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Investigation into the supramolecular properties of fibres regenerated from cotton based waste garments

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Abstract This paper investigated the supramolecular properties and accessibility of fibres regenerated from cotton-based waste garments and compared to typical lyocell fibres.

The supramolecular and accessibility properties of the cotton-based waste garments fibres regenerated from three sources (waste denim garments, easy care finished cotton fabrics and a blend of cotton-based waste garment with wood pulp) were analyzed and compared to the lyocell fibres. The Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy and Wide Angle X-ray Diffraction (WAXD) analyses indicated that the fibres from cotton waste garments had supramolecular properties similar to the typical lyocell fibres. The exception was spun from the cotton pulp reclaimed from easy care treated cotton fabrics and maybe related to increased amorphous cellulose content in its structure. The fibre's accessibility by reagents behaviour correlated well with the supramolecular properties. The results indicate that the waste garment purification process may affect the properties of the pulp and hence the supramolecular properties of the resultant fibres. Further research on the purification and regeneration of fibres from waste garments may lead to the use of cotton waste garments as an alternative feedstock source to the lyocell process.

Keywords: Waste cotton, supramolecular properties, accessibility, iodine sorption value, recycling.

1. Introduction

The increase in the number of fashion seasons has resulted in an increase in the amount of waste garments generated, particularly in the developed countries. It is reported that at least 50% of the waste apparel collected by developed countries is transported to developing countries to be used as second hand clothing (Ekström & Salomonson, 2014). In addition this second hand clothing business hinders the growth of textile and fashion industries in the developing countries, while the solid waste management cost in the developed source countries is also increasing (Amankwah-Amoah, 2015).

Cellulosic fibres contribute significantly in fashion textiles due to the ability of these fibres to provide comfort to the users. The main sources of cellulosic

fibres are cotton and wood pulp with the cotton fibres harvested from the cotton plant, while the wood pulp is used for the regeneration of viscose and lyocell fibres by chemical derivatisation and physical dissolution of the pulp, respectively. The viscose process is characterised by a high consumption of water and the generation of by-products which may pollute the environment. In contrast the lyocell process is more environmental friendly with a "closed" processing structure that generates little effluent. However while the viscose and lyocell fibre making industries become ever more efficient the challenge is to source cheap, readily available raw materials.

In order to globally combat the impact of high fashion affluence and the shortage of the raw material for fibre making, closed loop recycling has been suggested (Danish Fashion Institute, 2012). As part of closed loop recycling, garments and bottles made from polyethylene terephthalate can be depolymerised into monomers and commercially re-polymerised into new filaments for textile application (DEFRA, 2009; Shen, Worrell & Patel, 2010).

Recent research on closed loop recycling of cellulosic waste garments has suggested the use of the garments as feedstock for regeneration of fibres via the lyocell process (Haule, Carr & Rigout, 2014; Haule, Carr & Rigout, 2016b). These studies demonstrated the approach to remove the easy care finishes from the cotton waste garments and subsequent regeneration of fibres via the lyocell process. Further the mechanical properties of the fibres reclaimed from cotton based waste garments were found to be superior to the traditional lyocell fibres (Haule, Carr & Rigout, 2016a). In addition the work demonstrated that wood pulp can be blended with the pulp from cotton waste garments and regenerated into fibres with improved mechanical properties. The work reported in this study builds on the previous investigations by studying the supramolecular properties in order to characterize the structure of the fibres reclaimed from cotton waste garments and compare the fibre properties with traditional lyocell fibres. The supramolecular properties relate to the interaction of the cellulose polymer chains above the molecular level. In particular the supramolecular properties investigated were the interactions of the cellulose polymer molecules within the polymers chains and with neighbouring chains, the degree of order of the chains and the

proportion of crystalline material in the fibres. Associated with this characterisation the relative fibre accessibility by reagents of a range of fibres with respect to the supramolecular properties was investigated.

The influence of structural properties on the fibre accessibility by reagents was also discussed. The fibres were characterized by the use of Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and the results correlated with Wide Angle X-ray Diffraction (WAXD) analyses.

2. Methodology

2.1 Preparation and purification of the fabrics

The material for the spinning of the fibres was prepared as per previously reported procedures (Haule, Carr & Rigout, 2016a) and described hereunder.

In order to simulate the effect of extended washing during domestic usage the plain woven cotton fabric was washed 50 times with ECE-phosphate based detergent in a Wascator FOM-71 machine, (Haule, Rigout, Carr & Jones, 2012), and this fabric was the source material for deconstruction into pulp and spinning of regenerated lyocell (*ReCell-1*) fibres. Similarly in order to prepare cross-linked, crease resistant fabrics the plain woven cotton fabric was treated with 100g/L Dimethylol dihydroxyethylene urea (DMDHEU) easy care finish (Haule, Rigout, Carr & Jones, 2012) and the easy care finished cotton fabric was then Wascator washed 50 times with ECE-phosphate based detergent and subsequently purified in acid/alkali solutions to produce a component source for the *ReCell-2* fibres (Haule, Carr & Rigout, 2014). The *ReCell-2* fibres were prepared from a blend of 20% cellulose recovered by purification of the DMDHEU treated cotton fabrics and 80% wood pulp. In order to prepare the waste indigo dyed denim garments for deconstruction into pulp for spinning, 5 pairs of indigo dyed waste denim were washed once with European Colourfastness Establishment (ECE)-phosphate based detergent, tumble dried, zippers, buttons and threads removed manually and considered the source of *ReCell-Denim* fibres.

