Haslinger, Simone; Hummel, Michael; Anghelescu-Hakala, Adina; Määttänen, Marjo; Sixta, Herbert

Upcycling of cotton polyester blended textile waste to new man-made cellulose fibers

Published in:
Waste Management

DOI:
10.1016/j.wasman.2019.07.040

Published: 01/09/2019

Please cite the original version:
Upcycling of cotton polyester blended textile waste to new man-made cellulose fibers

Simone Haslinger a, Michael Hummel a, Adina Anghelescu-Hakala b, Marjo Määttänen b, Herbert Sixta a,⇑

a Department of Bioproducts and Biosystems, Aalto University, Espoo, P.O. Box 16300, FI-00076 Aalto, Finland
b VTT Technical Research Centre of Finland Ltd, Espoo, P.O. Box 1000, FI-02044 VTT, Finland

Article info

Article history:
Received 13 February 2019
Revised 31 May 2019
Accepted 30 July 2019

Keywords:
Dry-jet wet spinning
Loncell
Ionic liquid
Polyethylene terephthalate
Textile recycling
Cellulose PET separation

Abstract

The creation of a circular economy for cellulose based textile waste is supported by the development of an upcycling method for cotton polyester blended waste garments. We present a separation procedure for cotton and polyester using [DBNH][OAc], a superbase based ionic liquid, which allows the selective dissolution of the cellulose component. After the removal of PET, the resulting solution could be employed to dry-jet wet spin textile grade cellulose fibers down to the microfiber range (0.75–2.95 dtex) with breaking tenacities (27–48 cN/tex) and elongations (7–9%) comparable to commercial Lyocell fibers made from high-purity dissolving pulp. The treatment time in [DBNH][OAc] was found to reduce the tensile properties (<52%) and the molar mass distribution (<51%) of PET under certain processing conditions.

© 2019 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Ever since fast fashion has attempted to satisfy the demands of a rapidly growing population (Hämmerle, 2011), the global waste pollution has increased tremendously. Europe disposes 75% (4.3 million tons) of textiles waste annually due to the absence of viable recycling strategies. (Briga-Sá et al., 2013) Interwoven cotton polyester blends represent one of the most prominent mixtures on the market, which are difficult to recycle because of their heterogeneity. Conventional fiber spinning processes can partly reuse pure cellulose waste (Shen and Patel, 2010), but they are unable to handle blended waste garments. Therefore, the recycling of cotton polyester blends has yet demanded either the depolymerization or dissolution of either component. The dissolution of polyester usually involves toxic solvents and elevated temperatures (DMSO), which can influence the properties of the cellulose component (Serad, 1993). Accordingly, polyester is preferably subjected to alcoholysis, hydrolysis, or glycolysis reactions (Barot and Sinha, 2015; Oakley et al., 1992; Palme et al., 2017; Shen et al., 2013).

Similar approaches have also been used to degrade cellulose under acidic conditions (Cowan, 1981; Gruntfest and Turner, 1974; Ouchi et al., 2010; Shen et al., 2013). An example is the hydrolysis of cotton employing hydrochloric acid to generate a microcrystalline cellulose powder, which can be separated from the remaining polyester fabric. The recovered polyester is re-spun to PET yarns that can then be used to manufacture new textiles (Sun et al., 2018a, 2018b).

Less destructive methods utilize ionic liquids (ILs) or NMMO to dissolve the cellulose component. Negulescu et al. prepared a 1–2% cellulose solution from cotton polyester blends, and removed the polyester residue by filtration. Afterwards, the cellulose solution was further concentrated up to 15–17% using cotton material from an alternative feedstock (Negulescu et al., 1998). A recent patent further elaborates this approach. An amine oxide solvent such as NMMO is supposed to dissolve the cellulose component of various blended textile products to yield cellulose solutions of up to 35% (Brinks et al., 2013). Similarly, 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) and 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) have been described to foster the recycling of blended textile waste. The process steps are comparable to NMMO. The ionic liquid dissolves the cellulose component, while filtration removes the polyester residue, and subsequent coagulation recovers the cellulose (de Silva et al., 2014). Although both NMMO and IL-based approaches highlight the potential of the generated cellulose solutions to be used in a film or fiber spinning process, neither of them provides any relevant data that could serve as a proof of concept.

https://doi.org/10.1016/j.wasman.2019.07.040
0956-053X/© 2019 The Author(s). Published by Elsevier Ltd.
This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
It is evident that there is a strong need to further develop recycling strategies for textile industry. A viable, ecofriendly concept for circular economy should allow quantitative and “green” recycling of all material components without the generation of additional waste streams, or an increase in energy consumption resulting from complex processing steps. In many cases, the approaches discussed so far involve the degradation of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous recycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process. Even more significantly, however, they fail to show the conversion of either cotton or polyester, and therefore impede the simultaneous upcycling of both components within one process.

