutin (PDF)

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H.S. and K.M. designed and interpreted the results of all the experiments. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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