2.2 Dissolution and spinning of fibres

The dissolution and spinning of the fibres were as per previously reported methods (Haule, Carr & Rigout, 2016a) and involving preparing the requisite spinning dope by mixing 300g of 50% N-methylmorpholine N-oxide (NMMO) solution with 27g pulp and 0.2g n-propyl gallate using a mechanical kneader. The dissolution process was made possible by mixing the pulp and NMMO solution at increasing temperature and vacuum at suitable intervals until the final spinning dope was composed of 9-13% cellulose, 10-13% water and 77-78% NMMO. For every sample the dissolution dope was checked for fibre solubility using a light microscope. The

fibres were then spun in filament form from a laboratory scale spinning machine at Lenzing AG, Austria. The spinneret used had 19 holes of 100 μ m in diameter and the spinning temperature was 115°C. The dope throughput was 0.03g/min per hole and the air gap conditions were set at 30mm, 24°C and 53% relative humidity. The fibre fineness and molecular weight were determined as per previously reported methods (Haule, Carr & Rigout, 2016a) are presented in Table 1.

Table 1. Molecular and fineness properties of the Lyocell, ReCell-1, ReCell-2 and ReCell-Denim fibres

| Fibre type | % cellulose in a spin dope | Fineness (dtex) | Viscosity - average Molecular Weight (Mv) [g/mol] |
|--------------|----------------------------|-----------------|---|
| Lyocell | 13 | 1.30 | 494 |
| Recell-1 | 9 | 1.33 | 1066 |
| Recell-Denim | 9 | 1.30 | 623 |
| Recell-2 | 13 | 1.30 | 517 |

2.3 ATR-FTIR analysis of the fibres

The ATR-FTIR spectra were collected on a Nicolet 5700 instrument with a diamond crystal. Scanning was performed from 4000 to 600 cm^{-1} with 128 scan repetitions and a resolution of 8 cm^{-1} . For consistency and reproducibility all spectra were normalized against the C-O-C asymmetric stretching vibration at 1155 cm^{-1} .

The ATR-FTIR crystallinity indices of the ReCell fibres were determined in accordance to the method proposed by Nelson and O'Connor (Nelson & O'Connor, 1964a, b). The method was specifically proposed and applied to cellulose polymers with either crystalline cellulose I or II, or mixtures of both cellulose I and II forms. Infrared absorption results in molecules in the crystalline fractions vibrating at a different frequency to similar molecules in the amorphous fraction and the resultant vibrational intensities of the crystalline and amorphous fractions can be used to estimate the Total Crystallinity Index (TCI) and Lateral Order Index (LOI) of the fibres. The TCI provides information about the crystallinity degree of the cellulose II while the LOI gives an indication of the degree of order of the cellulose II structure. Nelson and O'Connor defined the TCI and the LOI as the ratios of the FTIR 1372/2900 cm^{-1} and 1420/893 cm^{-1} peak intensities, respectively and in this work similar absorption intensities were observed at 1375 cm^{-1} , 2892 cm^{-1} , 1420 cm^{-1} and 894 cm^{-1} , respectively. Previous research indicated that absorption band in the 1372-1375 cm^{-1} region was related to crystallinity in cellulose, and the ratio of this band to the absorption band at 2900 cm^{-1} could provide useful TCI data (Nelson & O'Connor, 1964a) The ratio of 1420 cm^{-1} and 894 cm^{-1} absorption intensities was used for the determination of LOI because the two are related to the

amount of crystalline structure and the amorphous region in cellulose II, respectively. Therefore in this work the TCI and LOI were determined at the 1375/2892 cm⁻¹ and 1420/894cm⁻¹ absorption bands, respectively.

The ATR-FTIR data were processed using Origin Pro 8.1 SR3 application software.

2.4 Wide Angle X-ray Diffraction (WAXD) analysis of the fibres

The Xpert Phillips (Power 45kV and current 40mA) instrument with a copper anode with an X-ray wavelength of 1.54060 Å was used for WAXD analysis. Scans were recorded from 1 to 30° 2θ with a step size of 0.07 with both equatorial scans acquired for aligned fibres, taking the meridional axis as the orientation reference.

In order to account for instrument broadening contribution to the experimental peak width, the same experiment geometry was applied to a powdered silicon standard with the (111) reflection at 28.40° (2θ). The crystallinity of the fibres regenerated from cotton based waste garments and lyocell fibres were determined from the wide-angle X-ray diffraction patterns recorded perpendicular to the fibres axis. The percentage of crystalline material was calculated by the first determination of the peak height of the diffractograms at the position of the (002) plane at 2θ = 21.7° (I₀₀₂) and the peak height of the amorphous background at 2θ = 16° (I_{am}) (Nelson & O'Connor, 1964a) and crystallinity was calculated as Equation 1:

$$\text{crystallinity} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad \text{Equation 1}$$

The crystallite size was calculated using the Scherrer equation, Equation 2:

$$\text{crystallite size} = \frac{K\lambda}{B \cos \theta} \quad \text{Equation 2}$$

Where B describes the structural broadening which is the difference in integral profile between a standard (*B_{std}*) and unknown (*B_{obs}*) material and was calculated using Equation 3, and is in radians

$$B = B_{obs} - B_{std} \quad \text{Equation 3}$$

K is the shape factor and was 0.91.

The structural broadening (*B_{std}* and *B_{obs}*) was determined from the respective ratios of the area to intensity of the reflections of the silicon standard and the sample using PCACD Version 3.6 software.

In order to compare the WAXD data of the various fibres under investigation, the graphs were normalized against the diffraction angle of 2θ = 12.3° which is due to the 10^l crystal plane and which does not change for all the fibres. The crystallinity values of the fibres examined in this

investigation were calculated solely based on WAXD data and hence are specific to this study.

