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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

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Abstract 1,2,3,4-Butane tetracarboxylic acid (BTCA)-treated cotton fabrics were immersed in alkali for increasing time periods and the effectiveness of alkali in removing the cross-linking agent was investigated by surface (X-ray photoelectron spectroscopy, XPS) analysis, attenuated total reflectance Fourier transform infrared spectroscopy and solubility in specific solvents. The cellulose yield after the chemical 'stripping' processes was established and the effect of the alkali treatments on the degree of polymerization of the resultant cellulose determined. Surface analyses and solubility tests suggested that the alkali alone could successfully remove the BTCA from the crease resist-treated cotton fabric and
produced a commercially viable yield of cellulose.

Introduction

The increase in the number of fashion seasons and associated consumer behaviour is probably the main cause of the subsequent increase in textile waste generated (Baden & Barber, 2005). The commonest approach to reducing the environmental impact of this clothing 'waste' in Europe and North America is to export the second hand clothes to developing countries (DEFRA, 2006, 2009; Hawley, 2006a, 2006b). However, this approach is not sustainable long term because it is increasingly considered as a threat to the growth of local textile and apparel industries in the destination countries in Africa (Baden & Barber, 2005). Therefore, a potential solution to this growing textile waste stream could be the recycling of the used garments using them as a raw material for making new textile fibres. The technology for recycling of polyester-based waste garment by depolymerization of the fibres into monomers and then reconstituting the monomer into 'new polymer' is commercially available (Lebedev, 1995). However, in contrast while the regeneration of 'new' cellulosic fibres from cotton waste garments has also been reported (Firgo, Eichinger, & Eibl, 1997), it as yet is not a commercial process. In addition, the previous work was based on clean white cotton fabrics and the effect of finishes such as crease resist easy care treatments and colouration was not considered.

Easy care chemical finishes are applied to cellulosic fabrics in order to impart dimensional stability, crease resistance and crease recovery properties to garments (Carty & Byrne, 1987). Previous research has established that waste cotton garments contain residual dimethyloldihydroxyethylene (DMDHEU) easy care finish even at the end of garments' life cycle (Haule, Rigout, Carr, & Jones, 2012) and that the residual DMDHEU reduced the solubility of the waste cotton garments in solutions suitable for dissolution and regeneration of cellulosic fibres. Subsequently, a method for removal of the DMDHEU easy care finishes for reclaiming cellulose suitable for fibres regeneration was developed based on an acid and alkali 'stripping' treatment (Haule, Carr, & Rigout, 2014).

Although the DMDHEU easy care finish has outstanding functional and cost performance, possible health and environmental problems associated with formaldehyde release remains a major concern over its continuing use in textile finishing (Kottes Andrews, & Harper, 1980; Vail & Pierce, 1973; Weilin & Shyr, 2000; Xu & Shyr, 2001). In order to overcome the potential effects of methylol-based easy care finishes a number of alternative zero-formaldehyde finishes based on polycarboxylic acids (PCA) have been investigated and their relative performance demonstrated (Weilin & Shyr, 2000; Xu & Shyr, 2001; Yang, 1991a, 1991b, 2001; Yang & Andrews, 1991; Yang, Chen, Guan, & He, 2010; Yang & Dengjin, 2000; Yang, Hu, & Lickfield, 2003; Yang, Lan, Shiqi, & Yanqiu, 1998; Yun & Yang, 1999). It has been established that the PCA crosslinked the cellulose polymer, in the presence of a hypophosphite catalyst, through the formation of a fivemembered cyclic anhydride and then esterification of the cellulose polymer (Scheme 1). A series of polycarboxylic acids such as 1,2,3,4-butane tetracarboxylic acid (BTCA), citric acid and polymaleic acid have been investigated, but all have had limited commercial success either due to the high cost of the BTCA or the lower reactivity, overall performance and yellowing of the cheaper citric and polymaleic acid alternatives (Kang, Yang, Weishu, & Lickfield, 1998; Schramm & Rinderer, 2002; Yang et al., 2010; Yun & Yang, 1999). Nevertheless, BTCA has been used as a cross-linking agent in the pulp and paper industry as a wet strength and dimensional stability agent (Caulfield, 1994).

Previously, the removal of BTCA from cross-linkertreated cotton fabrics has been investigated in

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order to determine the effects of treatment conditions on the degree of cross-linking and the strength loss associated with the acid hydrolysed depolymerization (Kang et al., 1998; Yang et al., 2003). The alkali BTCA stripping treatment was based on immersion in 0.1–0.5 M sodium hydroxide (NaOH) solution at 50 °C for 48–96 h and was clearly not a viable fibre 'production-type' process. The effectiveness of the stripping method was evaluated by the determination of the crease recovery angle (CRA) performance, hydrolysis of the ester bonds and the loss in strength of the stripped cotton fabrics. The solubility and level of degradation of the reclaimed cellulose following alkaline hydrolysis was not determined. In this article, the stripping of BTCA easy care finishes from cotton fabric under alkaline conditions was investigated and the treatment conditions optimized with a view to commercial reclamation of the first lifetime cellulosic textile. The efficiency of the stripping process was quantified microscopically and using X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATRFTIR), solubility tests and retention of the cellulosic molecular properties of the treated cotton fabrics.