2. Materials and methods

2.1. Synthesis of [DBNH] [OAc]

The synthesis of [DBNH] [OAc] is a neutralization reaction of an equimolar amount of 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) and glacial acetic acid. During the addition of acetic acid, permanent cooling is necessary because of the exothermic nature of the reaction. The resulting ionic liquid shows a melting point close to 65 °C and therefore requires stirring at elevated temperatures (80 °C, 1 h) in order to ensure a complete conversion.

2.2. Cotton polyester blend

The cotton polyester blend was supplied by SOEX (Germany) consisting of white postconsumer textiles, which were shredded and blended to obtain a mixture with an overall concentration of 50 wt% cotton and 50 wt% polyester. The sample was pretreated by VTT (Finland) using an ozone based sequence Ew-disk refining-Z-P-A. The target of the alkaline washing stage (Ew) was to remove silicate, whereas ozone (Z) and hydrogen peroxide (P) were used to both adjust the viscosity (DP) and to bleach the material. Acid washing (A) aimed to decrease the metal content. Disk refining targeted to homogenize the sample mixture and to improve the reactivity for the following pretreatment and dissolusion stages. The molar mass distributions (MMD) of both cellulose and the polyester fractions were determined by size exclusion chromatography, respectively, as described below. All samples were further disintegrated by the means of a Wiley Mill.

2.3. Molecular mass distribution (MMD) and intrinsic viscosity of cellulose

The MMD of the raw material and the spun fibers was determined by gel permeation chromatography (GPC) using a 5 column
set up with one precolumn (Plgel Mixed-A, 7.5 × 50 mm) and four analytical columns (4 × Plgel Mixed-A, 7.5 × 300 mm) equipped with an RI-detector (Shodex RI-101). The samples were dissolved in a 90 g l−1 LiCl/N,N-dimethylacetamide (DMAc) solution and diluted with pure DMAc in order to obtain a sample concentration of 1 mg ml−1 in 9 g l−1 LiCl/DMAc. 100 μl of the respective solution were injected at a flow rate of 0.750 ml min−1 (9 g l−1 LiCl/DMAc eluent) at 25 °C. The calibration was conducted with pullulan standards (Mw: 343–708,000 Da) based on a direct-standard-calibration model, in which the molar mass distribution was corrected according to the molar masses of cellulose equivalent pullulan standards (Berggren et al., 2003; Borrega et al., 2013; Michud et al., 2015a).

The limiting viscosity of the raw material before and after its pretreatment was determined according to the SCAN-CM 15:88 standard for viscosity in cupri-ethylendiamine solution.

### 2.4. Selective dissolution of cotton and recovered PET

The cotton polyester blend was mixed with [DBNH] [OAc] (1 h, 80 °C) using a vertical kneader system (cf. experiments [S1], [S2], and [M2] in Table 1) to yield a cellulose solution of 6.5 wt%. For [M1], [DBNH] [OAc] was prepared with an excess amount of HOAc in a ratio of 1:1.3 to reduce the degradation of PET. Subsequently, the undissolved polyester fraction was separated from the cellulose solution via hydraulic pressure filtration (70 °C, 1–8 MPa, metal filter mesh with 5–6 μm absolute fineness, Gebr. Kufferath AG, Germany). In experiment [M2], the filtered solution was transferred back to the kneader system and mixed with an additional amount of the cotton polyester blend (1 h, 80 °C) to obtain a final cellulose concentration of 10.5 wt% after filtration. Whereas the resulting cellulose solutions could be subjected to dry-jet wet spinning directly after solidification (storage at 8 °C for a couple of days), the recovered polyester fibers required further purification as they were still contaminated with residual cellulose. Therefore, the polyester residue was extracted with fresh ionic liquid (1 h, 80 °C, vertical kneader). Afterwards, the solvent was removed by filtration and subsequent washing with deionized water. This step was repeated for experiments [S2], [M1], and [M2].