2.5 Determination of water retention value (WRV)

The WRVs of the ReCell and Lyocell fibres were determined using a Heraeus Labofuge 400. The centrifuge equipment was operated under the conditions defined in the literature (Okubayashi, Griesser & Bechtold, 2004; Siroka, Noisternig, Griesser & Bechtold, 2008) with minor modifications as described:

About 0.5g of a cellulose fibre specimen was accurately weighed and immersed in deionised water for 24 hours at room temperature in order to allow the fibres to imbibe the water (Okubayashi, Griesser & Bechtold, 2004; Siroka, Noisternig, Griesser & Bechtold, 2008). The specimen was then removed and centrifuged at 2500 revolution per minute for 20 minutes. After centrifugation the specimen was reweighed (*W_w*) and then allowed to dry for 24 hours in oven set at 105°C. Subsequently the dried specimen was allowed to cool in a desiccator over anhydrous phosphorous pentoxide, and the weight of the dried specimen (*W_d*) was recorded. Finally the WRV in (g/g) was calculated using Equation 4:

$$WRV = \frac{W_w - W_d}{W_d} \quad \text{Equation 4}$$

The reported mean values were calculated based on four measurements.

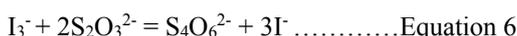
2.6 Determination of the iodine sorption value (ISV)

The ISVs of the ReCell fibres and Lyocell fibres was determined in accordance to method described by Nelson (Nelson, Rousselle, Cangemi & Trouard, 1970). A 0.3g specimen was placed in tared 250mL, glass stoppered Erlenmeyer flask and the weight of flask and contents was recorded. A volume of 2mL concentrated iodine solution (which was prepared from 5g iodine, 40g potassium iodide and 50mLs water) was added to the sample. The mixture was then stirred with a glass rod and the weight of the flask plus fibres plus iodine solution was recorded. After mixing the specimen with iodine, the mixture was allowed to stand for 3 minutes in order to reach sorption equilibrium between the fibres and concentrated iodine solution. The potassium iodide was added to the solution in order to convert the insoluble concentrated iodine (I₂) into soluble and non-volatile soluble triiodide (I₃⁻), Equation 5 and the specimen adsorbed the iodine in the form of I₃⁻

$$I_2 + I^- = I_3^- \dots \dots \dots \text{Equation 5}$$

At the end of sorption equilibration period, 100mL of saturated sodium sulphate solution (200g/L) was added into the flask containing the fibres and iodine solution in order to remove any excess iodine which was not bound to the specimen. After addition of the saturated solution of sodium sulphate the mixture was shaken on

mechanical shaker for one hour at $23\pm 1^\circ\text{C}$ to ensure complete desorption of the excess iodine. A blank solution was prepared by similar procedure omitting the sample. After one hour of the shaking of the mixture, the solution was filtered using tared coarse-frit glass crucible. An aliquot amount of sample and blank solution were then titrated with 0.02N sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution, Equation 6. The sample was then washed on tared crucible thoroughly with deionised water, dried in crucible at 105°C for 4 hours and finally the crucible was allowed to cool under phosphorus pentoxide and weighed to obtain the final mass of the fibres.



The ISV (mgI_2/g cellulose) was calculated according to Equation 7:

$$\text{ISV} = 126.91 \times N \times F \times \frac{T_s - t_s}{w} \quad \text{Equation 7}$$

Where $T_s = T_b \times I_s/I_b$ is the volume of sodium thiosulphate solution equivalent to the initial iodine in the aliquot of sample solution; I_s is the weight of concentrated iodine/potassium iodide solution in the sample solution; I_b is the weight of the concentrated iodine/potassium iodide solution in the blank solution; T_b is the volume of sodium thiosulphate solution for the aliquot blank; t_s is the volume of sodium thiosulphate solution for aliquot of supernatant filtered from sample; F is aliquot factor (total volume is 102mL; w , oven dry weight of sample in grams. Three replicates were conducted for each type of fibre and the mean reported.

2.7 Determination of the regain

The water regain of the fibres was determined gravimetrically with the fibres conditioned at 20°C and relative humidity of 65% for 24 hrs prior to testing. Conditioned samples weighing 50mg were contained in a pre-dried sample holder and then dried in an oven at 110°C for 2 hours. Upon cooling the samples were re-weighed in order to ensure that the dried samples absorbed no moisture from the surroundings. The samples were then allowed to cool in desiccators containing phosphorus pentoxide and weighed immediately. Finally the regain was calculated as the amount of moisture in the sample expressed as a percentage of its dry weight. The results are the average of five replicates.

3. Results and Discussion

3.1 ATR-FTIR and WAXD analyses of fibre supramolecular properties

After dissolution of the cotton waste garments in NMMO solvent and spinning of the fibres, the structure of the resultant fibres was investigated by ATR-FTIR spectroscopy. It is known that the Lyocell fibres

regenerated after the dissolution of wood pulp in NMMO solvent exhibited the cellulose II unit cell structure. Thus, the ATR-FTIR spectra of the ReCell-1, ReCell-2 and ReCell-Denim fibres were compared with the Lyocell fibre spectrum and the focus was on identifying the characteristic cellulose II structure vibrational fingerprint. Table 2 presents the most significant absorbance bands assigned to crystalline cellulose II based on previous publications.

Examination of the ATR-FTIR spectra for the fibres in the $4000\text{-}2400\text{ cm}^{-1}$ region indicated that both Lyocell and ReCell fibres exhibited the same cellulose II vibrational fingerprint, Figure 1. The broad band between $3600\text{-}3000\text{ cm}^{-1}$ was assigned to hydrogen bonds between OH groups of cellulose II structure, where the 3488 cm^{-1} and 3447 cm^{-1} absorptions were due to the general OH stretching and specific $\text{O}(3)\text{H}\dots\text{O}(5)$ vibration due to the intramolecular hydrogen bonds in the cellulose II unit cell, respectively. Similar FTIR peaks for the cellulose II has previously been reported (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010), however the previous studies reported the $\text{O}(3)\text{H}\text{---}\text{O}(5)$ vibration at 3442 cm^{-1} .