Experimental

Materials

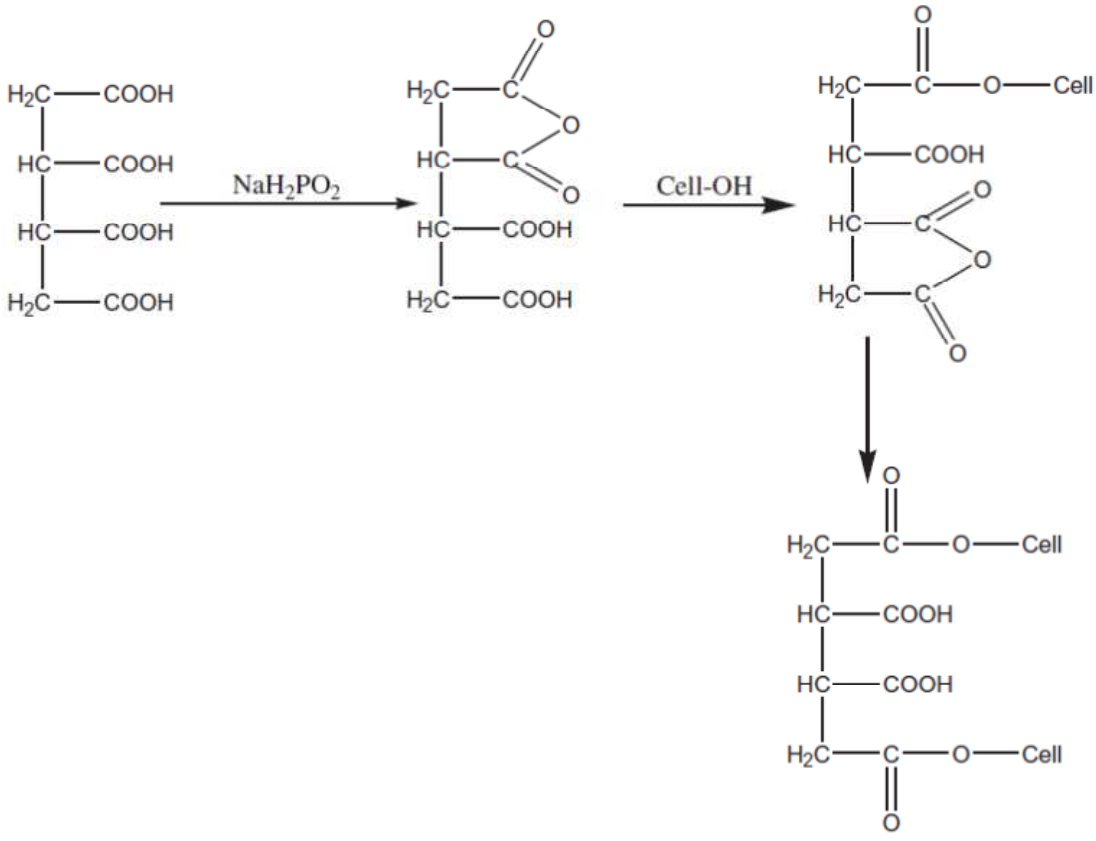
Scoured, bleached, 100% plain woven cotton fabric, 152 g/m2 was supplied by Phoenix Calico, UK. BTCA, sodium hydroxide and glycerol were supplied by Fisher Scientific, UK. Propyl gallate 98%, hydroxylamine sulphate 99% and 4-methylmorpholine-N-oxide (NMMO) solution (50% water) and sodium hypophosphite, laboratory reagent grade, were supplied by Acros Organics, UK. Cupriethylenediamine (CED) solution, (1 M), was supplied by Merck, UK.

Application of easy care finishes

In order to modify the cotton fabrics with the zero-formaldehyde finish solutions of 100 and 140 g/L BTCA and sodium hypophosphite (BTCA: sodium hypophosphite ratio 1:1), respectively, were padded onto the cotton fabrics at 80% wet pick up. The padded fabrics were then oven dried for 2.5 min at 100 °C with subsequent curing for 90 s at 180 °C. The cured fabrics were warm rinsed in distilled water to remove any finish residue and then air dried for further tests.

Alkali treatment of cross-linked fabrics

Both control and easy care finished cotton were 'stripped' in sodium hydroxide solution based on the following methods described in the literature (Abhyankar, Beck, Ladisch, & Bertoniere, 1987; Abhyankar, Beck, Ladisch, & Frick, 1986; Abhyankar, Beck, Ladisch, & Rowland, 1985) with some minor modifications (Haule et al., 2014). A solution of 23% w/w sodium hydroxide was prepared, cooled to 23 °C modifications (Haule et al., 2014). A solution of 23% w/w sodium hydroxide was prepared, cooled to 23 °C



Scheme 1. Crosslinking of cellulose polymer with BTCA easy care finish.

and then divided into two portions into two 250 mLs beakers. Cotton fabric, ~12.5 g, was placed in one of the sodium hydroxide solutions in order to impregnate the solution into the fabric. After 30 min immersion in the cold sodium hydroxide solution, the fabric was transferred into the boiling sodium hydroxide solution and allowed to boil for increasing time periods. The liquor:fabric ratio was 10:1. The treated fabrics were then removed, rinsed in hot water, neutralized in 0.5 mL/L acetic acid for 10 min, warm rinsed in distilled water and then air dried.

XPS analysis

XPS analysis was performed using a Kratos Axis system spectrometer. The fabric samples were cut from the middle of the specimen and attached to the sample holder using a double sided tape. Monochromatic AlKα X-rays (1486.69 eV) with a power of 150 W were used to irradiate the samples. A wide scan spectrum was recorded with pass energy of 160 eV from which the surface composition (C and O) was determined. High resolution Carbon (1s) spectra were recorded with pass energy of 40 eV. The binding energy (BE) values were calculated relative to the Carbon (1s) photoelectron at 285.0 eV. Charge compensation for the samples was achieved using a 4–7 eV electron beam at a flood current of approximately 0.1 mA, and an electrically ground 90% transmission nickel mesh screen adjacent to the fabric samples. Data analysis was performed using the CASA XPS software (Walton, Wincott, Fairley, & Carrick, 2010).

ATR-FTIR analysis

The ATR-FTIR spectra were collected on Nicolet 5700 instrument with a diamond crystal attachment. Analysis was performed from 4000 to 600 cm^{-1} and the data presented the average of 128 repetitions with a resolution of 8 cm^{-1}. The data were processed using Origin Pro 8.1 SR3 application software.

Light microscopy analysis

Light microscopy analyses were performed using Leica CTR 6000 microscope with a Leica 20x lens magnification.