### 2.5. Dry-jet wet spinning

The solidified cellulose solution was placed into a customized laboratory dry-jet wet piston spinning unit (Fourné Polymertechnik, Germany) and heated up according to its rheological properties. The melted spin dope was extruded through a multi hole spinneret (36 holes, 0.1 mm diameter, 0.02 mm capillary length) with a constant extrusion velocity of 1.6 cm3 min−1. The resulting cellulose solutions could be subjected to dry-jet wet spinning at 1 mm gap size, 25 mm plate diameter. Initial dynamic strain sweep tests were performed to define the linear-viscoelastic domain. A strain of 0.5% was chosen for the following frequency tests. All samples were subjected to a dynamic frequency sweep over an angular frequency (ω) range of 0.01–100 s−1 at relevant temperatures (40–100 °C). The complex viscosity (η′) and dynamic moduli (G′, G″) were recorded as a function of the shear rate. The zero shear viscosity (η0) was calculated using the cross model assuming that the Cox-Merz rule was valid (Sammons et al., 2008). The cross over points of storage and loss moduli were also determined.

### 2.7. Fiber properties and total orientation

Linear density (dtex), elongation at break (%), and tenacity (cN dtex−1) of all spun fibers and of 3.3 dtex PET filaments were measured by a Vibroskop and VibroDyn 400 set up (Lenzing Instrum., Austria) according to DIN 53816 standard (20 mm gauge length, 5.9 ± 1.2 mN/tex pretension, 20 mm/min test speed). The samples were conditioned prior to the measurement (20 °C, 65% humidity) and were tested in both dry and wet state (fiber count: 10). The young modulus (GPa) was calculated from the slope of the average stress strain curve based on the ASTM standard D2256/D2256.

The total orientation of the spun fibers was determined by a polarized light microscope (Zeiss Axio Scope) with a 5× Berek compensator. The birefringence (Δn) was calculated from the retardation of the polarized light divided by the fiber thickness assuming a density of 1.5 g cm−3 for cellulose. In order to obtain the total orientation factor fT, Δn was divided by the maximum birefringence value (0.062) of cellulose (Adusumalli et al., 2009).

### 2.8. Scanning electron microscopy (SEM)

The cross sections of the spun fibers were observed on a Zeiss Sigma VP, Zeiss FE-SEM. An acceleration voltage of 1.5 kV was used and all samples were sputter coated with Au prior to the measurement.

### 2.9. Degradation experiments of PET filaments

Virgin 3.3 dtex PET filaments (Swerea IVF, Sweden) were treated with [DBNH] [OAc] (6 wt% PET, 0.5–4 h, 80 °C) under permanent stirring. Afterwards, the filaments were rinsed with deionized water and their tensile strength was determined as described in the cellulose section above.

### 2.10. Gel permeation chromatography of PET

The molar mass distribution (MMD) of polyester was determined by gel permeation chromatography (VTT, Finland) using a 3 column setup with one precolumn (Stryragel WATT054405) and two analytical columns (Stryragel HR 4E 7.8 × 300 mm and Stryagel HR5 7.8 × 300 mm) equipped with a RI-detector (40 °C). The analysis was conducted with an 1,1,1,3,3-hexafluoro-2-propanol (HFIP)/5mM salt (sodium trifluoroacetate) eluent at a flow rate of

### Table 1
Experimental design. Summary of the conducted experiments describing the total concentration of cotton and polyester (CO/PET) before separation, the resulting cellulose concentration (Cellulose) in the spinning dope, the solvent used, and the washing steps employed for the polyester residue.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>CO/PET (wt%)</th>
<th>Cellulose (wt%)</th>
<th>Solvent</th>
<th>Washing of PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>[S1]</td>
<td>13</td>
<td>6.5</td>
<td>[DBNH] [OAc]</td>
<td>1x [DBNH] [OAc]</td>
</tr>
<tr>
<td>[S2]</td>
<td>13</td>
<td>6.5</td>
<td>[DBNH] [OAc]</td>
<td>2x [DBNH] [OAc]</td>
</tr>
<tr>
<td>[M1]</td>
<td>13</td>
<td>6.5</td>
<td>[DBNH] [OAc] + HOAc (molar ratio: 1:1.3)</td>
<td>1x [DBNH][OAc] + HOAc (molar ratio: 1:1.3)</td>
</tr>
<tr>
<td>[M2]</td>
<td>21</td>
<td>10.5</td>
<td>[DBNH] [OAc]</td>
<td>2x [DBNH][OAc]</td>
</tr>
</tbody>
</table>
The concentration of the residual cellulose in the recovered polyester fraction was estimated by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.