The intensities for the 3488 cm^{-1} and 3447 cm^{-1} were similar in both the ReCell and Lyocell fibres and are very weak. The band at 3350 cm^{-1} was due to the OH stretching intramolecular hydrogen bonds in both Cellulose I and Cellulose II structures and is unambiguous (Carrillo, Colom, Sunol & Saurina, 2004). Nelson and others (Nelson & O'Connor, 1964a, b) proposed the band at 2900 cm^{-1} was due to the C-H stretching in Cellulose I and Cellulose II structures and they used the intensity ratio of the 1372 cm^{-1} and the 2900 cm^{-1} bands as a measure of the total crystallinity index for cellulose fibres. In this study intense bands of the same magnitude were observed at 2892 cm^{-1} for both Lyocell and the ReCell fibres and similar absorption intensities were reported for other lyocell fibrous materials (Široký, Blackburn, Bechtold, Taylor & White, 2010).

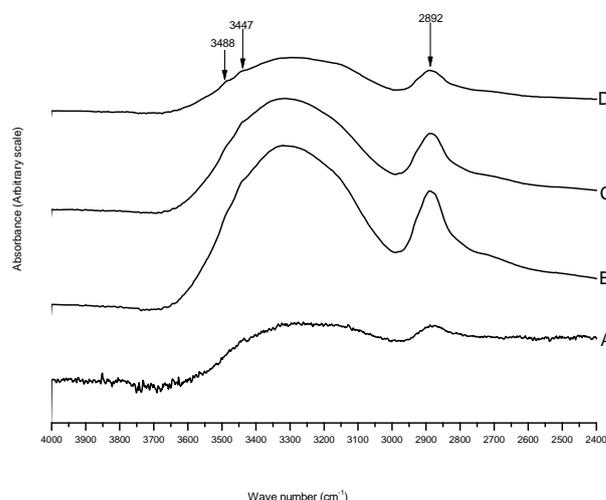


Fig. 1. FTIR spectra for the A - ReCell-2, B - Lyocell, C - ReCell-1 and D - ReCell-Denim fibres

Table 2. Characteristic vibrational infrared frequencies of Cellulose II fibres from research literature

| Frequency (cm ⁻¹) | Vibrational Assignments | References |
|-------------------------------|---|--|
| 3488 | stretching of intramolecular hydrogen bonded –OH groups | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 3447 | O(3)H...O(5) intramolecular hydrogen bond | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 3350 | O(3)H...O(5) intramolecular hydrogen bond | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 2900 | C-H stretching | (Carrillo, Colom, Sunol & Saurina, 2004; Nelson & O'Connor, 1964a; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1685-1655 | C=O stretching | (Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1635 | OH of water absorbed from cellulose | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1455 | OH in plane bending | (Carrillo, Colom, Sunol & Saurina, 2004) |
| 1420 | CH ₂ scissoring at C(6) | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1374 | CH bending | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1335 | OH in plane bending | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1315 | CH ₂ wagging | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1278 | CH bending | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1200 | OH in plane bending | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1155 | C-O-C asymmetric stretching | (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 1056 | C-O stretching | (Carrillo, Colom, Sunol & Saurina, 2004) |
| 996 | C-O valence vibration at C(6) | (Široký, Blackburn, Bechtold, Taylor & White, 2010) |
| 894 | C-O-C valence vibration | (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010) |

Examination of the ATR-FTIR spectra of the Lyocell and ReCell fibres in the 2000cm⁻¹ - 800cm⁻¹ region indicated that the fibres have similar structural features, Figure 2. The band between 1685 and 1600 cm⁻¹ comprises an overlap of the 1685-1655 cm⁻¹ and 1635cm⁻¹ bands and exhibits the same intensity and location for the Lyocell, ReCell-1 and ReCell-Denim fibres. The ReCell-2 fibres exhibited weaker absorption intensity relative to the other fibres in the 1685cm⁻¹-1600cm⁻¹ spectral range. The band between 1685-1655cm⁻¹ can be assigned to the C=O stretching in the cellulose II structure (Široký, Blackburn, Bechtold, Taylor & White, 2010) and the band at 1635cm⁻¹ was assigned to the OH water absorbed in the cellulose (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010) and is a characteristic of all cellulosic materials. The 1470cm⁻¹ and 1420cm⁻¹ absorption bands can be assigned to the OH in-plane bending and the CH₂ symmetrical bending of cellulose II structure, respectively, with these bands having similar intensities for all the fibres under investigation except the ReCell-2 fibres which exhibited relatively weaker absorption at 1470cm⁻¹. The absorption

bands at 1374 cm⁻¹, 1335 cm⁻¹ and 1315cm⁻¹ were assigned to CH bending, OH in-plane bending and CH₂ wagging of cellulose II and the amorphous cellulose structure (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a, b; Široký, Blackburn, Bechtold, Taylor & White, 2010), however for this study the CH bending and CH₂ wagging were observed at 1375cm⁻¹ and 1316cm⁻¹, respectively, and the peak intensities of the respective absorption bands were similar for Lyocell and ReCell fibres. Previous studies assigned the absorption band at 1280-1277 cm⁻¹ to C-H deformation in cellulose II (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002; Nelson & O'Connor, 1964a; Široký, Blackburn, Bechtold, Taylor & White, 2010) and it has been suggested that the absorption intensity in this region is weaker for amorphous cellulose and stronger for cellulose II. It was also suggested that the band observed at 1268 cm⁻¹ corresponds to the C-H deformation in cellulose II and amorphous cellulose and is an overlap of the 1278-1268cm⁻¹. The absorption band at 1278-1268cm⁻¹ was more obvious in the Lyocell and ReCell-1

spectra than the ReCell-Denim and ReCell-2 fibre spectra, suggesting that the ReCell-Denim and ReCell-2 fibres have a higher amount of amorphous cellulose than the Lyocell and ReCell-1 fibres. The source of the increased amorphous cellulose content in the ReCell-2 and ReCell-Denim fibres could be related to the treatment history of the feedstock. The band at 1235-1225 cm^{-1} has previously been reported as due to the O-H in plane deformation at C (6), and in this study similar band was observed at 1235 cm^{-1} with the intensity for this band very weak for both Lyocell and ReCell fibres.