Solubility in CED solution

The dissolution of cotton fabrics in CED solution was performed as per British standard test method BS ISO 5351:2010 (British Standards, 2010) as previously described (Haule et al., 2014), and the amount of cellulose dissolved in the CED solution was determined as per Equation (1).

$$s = \frac{x - (w - f)}{x} \times 100\%, \quad (1)$$

where I is the solubility of the cellulose in %, I is the oven dry (OD) weight of the sample before dissolution in g, and *w* and *f* are the OD weights in grams of the filter paper after and before filtration, respectively. Only samples which did not show any insoluble particles on the microscope and with s = 100% were considered as 100% soluble and tested for limiting viscosity.

Analysis of the degree of polymerization (DPv) of cellulose

The DPv of the purified cellulose was derived from the limiting viscosity of the cellulose. The limiting viscosity of the cellulose material was measured using Scan CM 15:99 C for calibration and Scan CM 15:99 T for testing-Rheotek capillary viscometers (as described by the British standards test method, BS ISO 5351:2010 as previously described (Haule et al., 2014). The DPv values were then calculated from the mean limiting viscosity (Marx-Figini & Figini, 1995).

Dissolution of cellulose in NMMO

The method for dissolution of cellulose was based on previous work (Chanzy, Paillet, & Hagège, 1990) and were described previously (Haule et al., 2014). The solubility of the cotton specimen in NMMO solution was established by adding 14 g of 50% w/w NMMO solution to a 200 mLs spherical flask, followed by 80 mg of n-propyl gallate anti-oxidant and then stirred until all the anti-oxidant dissolved in the NMMO solution. Then, 0.280 g of cellulose was added to the solution, the flask was connected to a rotor evaporator, heated to 100 °C and connected to a 15 mm Hg vacuum system. After 60–90 min of evacuation/rotation, a yellowish, transparent, bubble free film was formed on the wall of the flask. The flask was then removed from the rotor evaporator and immersed in silicone oil bath at 130 °C for 20 min in order to convert to a free flowing solution. The solution was sampled on a glass slide and observed using a Leica CTR 6000 polarizing light microscope to confirm the solubility. The simple criterion for solubility in the NMMO solution was designated as either ‘fully soluble’ or ‘insoluble’. If microscopic images indicated the presence of any fibres then the sample was considered as ‘insoluble’. If the microscopic images indicated no fibres present then the sample was considered as ‘soluble’.

Results and discussion

Removal of BTCA easy care finish from cotton fabric: XPS and ATR-FTIR analysis

Examination of the C(1s) XP spectra of the untreated and 100 g/L BTCA-treated cotton fabric surface indicated that the surface was not purely cellulosic, due to the presence of the hydrocarbon C–H peak intensity at a BE of 285.0 eV, and the spectral peak intensity at a BE of 289.0 eV, assigned to the –C(=O)–OH and –C (=O)–O–Cell species, (Scheme 1 and Figures 1 and 4) (Ratner & Castner, 1997). The relative increase in peak intensity at 289.0 eV with the BTCA-treated cotton suggests the presence of the PCA at the fibre surface. The peak intensity at 286.6 and 288.0 eV can be assigned to the C–OH and O–C–O and C=O species,

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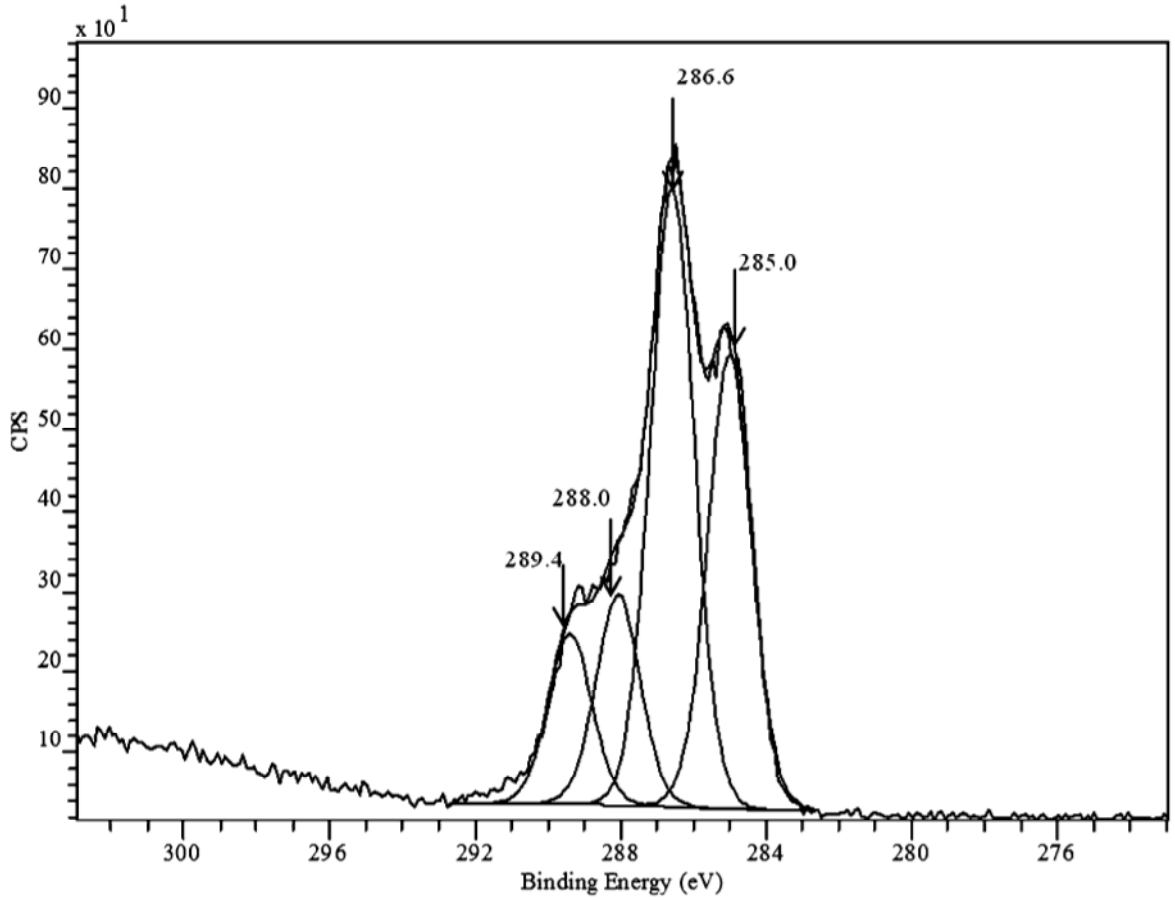

Figure 1. C(1s) XP spectrum of 100 g/L BTCA finished cotton fabric.

respectively, (Ratner & Castner, 1997). Examination of the XP spectrum of the 140 g/L BTCA-treated cotton similarly showed an even larger increase in the spectral peak at 289.0 eV due the increased ester and carboxyl surface functionalities. Following treatment of the 100 g/L BTCA finished cotton fabric with 23% sodium hydroxide at 100 °C for 30 s, the peak intensity at BE 289.0 eV was reduced (Figure 2).