A sigmoidal calibration model was employed to quantify the cellulose content in the polyester residue. The ratios of the peak areas of C1 (cellulose) and C1-8 as well as C2-3-4-5-6 (polyester) were plotted as a function of the cellulose concentration. The concentration of the residual cellulose in the recovered PET was determined by $^{13}$C CP-MAS NMR. All samples were analyzed on a Bruker AVANCE III spectrometer with a probe size of 4 mm employing an UltraShield Plus 400 MHz magnet running at 100.6 MHz. The spectra were recorded at a spinning speed of 8 kHz using a relaxation delay of 5 s and a CP contact time of 2 ms. 8000 scans with an acquisition time of 34 ms were measured. During contact time, a variable crosspolarization increasing from 50% to a maximum amplitude of 85 kHz was used. A SPINAL64 1H decoupling aimed to decouple the protons during acquisition.
entanglements between the polymer chains tend to be disrupted (Chen et al., 2009). Most samples studied herein correspond to this trend. The critical shear rate for shear thinning decreases with a broad MMD and the concentration being raised from 6.5 wt% to 10.5 wt%, while the measured complex viscosities potentiate. Assuming that the Cox–Merz rule is valid for solutions of cellulose in [DBNH] [OAc], the zero shear viscosities ($\eta_0$) can be determined based on the Carreau and the Cross model (Sammons et al., 2008). The high zero shear viscosity calculated for [M1] implies that the excess amount of acetic acid reduced the ILs power to dissolve cellulose. Throughout the angular frequency range, [M1] also displays higher values for $G'$ than for $G''$ indicating the formation of a gel rather than a solution. The remaining samples show a viscous domain, whose range is dependent on the cellulose content (Chen et al., 2009). The COPs of [S1] and [S2] (6.5 wt%) can be found at considerably high shear rates, whereas the COP of [M2] moves to lower angular frequencies with an increasing concentration (10.5 wt%).

In this context, it is important to note that the spinning conditions are determined by the rheological properties of the solution. In principle, any fluid is spinnable as long as the formed filaments can withstand the applied deformation and surface forces (Ziabicki and Takserman-Krozer, 1964a, 1964b). During spinning, a certain DR ($\nu_{in}/\nu_{c}$) is exerted on the extruded filaments in order to align the cellulose chains coaxially to obtain a higher fiber tenacity and a lower fiber diameter (Hauru et al., 2014; Sixta et al., 2015). A cellulose solution in [DBNH] [OAc] should thus display a $\eta_0$ of 20,000–30,000 Pas and a COP of 2000–5000 Pa to yield optimum spinning conditions (Asaadi et al., 2016; Ma et al., 2018, 2016; Michud et al., 2015a, 2015b; Sixta et al., 2015). Besides varying concentration and MMD, these parameters can be reached through adjusting the spinning temperature. However, the melting point of [DBNH] [OAc] restricts the spinning window of cellulose solutions of lower concentrations and is evident in the values summarized in Table 3.

The spinnability under standardized conditions has been described as follows, DR < 2 non spinnable, 2–8 poor, 8–14 good, 14 < excellent (Asaadi et al., 2016). We redefined these criteria for cellulose solutions of lower concentrations to DR < 2 non spinnable, 2–4 poor, 4–8 good, 8 < excellent, as they require lower DRs to reach fibers with textile grade properties. All samples prepared from pure [DBNH] [OAc], i.e. [S1], [S2], and [M2], showed a good spinnability with maximum DRs of 8, 6, and 8.8, respectively. In case of [S1], the spinning at a DR of 8 led to fibers with a titer of 0.75 dtex, which classifies them as microfibers. The spinning of [M1] was accompanied by the formation of aggregates on the spinneret surface, which led to a maximum DR of 4. As mentioned before, the excess amount of acetic acid reduces the solvent power of the IL and therefore the solubility of cellulose therein, which is consequently reflected in the poor spinnability of [M1].

Besides additives, both the spin dope concentration and the draw ratio influence the tensile properties of dry-jet wet spun fibers. Due to shear forces, the cellulose molecules experience a pre-orientation in the spinneret during extrusion and are further aligned when stretched in the air-gap. As a result, the cohesive forces within the cellulose network increase, which eventually fosters the formation of a dense fibrillar cellulose II structure (Fink et al., 2001). A raise in the cellulose content can improve this effect. The properties of the fibers presented in Fig. 2 confirm this principle.