The absorption band due to the OH in plane bending was observed at 1200 cm^{-1} with similar intensity for both the ReCell and Lyocell fibres, with similar absorptions being previously reported in the 1205-1200 cm^{-1} region (Carrillo, Colom, Sunol & Saurina, 2004; Schwanninger, Rodrigues, Pereira & Hinterstoisser, 2004). Previous research has also indicated that the absorption band at 1162 - 1125 cm^{-1} is due to C-O-C stretching of the β -glycosidic link in cellulose II (Carrillo, Colom, Sunol & Saurina, 2004; Liang & Marchessault, 1959a, b) whereas in this study a similar band was observed at 1135 cm^{-1} with similar intensity for both Lyocell and ReCell fibre.

The band at 1056 cm^{-1} was more obvious for ReCell-2 fibres than in Lyocell, ReCell-1 and ReCell-Denim fibres. Previous research has indicated that this band is characteristic of amorphous cellulose (Carrillo, Colom, Sunol & Saurina, 2004; Široký, Blackburn, Bechtold, Taylor & White, 2010). The presence of this absorption band in the ReCell-2 fibres may be due to the chemical removal of the easy care finish in the acid-alkaline solutions which may convert the reclaimed pulp into amorphous cellulose. The absorption band at 1018 cm^{-1} appears in both ReCell and Lyocell fibres with similar intensity. In this study the 1018 cm^{-1} absorption is considered to be similar to the 1035 cm^{-1} band which was previously reported to be due to C-O stretching in cellulose II (Carrillo, Colom, Sunol & Saurina, 2004)

An intense band was also observed at 996 cm^{-1} for the ReCell-2 fibres while the comparable band appears to be relatively weaker for the Lyocell, ReCell-1 and ReCell-Denim fibres. This band was previously reported to increase when cellulose II was treated with sodium hydroxide of increasing strength (Široký, Blackburn, Bechtold, Taylor & White, 2010). The highest peak intensity at 996 cm^{-1} for the ReCell-2 fibres may be due to the fact that the ReCell-2 fibres were produced from a blend of pulp reclaimed from waste garments by stripping off the easy care finish in acid-alkaline solutions. Thus it is the portion of the sodium hydroxide treated pulp which contributes to this intense band, hence no strong peak intensities were observed for the ReCell-Denim, ReCell-1 and Lyocell fibres at 996 cm^{-1} .

The absorption bands at 897 cm^{-1} and 893 cm^{-1} have previously been reported to be due to valence vibration of the C-O-C group in mainly cellulose I and cellulose II,

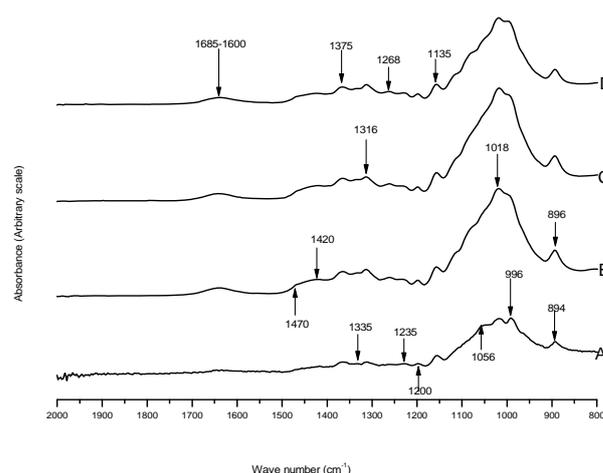


Fig. 2. FTIR spectra of A - ReCell-2, B - Lyocell, C - ReCell-1 and D - ReCell-Denim fibres

respectively (Široký, Blackburn, Bechtold, Taylor & White, 2010). The band at 897 cm^{-1} has previously also been reported to be due to the presence of cellulose III (Nelson & O'Connor, 1964b). In this study, the ReCell-2 fibre spectrum exhibited a strong distinct band at 894 cm^{-1} while the Lyocell, ReCell-1 and ReCell-Denim fibres exhibited a broad absorption band at 896 cm^{-1} . The band seems to be an overlap of the 894 cm^{-1} and 897 cm^{-1} spectral intensities and it is suggested that the Lyocell, ReCell-1 and ReCell-Denim fibres have some components of cellulose II.

From the FTIR results it can be concluded that while the Lyocell and ReCell fibres are similar, the ReCell-2 fibres in particular exhibited minor structural differences. The observed differences in the ReCell-2 fibre spectrum maybe due to the increased proportion of amorphous cellulose derived from the process of stripping off the easy care finishes in order to improve the cellulose solubility in the solvent.

Examination of the WAXD patterns for the ReCell and Lyocell fibres, Figure 3, showed cellulose with reflections mainly at the 101, 10 $\bar{1}$ and 002 planes which occur at angles of $2\theta = 12.3^\circ$, $2\theta = 20.2^\circ$ and $2\theta = 21.7^\circ$, respectively, with the 10 $\bar{1}$ and 002 planes overlapping each other. These observed reflections agree with previous publications on the WAXD patterns of the cellulose II structure (Kim, Pak, Jo & Lee, 2005; Kreže & Malej, 2003; Nelson & O'Connor, 1964a; Sfiligoj Smole, Peršin, Kreže, Stana Kleinschek, Ribitsch & Neumayer, 2003; Wang, Koo & Kim, 2003). The intensity of the 101 reflection was lower than the intensity of the 10 $\bar{1}$ and 002 plane reflections for both Lyocell and ReCell fibres, however no comparison was made on the peak intensity between the 10 $\bar{1}$ and 002 planes.