Further increases in the treatment times caused a gradual decrease in the peak intensity at BE 289.0 eV, and after 5 min, the intensity was reduced nearly to the level of the original untreated control cotton fabric (Figures 3 and 4 and Table 1).

It is known that during the cross-linking process, the carboxylic groups of the BTCA dehydrate into five membered cyclic anhydride intermediates, which subsequently forms the ester cross-links with the cellulose polymer, (Scheme 1), that provides the crease resistance and recovery under mechanical deformation of the fibre. Under strong alkaline conditions and high temperature, the cross-links in the 100 g/L BTCA-treated cotton appear to be hydrolysed leaving the cellulosic surface with its original level of cellulosic carboxylic acid species content (Sauperl, Stana-Kleinschek, & Ribitsch, 2009; Yang, 1991a, 1991b, 2001; Yang & Andrews, 1991; Yang et al., 1998). Similarly, treatment of cotton fabric with 140 g/L BTCA with alkali resulted in a clear decrease in the spectral peak intensity at a BE of 289.0 eV, assigned to –C(=O)–OH and –C(=O)–O– Cell and with increasing immersion periods in the 23% w/w sodium hydroxide solution, the peak intensity at 289.0 eV decreased to the levels of the original untreated cotton due to ester hydrolysis.

The effectiveness of the NaOH treatment on the BTCA cross-linked cotton fabric was also analysed using FTIR spectroscopy. In order to clearly observe and differentiate the changes in the FTIR spectral profiles before and after NaOH treatment, the spectra were normalized against the 2900 cm^{-1} vibrational band which is assigned to C–H stretching (Carrillo, Colom, Sunol, & Saurina, 2004; Nelson & O'Connor, 1964a; Široký, Blackburn, Bechtold, Taylor, & White, 2010) and which remained unchanged with the NaOH treatment. The normalized spectra were then analysed in detail between 1800–1500 and 1500–800 cm^{-1} in order to identify any compositional changes occurring following the alkali hydrolysis process. Examination of the FTIR spectra of the cotton fabric treated with 100 g/L BTCA easy care finish indicated an obvious 'new' absorption band at 1725 cm^{-1} which can be attributed to the chemically bound BTCA finish and was assigned to the carbonyl stretch in the ester bond of the cross-linked polycarboxylic acid (Figure 5). Treatment of the BTCA finished cotton fabrics in alkaline solution indicated that the observed absorption band diminished in intensity with increasing sodium hydroxide treatment time (Figure 5).

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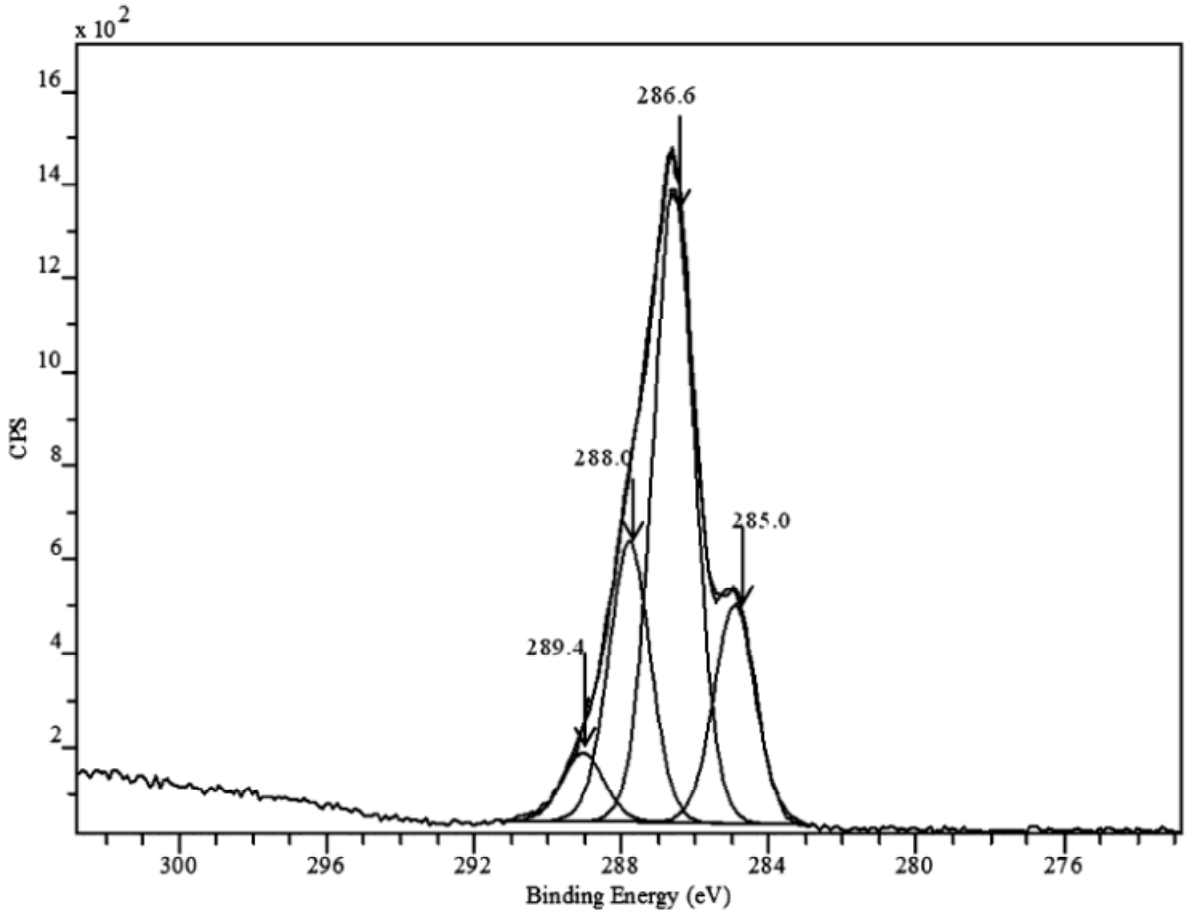

Figure 2. C(1s) spectrum of 100 g/L BTCA finished cotton fabric treated in 23% NaOH solution at the boil for 30 s.