Sample [M2] exhibits the highest tenacity followed by [S1], [S2] and [M1], which also corresponds to the draw ratios and concentrations employed. These properties are comparable in conditioned and wet state, with their elastic moduli (15–20 GPa) exceeding those of commercial Viscose and Tencel fibers as illustrated in the slope of the respective stress strain curves. The higher fiber strength is also explained by a higher total orientation $\nu_{total}$ of the fibers (s. Table 4) and an increase in the fibrillar density

### Table 3

Rheology data. The zero shear viscosities $\eta_0$ were calculated using the cross model, and the crossover point (COP) of the dynamic moduli ($G', G''$) was determined as function of the shear rate $\omega$. All values were calculated for 60 °C representing the measured temperature closest to the spinning temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO (wt%)</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\omega$ (s$^{-1}$)</th>
<th>$G' = G''$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[S1]</td>
<td>6.5</td>
<td>1439 ± 12</td>
<td>6.9</td>
<td>1495</td>
</tr>
<tr>
<td>[S2]</td>
<td>6.5</td>
<td>686 ± 6</td>
<td>6.9</td>
<td>939</td>
</tr>
<tr>
<td>[M1]</td>
<td>6.5</td>
<td>175660 ± 3621</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>[M2]</td>
<td>10.5</td>
<td>13294 ± 203</td>
<td>1.4</td>
<td>3224</td>
</tr>
</tbody>
</table>

Fig. 1. Rheology data. Complex viscosity ($\eta'$) and dynamic moduli ($G', G''$) of the solutions [S1] and [S2] with a concentration of 6.5 wt%, and [M2] with 10.5 wt% in [DBNH] [OAc], as well as [M1] with a cellulose content of 6.5 wt% in a DBN:HOAc mixture with a molar ratio of 1:1.3 as a function of the angular frequency at 60 °C.
Based on the concentration and draw ratio applied. Compared to commercial Tencel and Viscose fibers, the spun fibers show a lower elongation, because of a missing air gap conditioning on our lab-scale equipment, which could apply moisture as a plasticizer during the spinning process. Despite the difference in the fiber properties obtained, the processing conditions did not have any significant impact on MMD of the cellulose fraction as displayed in Table 4 and Fig. 3a. Evidently, the Mn and Mw of the starting material even seem to show lower values than the final products, which is a good representation of the heterogeneity of the waste substrate studied.

3.3. The effect of [DBNH] [OAc] on PET

In preliminary trials, we could observe a visible degradation of the recovered PET after its processing in [DBNH] [OAc] at 80°C because of a change in color. PET is usually hydrolyzed under the presence of water and temperatures higher than 100°C (Buxbaum, 1968). However, several imidazolium based ionic liquids, among them also [BMIM] [OAc], have been described to degrade and partly dissolve PET at elevated temperatures (Wang et al., 2009). These ionic liquids are supposed to catalyze the hydrolysis of PET, whose effectiveness is strongly influenced by the choice of their anion (Liu et al., 2009). Although reported in a number of publications (Brinks et al., 2013; Negulescu et al., 1998; de Silva et al., 2014), a separation of cotton and polyester without any degrading effect on the latter seems questionable.

In initial degradation studies, the decrease in tensile strength of virgin PET filaments (6 wt%) was monitored in [DBNH] [OAc] at 80°C (s. Fig. 3b). Although no substantial weight loss of the PET filaments could be observed, their tenacity was more than cut into half over a treatment time of 4 h. The decrease from 38 to 18 cN tex is exponential, and exhibits the largest drop already after 0.5 h, while the degrading effect of the ionic liquid flattens out with an increased treatment time.

The recyclability of PET fibers strongly depends on its degree of polymerization and purity. Only a high-grade PET substrate is suitable to be re-spun in a melt spinning process, fractions with a
lower DP require alternative processing techniques (Venkatachalam et al., 2012). These circumstances inevitably denote the most substantial challenge in the recycling of PET. Any degradation occurring during a separation and recovery process is categorically unwanted. Nevertheless, a fact that yet has often been ignored is that virgin PET, which is converted into textile fibers, already loses its ability to be re-spun during its first melt spinning cycle. Various degradation reactions cause a decrease of the DP of PET before the spun fibers have even been worn once (Samperi et al., 2004). This makes it strictly speaking impossible to recycle PET based textile waste to new fibers without applying any chain extension (Awaja and Pavel, 2005) or depolymerization and repolymerization concepts (Sun et al., 2018a, 2018b). Alternative recycling strategies therefore suggest to separate the PET mechanically from the cellulose component in order to keep a further degradation as low as possible (Sun et al., 2018b).