Both the ATR-FTIR and WAXD spectra of the ReCell fibres indicated typical cellulose II features and were similar to ATR-FTIR and WAXD spectra of Lyocell fibres.

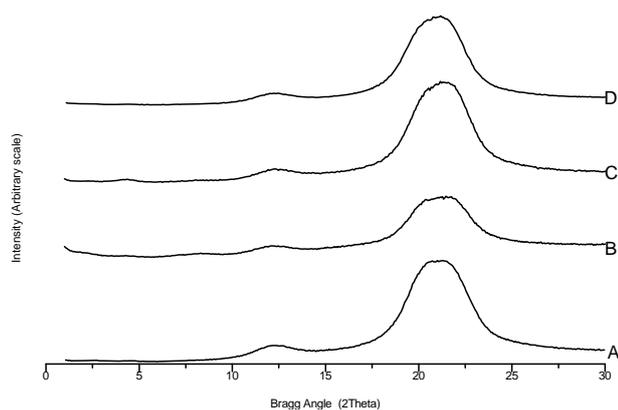


Fig. 3 .WAXD spectra for the A - ReCell-2, B - Lyocell, C - ReCell-1 and D - ReCell-Denim fibres

3.2 Crystallinity analysis of the fibres

Examination of the ATR-FTIR crystallinity indices of the fibres indicated that the ReCell-1, ReCell-2 and ReCell-Denim fibres have slightly higher TCI and LOI than the Lyocell fibres, Table 3. The TCI of Lyocell fibres was 1.10 whereas the ReCell-2 and ReCell-Denim fibres have a TCI of 20-26% higher than the Lyocell fibres. In contrast the TCI value for the ReCell-1 fibre was almost identical to the Lyocell fibres. The LOI for Lyocell fibres was 0.42 and the corresponding ReCell-1 and ReCell-Denim fibres had a LOI of 12-14% higher than the Lyocell fibres. The higher crystallinity indices of the ReCell-type fibres was probably due to the high molecular weight and degree of polymerization (DP) of the cotton pulp as previously reported (Haule, Carr & Rigout, 2014) which was again observed in the molecular weight of the fibres, Table 1. Although the Lyocell and ReCell fibres were regenerated by the same method, the nature of the feedstock appears to influence dissolution, fibre formation and structural development. Indeed previously it has been reported that the structure and formation of the solvent spun fibres is affected by the dissolution, spinning and regeneration conditions (Fink, Weigel, Purz & Ganster, 2001). Rheological parameters such as DP, viscosity and cellulose concentration are defined at the dissolution stage and have impact on chain orientation and fibres formation at subsequent stages (Chanzy, Paillet & Hagège, 1990; Fink, Weigel, Purz & Ganster, 2001; Kim, Shin, Cho, Kim & Chung, 1999).

Blending of 80% wood pulp and 20% waste cotton reclaimed pulp produced fibres (ReCell-2) that demonstrated a clear increase in TCI and LOI values,

26% and 40%, respectively, higher than the Lyocell fibres and 24% and 26%, respectively, above that observed for the ReCell-1 fibres and 5% and 23%, respectively, above that observed for the ReCell-Denim fibres. This increase in TCI and LOI was considered to be unusual because the two pulps (as they are both cellulosic and have the same molecular size) would be expected to follow the linear mixing rules of homogeneous polymers.

Previous publications indicated that Lyocell fibres have TCI and LOI values of 0.76 and 0.35, respectively (Carrillo, Colom, Sunol & Saurina, 2004; Colom & Carrillo, 2002) and TCI and LOI of 1.4 and 0.5, respectively (Široký, Blackburn, Bechtold, Taylor & White, 2010). Moreover Young-Soo Wang and others (Wang, Koo & Kim, 2003) reported the TCI of regenerated fibres at various cellulose concentrations and winding speeds was in the range of 0.228-0.642. The previously published FTIR crystallinity indices of Lyocell fibres varied slightly from the results, using a similar method, to those reported in this work, Table 3, and the observed difference could be due to the possible changes in physical spinning parameters such as solution state, spinning bath composition, length to diameter of the spinning nozzle, air gap length, spinning speed, take off tension, draw ratio, temperature and humidity and the precipitation and post-treatment conditions (Fink, Weigel, Purz & Ganster, 2001).

Examination of the WAXD crystallinity of the ReCell and Lyocell fibres indicated that the Lyocell fibres has a crystallinity of 79.6% whereas the ReCell-1 and ReCell-Denim fibres have a crystallinity of almost 9% higher than the Lyocell fibres. The ReCell-2 fibres have a lower crystallinity than the ReCell-1 and ReCell-Denim fibres but slightly higher than Lyocell fibres. This trend in the degree of crystallinity mirrors the change in the molecular weight of the fibres, Table 1. However, the trend WAXD crystallinity results do not correlate with the ATR-FTIR crystallinity indices, Table 3 and indicates that further studies should be conducted to understand the properties of the pulp recovered from the waste garments. The percentage crystallinity for Lyocell fibres in Table 3 agreed with the crystallinity index previously determined by similar methods (Sfiligoj Smole, Peršin, Kreže, Stana Kleinschek, Ribitsch & Neumayer, 2003; Wang, Koo & Kim, 2003) though was lower than the value reported by Kreže and others (Kreže & Malej, 2003).