The decrease of the absorption band at 1725 cm^{-1} with increasing in treatment times was due to the hydrolysis of the ester cross-links by the strong alkaline solution. Previous studies have indicated that during cross-linking of cellulose polymer with BTCA the latter exists in three forms, that is, as an ester species with an associated vibrational band at 1725 cm^{-1}, as a carboxylic acid species and as a carboxylate ion with an absorption band at 1576 cm^{-1}. The proportion of the three forms depends on the catalyst, temperature and curing time during application of the BTCA on the cotton fabrics (Yang, 1991a). The lack of strong absorption band at 1576 cm^{-1} in both the control and the BTCA finished cotton fabrics indicated that to the large extent the conditions for application of the BTCA into cotton fabrics favoured formation of ester cross-links and carboxylic acid. It is clear from this study that the ATRFTIR analysis correlates well with the surface XPS results in terms of cellulosic modification and durability to hydrolysis.

Treatment of cellulose with strong sodium hydroxide solution under conditions similar to mercerization causes rearrangement of the super molecular structure of the cellulose material (Fink, Philipp, Zschunke, & Hayn, 1992; Nelson & O'Connor, 1964a, 1964b). Thus, the effect of sodium hydroxide solution stripping on the 100 g/L BTCA-treated cotton fabric was also analysed by ATR-FTIR in the cellulosic fingerprint region (1500– 800 cm^{-1}) (Figure 6).

The 1163 cm^{-1} absorption band, which is due to the C–O–C symmetric stretching vibration in the cellulose I form of cotton (Nelson & O'Connor, 1964a, 1964b) was stronger for the BTCA-treated fabrics due to the additional C–O–C content after chemical modification. The application of sodium hydroxide solution to the BTCA-treated cotton fabric over increasing time caused a gradual disappearance of the 1163 cm^{-1} absorption band and an emergence of the 1156 cm^{-1} absorption band which has previously been assigned to the C–O–C symmetric stretching in cellulose II (Carrillo et al., 2004; Široký et al., 2010). Therefore, there was a proportional increase of the cellulose II form as observed by a shift of C–O–C stretching band from 1163 to 1156 cm^{-1} with increasing treatment times. Furthermore, the NaOH treatment on the BTCA-crosslinked cotton fabric resulted in the complete disappearance of the absorption band at 1111 cm^{-1}, which has been assigned to the asymmetrical ring stretching in cellulose I (Carrillo et al., 2004; Nelson & O'Connor, 1964a, 1964b; Široký et al., 2010). The disappearance of the 1111 cm^{-1} absorption band on treatment with NaOH indicated that the sodium hydroxide solution was converting the cotton fabric from cellulose I into the cellulose II form. In addition, the treatment of the BTCA-finished cotton fabric with

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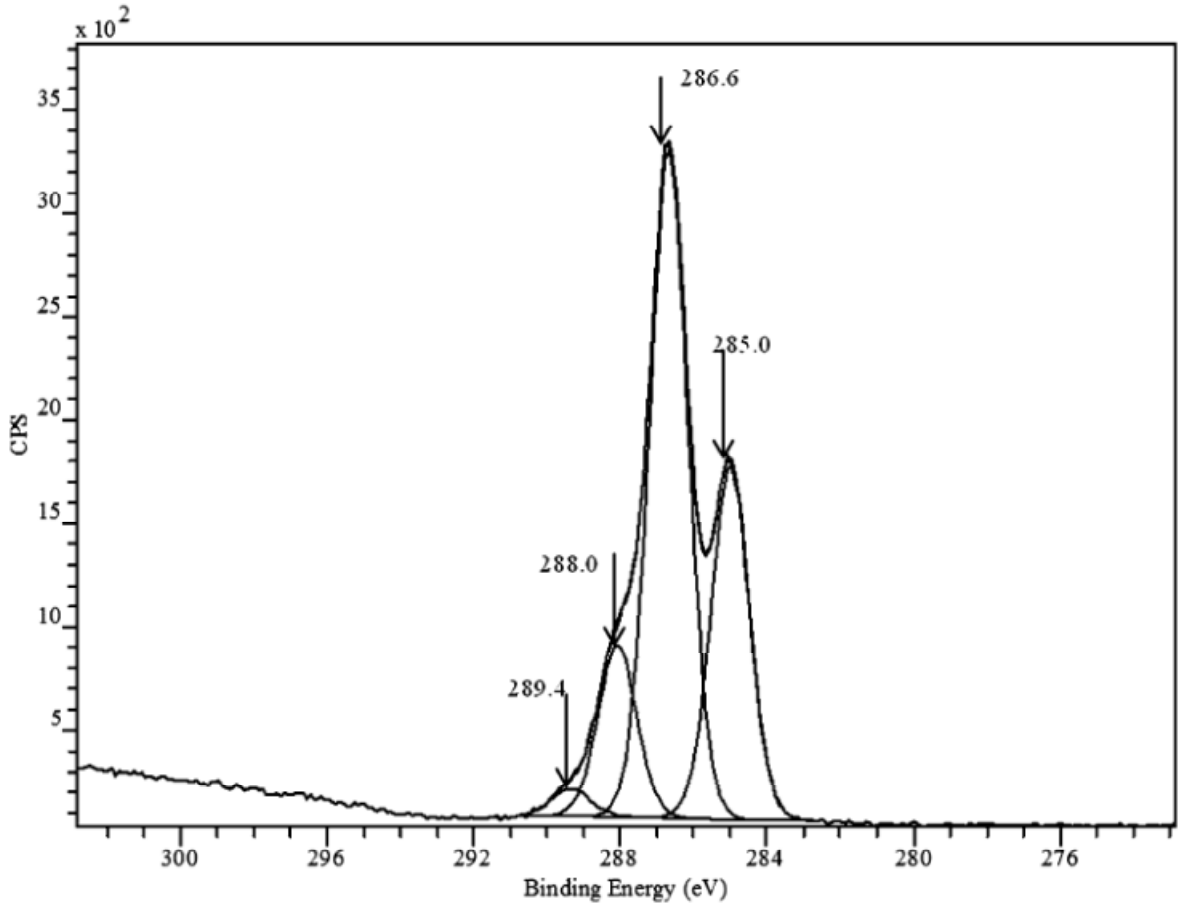