However, we still tried to avoid any unnecessary degradation of PET by keeping its treatment time in [DBNH][OAc] as short as possible during the separation experiments. According to previous results, 1 h appeared effective enough to ensure a complete dissolution of the cotton fraction, and to prevent an extensive degradation of PET (Michud et al., 2015a). To remove any residual cellulose, the PET fraction was filtered off from the cellulose solution and washed with IL and water as described in the experimental section. Table 5 depicts the cellulose content in the recovered PET after the separation experiments. The respective NMR spectra can be found in Fig. S4 in the supporting information.

One washing step in [DBNH][OAc] (1 h, 80 °C) was sufficient to decrease the concentration of residual cellulose to 2.5 ± 0.5 wt% (cf. [S1]). The addition of one more washing step further lowered the amount of cellulose to 1.7 ± 0.4 wt% (cf. [S2]). The purity of PET is also confirmed by the TGA shown in Fig. 3c, and does not reveal a major change in the onset temperature T_0 of the recovered fractions [S1] = 397 °C, [S2] = 398 °C, [M1] = 393 °C, and [M2] = 397 °C.

As expected, the treatment time in [DBNH][OAc] affected the molar mass distribution of PET as shown in Fig. 3d and in Table 5. The MMD of the treated substrate noticeably decreased throughout the different treatment steps and time until it almost reached a
bisection of $M_M$ and $M_N$ after a total of 3 h in [DBNH][OAc] (cf. [S1] and [S2]). [M2] exhibits a bimodal MMD, as it consisted of two separate PET fractions, which were added to the IL consecutively. The excess amount of acetic acid added to [M1] seemed to prevent the degradation of PET to some extent. Although the acetic acid caused a decrease in the viscosity of the solution, the cellulose content could be reduced in a similar manner as in the trials that employed pure [DBNH][OAc]. Neither of the approaches seemed to have a substantial impact on the PDI of the samples, implying that [DBNH][OAc] most likely induced a uniform cleavage of the polymer chains.

Alternatively, a reduction of the temperature during dissolution to 75 °C or lower might further decrease the degradation of PET, which is favorable especially on an industrial scale as larger kneaders utilize significantly shorter dissolution times (5–10 min).

4. Conclusions

The heterogeneity of textile waste represents both a challenge and an opportunity. The different chemical nature of cotton and polyester enables them to be separated efficiently, but also demands very specific processing conditions. [DBNH][OAc] allows a selective dissolution of the cotton component, and a subsequent dry-jet wet dissolution of cellulose to textile grade fibers. The spun fibers were found to have properties similar to Lyocell with linear densities between 0.75–2.95 dtex, breaking tenacities of 27–48 cN/tex, and elongations of 7–9%. The recovered PET fraction showed a very low cellulose content (1.7–2.5 wt%), which could further be reduced on an industrial scale by a multi-stage dissolution process. However, PET undergoes visible degradation once dispersed in [DBNH][OAc], which becomes evident in a decrease of its MMD (<51%) and tensile properties (<52%). The presented data clearly demonstrate that cellulose based, blended textile waste has the potential to serve as a feedstock for conventional fiber spinning processes. Commercialization, nonetheless, requires the development of efficient, reliable techniques for sorting and material identification to be able to deal with a heterogeneous substrate such as textile waste. Moreover, further optimization of the process conditions, especially in terms of dissolution and filtration, might be necessary to limit the degradation of PET. Whereas a certain degradation of cotton is favorable to reduce the consumption of water and chemicals, a high DP of PET is essential to convert it to textile fibers. Therefore, a further possible pathway to recycle the recovered PET fraction might rather include the manufacture of composites or plastic based packaging materials (Joshi, 2001; Zou et al., 2011).

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 646226. The authors also gratefully acknowledge Dr. Ali Harlin, Dr. Christiane Laine, and Dr. Sari Asikainen (VTT, Finland) for their support in material pretreatment and in the analysis of PET as well as Dr. Zhengwei Guo (RISE IVF, Sweden) for his expertise regarding the recyclability of PET. We also thank Hilda Zahra (Aalto University, Finland) for conducting the TGA measurements.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2019.07.040.

References