Table 3. Crystallinity of Lyocell and ReCell fibres as determined by FTIR and WAXD analyses

| Fibre Sample | Total Crystallinity Index (1375/2892 cm^{-1}) | | Lateral Order Index (1420/894 cm^{-1}) | | Crystallite size [Å] | WAXD Crystallinity (%) |
|--------------|---|------|--|------|----------------------|------------------------|
| | Mean | SD | Mean | SD | | |
| Lyocell | 1.10 | 0.02 | 0.42 | 0.04 | 20 | 79.6 |
| ReCell-1 | 1.12 | 0.06 | 0.47 | 0.03 | 20 | 86.6 |
| ReCell-Denim | 1.33 | 0.08 | 0.48 | 0.09 | 21 | 87.1 |
| ReCell-2 | 1.39 | 0.1 | 0.59 | 0.07 | 24 | 81.7 |

Table 4. Accessibility and regain values for Lyocell and ReCell fibres

| Fibre Type | WRV (g/g) | ISV (mg I ₂ /g Cellulose) | Regain (%) |
|--------------|-----------|---|------------|
| Lyocell | 0.78±0.03 | 288±4.2 | 12.4±0.8 |
| ReCell-1 | 0.62±0.04 | 248±4.5 | 9.5±0.3 |
| ReCell-Denim | 0.61±0.04 | 259±2.4 | 10.1±1.1 |
| ReCell-2 | 0.75±0.01 | 262±5.2 | 12.9±0.4 |

Table 3 presents the results for the crystal size [\AA] of the ReCell and Lyocell fibres as determined by WAXD at the diffraction angle 2θ [$^\circ$] of reflections of the 002 plane. The ReCell-2 and ReCell-Denim fibres have slightly higher crystallite sizes than the Lyocell and ReCell-1 fibres. The Lyocell and ReCell-1 fibres have a crystallite size of 20\AA whereas the ReCell-2 fibres have a crystallite size of 20% higher than the Lyocell and ReCell-1 fibres. The crystallite size of the Lyocell fibres was previously determined and found to be $34.2\text{-}47.3\text{\AA}$ (Kreze & Malej, 2003) which is higher than is reported in this work. The similarity in the crystallite size of the ReCell and Lyocell fibres can also be confirmed from the similar shape and size of the diffraction peak at the 002 plane, Figure 3.

3.3 Fibre regain and accessibility by reagents

One of the important properties of textiles fibres is its accessibility by chemicals/reagents. This property determines the ease with which the fibres can be modified by wet processes in order to achieve the desired performance properties of the final garments. Moisture regain is also an important aspect of the comfort of the garments. Fortuitously cellulosic fibres exhibit substantial regain and easy accessibility by wet chemical reagents. However these properties vary among the cellulosic fibres depending on the nature and method of fibre production as the two affect the structure of the resultant fibres.

Table 4 presents the WRV, ISV and moisture regain values of Lyocell fibres and the fibres regenerated from cotton waste garments. The Lyocell fibres proved to have the highest WRV among the investigated fibres followed by the ReCell-2 fibres. The ReCell-1 and ReCell-Denim fibres have a WRV which is at least 20% lower than the Lyocell fibres. The ISV of the Lyocell fibres was 10-13% above the ISV of ReCell fibres. Blending of 80% wood pulp and 20% reclaimed cotton pulp improved both the WRV and ISV of the resultant fibres (ReCell-2) to between that of ReCell-1 and Lyocell fibres. The regain of the ReCell fibres was at least 23% lower than the Lyocell fibres, however ReCell-2 fibres have regain values marginally higher than the Lyocell fibres.

The higher accessibility properties in Lyocell fibres in comparison to ReCell fibres is due to the difference in their supramolecular properties and correlates well with the crystallinity percentages determined by WAXD. The cellulose molecules retain water and iodine by interactions between the reagents polar molecules and

the cellulose hydroxyl groups in the amorphous fraction of the cellulose system. Owing to the high order and strong forces holding the crystalline regions, the water and iodine cannot access the crystalline region. Thus the ReCell fibres exhibited lower accessibility values than the Lyocell fibres due to the lower amorphous fraction in ReCell fibres in comparison to the Lyocell fibres. Blending of 80% wood pulp and 20% reclaimed cotton pulp resulted in a reduction of the crystalline fraction and an increase in the accessibility of the ReCell-2 fibres.

4. Conclusions

This work has characterized the properties of fibres regenerated from cotton waste garments. The supramolecular properties of ReCell-1, ReCell-2 and ReCell-Denim fibres were determined using ATR-FTIR and WAXD techniques, respectively, and compared to the properties of Lyocell fibres. The ATR-FTIR results indicated that the ReCell-2 fibres have increased amorphous cellulose which may be due to the purification of the feedstock under acid/alkaline conditions. More research is required to understand the molecular properties of the pulp reclaimed from cotton waste garments prior to regeneration into new fibres. The WAXD crystallinity index of the fibres did not correlate well with the ATR-FTIR, LOI and TCI data. The accessibility determined by ISV and water retention value and regain properties of the ReCell-1, ReCell-2 and Lyocell fibres correlated well with the supramolecular properties of the investigated fibres. The Lyocell fibres demonstrated the highest accessibility and regain properties among the tested fibres due to its relatively high amorphous fraction. From the results of the current study, further analysis of the fibres may be conducted so as to understand the properties correlation of the ATR-FTIR and WAXD analysis hence consider cotton waste garments as an alternative future source of feedstock for the regeneration of lyocell fibres. The alternative source may contribute to the reduction of the negative environmental and economic impact of the textile waste in the developing world.