Figure 3. C(1s) spectrum of 100 g/L cotton fabric treated in 23% NaOH solution at the boil for 5 min.

Table 1. XP peak position and height for various components of cotton fabrics finished with 100 g/L BTCA and then treated in 23% NaOH solution at the boil at increasing times.

Component	Peak position (eV)	0 min Intensity (CPS)	30 s Intensity (CPS)	5 min Intensity (CPS)	Control Intensity (CPS)
C–H, C–C	285.0	593.7	503.1	1770.6	425.3
C–O	286.6	801.5	1390.6	3304.0	1006.0
C=O, O–C–O	288.0	297.0	638.6	913.1	271.6
O=C–O	289.4	247.3	188.5	220.6	59.9

NaOH solution at increasing time resulted in an increase in the absorption band at 893 cm^{-1} and this has also been assigned to the C–O–C valence vibration of the cellulose II form (Nelson & O'Connor, 1964a, 1964b).

Similarly, the ATR-FTIR spectra of cotton fabric treated with 140 g/L BTCA and then stripped in sodium hydroxide solution for increasing times exhibited the same spectral behaviour as the fabric treated with 100 g/L BTCA.

Cellulose solubility in the CED and NMMO solutions

The effect of the NaOH treatment was to increase the solubility of the BTCA-treated cross-linked cotton fabric in CED and NMMO solutions. The microscopic visual inspection of the CED and NMMO cellulose containing solutions indicated that some undissolved fibres were still apparent in the solutions after the cotton fabrics treated with BTCA easy care finish were immersed in the CED and NMMO solutions, respectively. Similarly, the BTCA-finished cotton fabrics stripped in 23% w/w sodium hydroxide solution at the boil for 30 s did not completely dissolve in either the CED or NMMO solutions. However, with stripping times greater than 30 s there was complete dissolution of the treated fabrics in both the CED and NMMO solutions. The inability of the CED and NMMO solutions to completely dissolve the cotton fabric treated with BTCA easy care finish was due to limited accessibility to the cellulose in the crosslinked fabric. When the cotton fibre was cross-linked by the BTCA the cellulose hydroxyls in the amorphous fraction of the fibre, which react with the BTCA to form the ester links, become 'inaccessible' to swelling solvents. For

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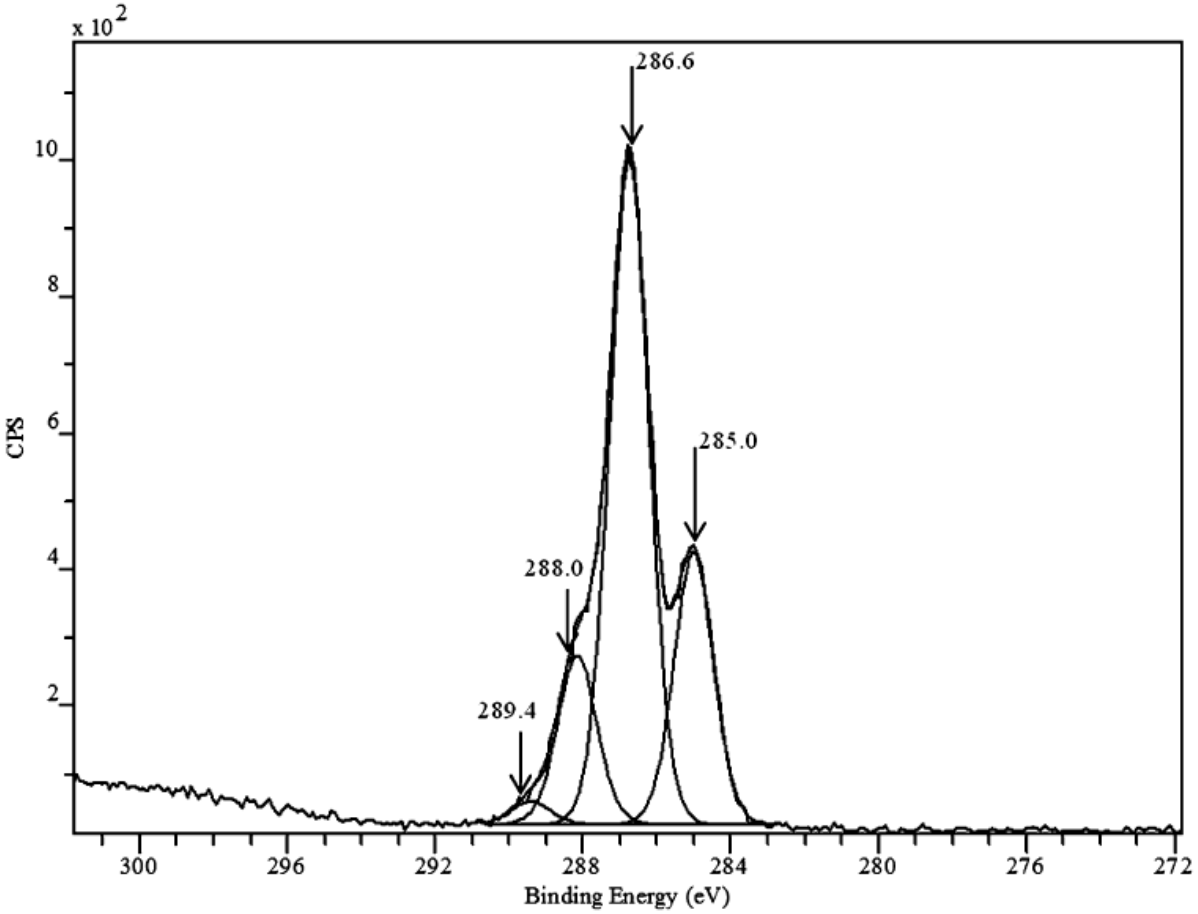

Figure 4. C(1s) spectrum of bleached, scoured, untreated cotton fabric.

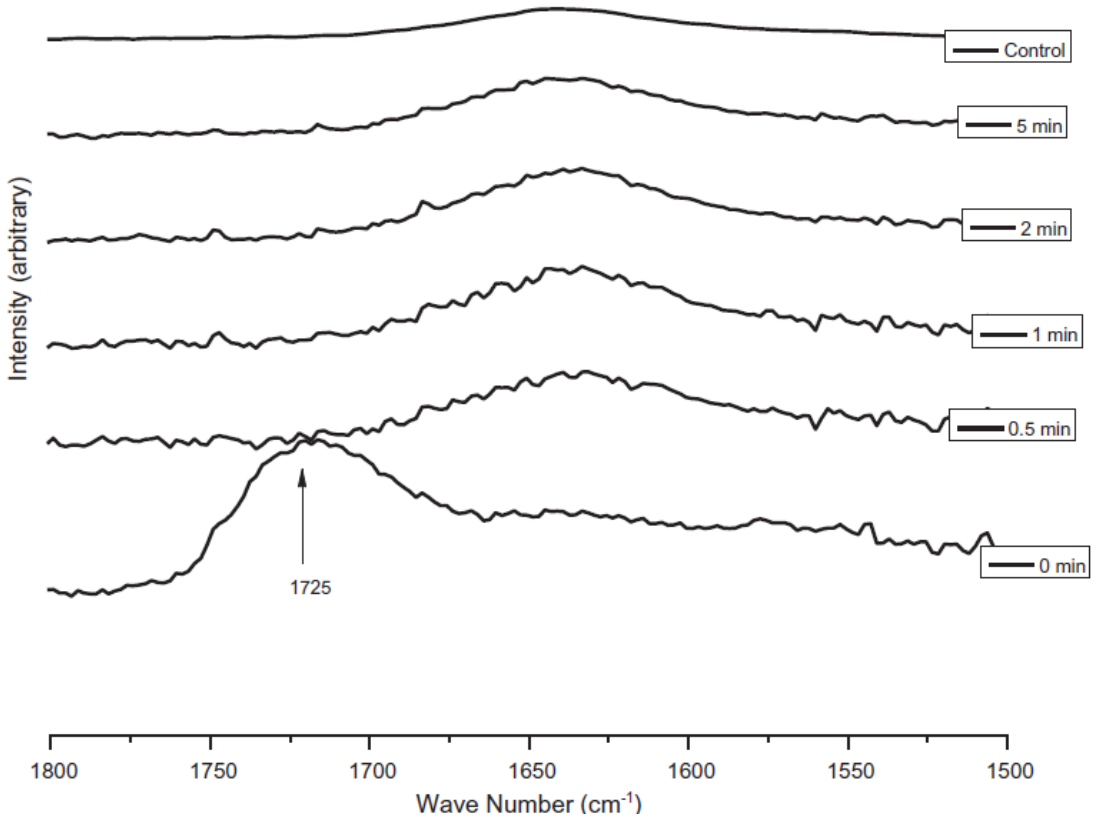

Figure 5. FTIR spectra of cotton fabrics finished with 100 g/L BTCA and then treated in 23% NaOH solution at the boil for increasing times (1800–1500 cm-1).

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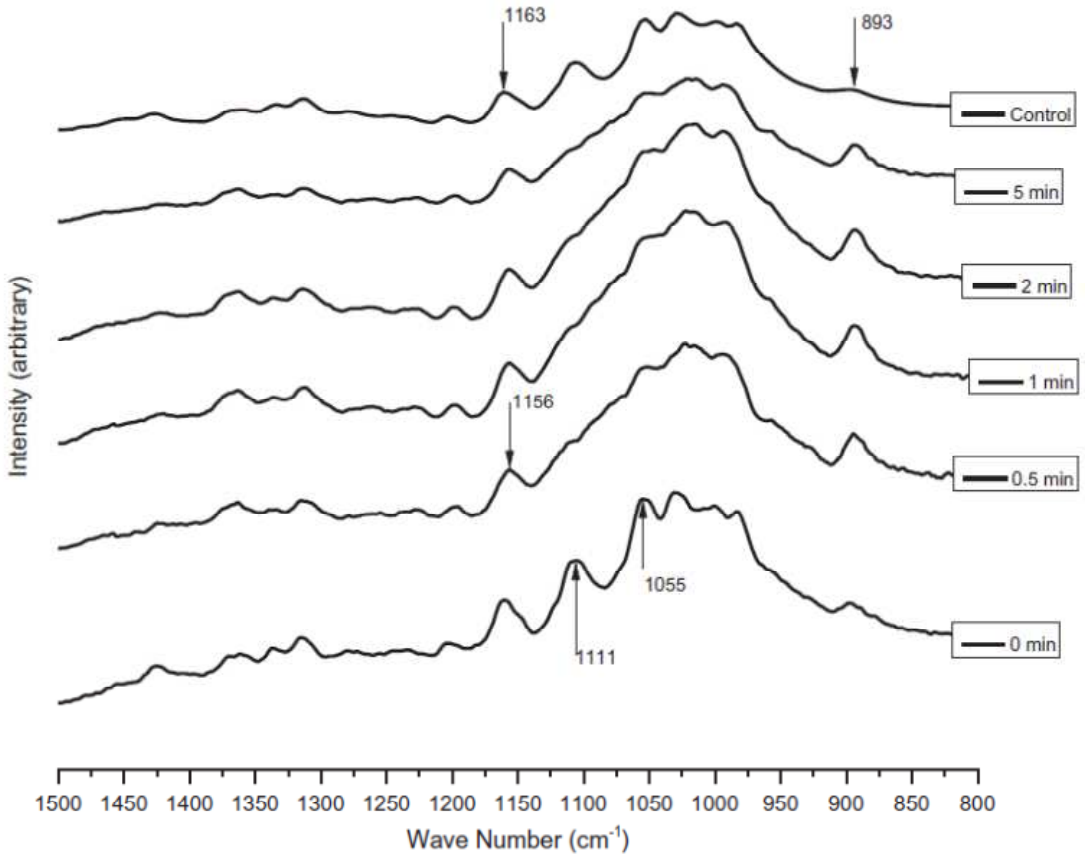