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References

- Amankwah-Amoah, J. (2015). Explaining declining industries in developing countries: The case of textiles and apparel in Ghana. *Competition & Change*, 19(1), 19-35.
- Carrillo, F., Colom, X., Sunol, J. J., & Saurina, J. (2004). Structural FTIR Analysis and Thermal Characterisation of Lyocell and Viscose-type Fibres. *European Polymer Journal*, 40(9), 2229-2234.
- Chanzy, H., Paillet, M., & Hagège, R. (1990). Spinning of Cellulose from N-methylmorpholine N-oxide in the Presence of Additives. *Polymer*, 31(3), 400-405.
- Colom, X., & Carrillo, F. (2002). Crystallinity Changes in lyocell and Viscose-type Fibres by Caustic Treatment. *European polymer journal*, 38(11), 2225-2230.
- Danish Fashion Institute (2012). Copenhagen Fashion Summit on Sustainability in Fashion. Danish Fashion Institute.
- DEFRA (2009). Maximising Reuse and Recycling of UK Clothing and Textiles. (p. 42). London: The Department for Environment, Food and Rural Affairs-UK.
- Ekström, K. M., & Salomonson, N. (2014). Reuse and Recycling of Clothing and Textiles—A Network Approach. *Journal of Macromarketing*, 34(3), 383-399.
- Fink, H. P., Weigel, P., Purz, H. J., & Ganster, J. (2001). Structure Formation of Regenerated Cellulose Materials from NMMO-solutions. *Progress in Polymer Science*, 26(9), 1473-1524.
- Haule, L. V., Carr, C. M., & Rigout, M. (2014). Investigation into the removal of an easy-care crosslinking agent from cotton and the subsequent regeneration of lyocell-type fibres. *Cellulose*, 21(3), 2147-2156.
- Haule, L. V., Carr, C. M., & Rigout, M. (2016a). Preparation and physical properties of regenerated cellulose fibres from cotton waste garments. *Journal of Cleaner Production*, 112(5), 4445-4451.
- Haule, L. V., Carr, M. C., & Rigout, M. (2016b). Investigation into the removal of a formaldehyde-free easy care cross-linking agent from cotton and the potential for subsequent regeneration of lyocell-type fibres. *The Journal of The Textile Institute*, 107(1), 23-33.
- Haule, L. V., Rigout, M., Carr, C. M., & Jones, C. C. (2012). Surface and bulk chemical analysis of the durability of an easy care finish on cotton. *Cellulose*, 19(3), 1023-1030.
- Kim, D. B., Pak, J. J., Jo, S. M., & Lee, W. S. (2005). Dry Jet-Wet Spinning of Cellulose/N-Methylmorpholine N-oxide Hydrate Solutions and Physical Properties of Lyocell Fibers. *Textile Research Journal*, 75(4), 331-341.
- Kim, S. O., Shin, W. J., Cho, H., Kim, B. C., & Chung, I. J. (1999). Rheological Investigation on the Anisotropic Phase of Cellulose-NMMO/H₂O Solution System. *Polymer*, 40(23), 6443-6450.
- Kreze, T., & Malej, S. (2003). Structural Characteristics of New and Conventional Regenerated Cellulosic Fibers. *Textile Research Journal*, 73(8), 675-684.
- Liang, C. Y., & Marchessault, R. H. (1959a). Infrared Spectra of Crystalline Polysaccharides. I. Hydrogen Bonds in Native Celluloses. *Journal of Polymer Science*, 37(132), 385-395.
- Liang, C. Y., & Marchessault, R. H. (1959b). Infrared Spectra of Crystalline Polysaccharides. II. Native Celluloses in the Region from 640 to 1700 cm⁻¹. *Journal of Polymer Science*, 39(135), 269-278.
- Nelson, M. L., & O'Connor, R. T. (1964a). Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part II. A New Infrared Ratio for Estimation of Crystallinity in Celluloses I and II. *Journal of Applied Polymer Science*, 8(3), 1325-1341.
- Nelson, M. L., & O'Connor, R. T. (1964b). Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part I. Spectra of Lattice Types I, II, III and of Amorphous Cellulose. *Journal of Applied Polymer Science*, 8(3), 1311-1324.
- Nelson, M. L., Rousselle, M.-A., Cangemi, S. J., & Trouard, P. (1970). The Iodine Sorption Test. Factors Affecting Reproducibility and a Semimicro Adaptation. *Textile Research Journal*, 40(10), 872-880.
- Okubayashi, S., Griesser, U. J., & Bechtold, T. (2004). A Kinetic Study of Moisture Sorption and Desorption on Lyocell Fibers. *Carbohydrate Polymers*, 58(3), 293-299.
- Schwanninger, M., Rodrigues, J. C., Pereira, H., & Hinterstoisser, B. (2004). Effects of Short-time Vibratory Ball Milling on the Shape of FT-IR Spectra of Wood and Cellulose. *Vibrational Spectroscopy*, 36(1), 23-40.
- Sfiligoj Smole, M., Peršin, Z., Kreže, T., Stana Kleinschek, K., Ribitsch, V., & Neumayer, S. (2003). X-ray Study of Pre-treated Regenerated Cellulose Fibres. *Materials Research Innovations*, 7(5), 275-282.
- Shen, L., Worrell, E., & Patel, M. K. (2010). Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling. *Resources, Conservation and Recycling*, 55(1), 34-52.
- Siroka, B., Noisternig, M., Griesser, U. J., & Bechtold, T. (2008). Characterization of Cellulosic Fibers and Fabrics by Sorption/Desorption. *Carbohydrate Research*, 343(12), 2194-2199.
- Široký, J., Blackburn, R., Bechtold, T., Taylor, J., & White, P. (2010). Attenuated Total Reflectance Fourier-transform Infrared Spectroscopy Analysis of Crystallinity Changes in Lyocell Following Continuous Treatment with Sodium Hydroxide. *Cellulose*, 17(1), 103-115.
- Wang, Y.-S., Koo, W.-M., & Kim, H.-D. (2003). Preparation and Properties of New Regenerated Cellulose Fibers. *Textile Research Journal*, 73(11), 998-1004.