Figure 6. FTIR spectra of cotton fabrics finished with 100 g/L BTCA and then treated in 23% NaOH solution at the boil at increasing times (1500–800 cm^{-1}).

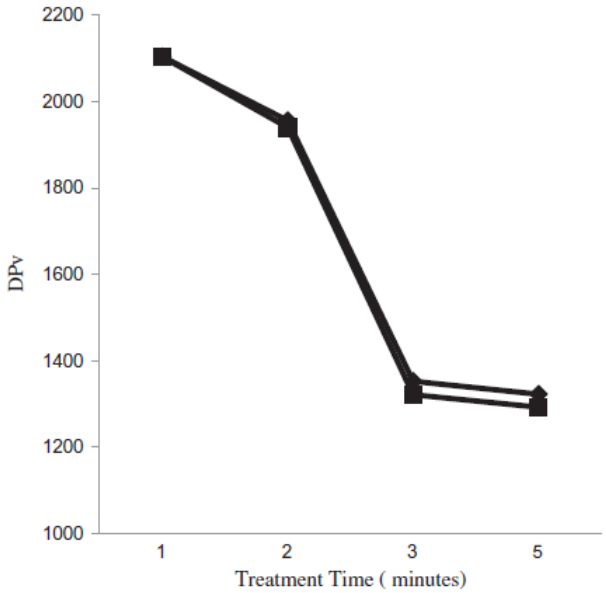

Figure 7. Effect of NaOH treatment on the DPv of cotton fabric treated ■ – 100 g/L and ♦ – 140 g/L BTCA easy care finish

the CED solution to dissolve cellulose, it must first form hydrogen bonds with the cellulose hydroxyl groups in the amorphous region, swell the cellulose and finally disrupt the crystalline region of the cellulose. The cross-linked cotton fibre has limited swelling ability and the cross-links are strong enough to resist the disruptive action of the CED and NMMO solutions.

Examination of the effect of subsequent alkali treatment on the DPv of the cotton fabrics treated with BTCA was to decrease the DPv value and this decreased further as the stripping time increased (Figure 7). However, the decrease was most obvious between 1 and 5 min of hydrolytic stripping. Nevertheless, the DPv value did not decrease to the same level observed with DMDHEU-treated cotton fabrics stripped under the sequential acid/alkaline conditions (Haule et al., 2014). Accordingly, the lower loss in DPv of the alkali-treated material may be due to higher stability of the cellulose polymer to alkali rather than mineral acids. Furthermore, the DPv of the cellulose recovered from the BTCA finished cotton fabrics hydrolysed in alkali alone was higher than that of the 'standard' wood pulp previously reported (Haule et al., 2014) and clearly offers an advantage in terms of cellulose processing and blending flexibility. (The DPv was only determined for samples which completely dissolved in CED and NMMO solutions).

The reduction of the DPv with increasing alkali exposure time was due to the degradation of the cellulose molecules at high temperature and aggressive alkaline conditions leading to probable chain scission of the cellulose glycosidic links, thus producing shorter polymer chains. This degradation may be undesirable if the reclaimed cellulose is to be used for applications other than fibre regeneration (Haule et al., 2014).

Garments are exposed to a range of environmental during the garment life time. Thus at the end of the

garment's useful life time, not all garments will have degraded to the same extent and this will result in the polydispersity of the DPv of the reclaimed material after purification. In cases where the DPv of the reclaimed material is below the processing requirements necessary for making lyocell fibres, blending with virgin wood pulp would be recommended.

The potential introduction of this new alternative supply chain in the regenerated fibre making process has both environmental and technological benefits. Economically, the reclaimed pulp may be used to supplement the shortage of wood pulp during production of lyocell fibres. Furthermore, the new supply chain would divert the shipping of second hand clothing to developing countries hence providing potential growth in the textile and fashion industries of the developing countries while reducing the environmental impact caused by waste garments. However, in order to have a comprehensive approach to the removal of the easy care finishes, further research is necessary to establish effective methodologies to remove not only easy care finishes but also dyes and in particular reactive dyes from the waste garments.

Conclusions

The lower solubility of BTCA easy care finished cotton fabrics in CED and NMMO solutions was confirmed by microscopic examination of the solutions. Accordingly, a simple method to assess the effectiveness of chemically removing the covalently bound BTCA finish from cotton garments was established and the effectiveness of the 'stripping' conditions was evaluated by solubility tests in CED and NMMO solution, XPS analysis, ATR-FTIR analysis and the DPv of the purified cotton fabrics. It was found that the easy care finish was effectively stripped by treatment of the BTCA finished fabric in a solution of 23% NaOH solution at the boil for at least 5 min. XPS and ATR-FTIR analysis of the purified cellulose indicated that after five minutes at the boil, the covalently bound BTCA was completely removed leaving the cotton fabric with no cross-linking residue. The molecular properties of the alkali purified cotton fabrics indicated that the DPv of the latter was higher than that of wood pulp and comparable acid-/alkali-treated, DMDHEU-treated cotton. The research findings in this study highlight the potential to establish a new fibre manufacturing supply chain based on the sustainable use of cellulosic materials that will benefit the textile industry in both developing and developed countries.

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