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Investigation into the removal of an easy-care crosslinking agent from cotton and the subsequent regeneration of lyocell-type fibres

L. V. Haule · C. M. Carr · M. Rigout

Abstract Dimethylol dihydroxyethylene urea (DMDHEU)-treated cotton fabrics were treated with alkali or alternatively acid followed by alkali for increasing time periods, and their effectiveness in removing the crosslinking agent was investigated by surface (X-ray photoelectron spectroscopy) analysis, bulk analysis, crease recovery angle performance and solubility in specific solvents. The cellulose yield after the chemical stripping processes was established and the effect of the acid and alkali treatments on the degree of polymerisation of the resultant cellulose determined. Surface and bulk analyses and solubility tests suggested that alkali alone could not remove the DMDHEU from the crease-resist-treated cotton fabric. However, a sequential acid/alkali treatment effectively removed the easy-care finish from the cotton fabric and produced a commercially viable yield of cellulose.

Introduction

The impact of textile waste on the environment has increased dramatically in recent years because of the increase in the number of fashion seasons and the associated built-in fashion lifetime. Nowadays, a garment lifecycle is more dependent on the durability of the garment's fashion than the physical performance of the garment (DEFRA 2006; Bianchi and Birtwistle 2012; Birtwistle and Moore 2007; Bromley and Dunstan 1978; Haggblade 1990). The main avenue for disposal of the waste garments is by reuse as second-hand clothing in developing countries (Baden and Barber 2005; DEFRA 2006, 2009; Hawley 2006a, b; Haggblade 1990). However, this approach lacks sustainability and has already been challenged by these developing countries because it contributes to the failure of their textile and garment industries (Hawley 2006ab; Baden and Barber 2005). This has led to a total import ban and/or an increase in administrative bureaucracy effectively slowing the importation of second-hand clothing (Hawley 2006a).

Therefore, in order to ensure sustainable production of textiles and garment materials, a ‘‘closed loop’’ production system could be an ideal solution when compared to the current linear system. With the closed loop system, the garment fabric that has reached the end of its ‘‘first life’’ could be collected, separated and then used as a raw material for regeneration of new fibres. The current option of reclamation of fibres from waste garments involves pulling out the fibres (shredding) and then spinning the separated strong fibres into yarn (Lebedev 1995; DEFRA 2006; Hirsch and Woodside 2002; Morel 1984; Ball and Hance 1994; Campman and Barbod 1970). However, the yarns spun from fibres obtained by the shredding process always have poorer mechanical properties and associated limitations (Lebedev 1995). Other end-use markets for the recycled textiles include wipes, sound proofing, thermal insulation, composites and reinforcement for road constructions and geotextiles (DEFRA 2006, 2009). However, some markets reject recycled materials because of the standards set under specific groups of applications (DEFRA 2009).

The two main classes of cellulosic fibres are those from natural materials such as cotton and flax and the manmade cellulosic fibres, derived from wood and cotton, such as viscose and lyocell fibres. The viscose process involves chemical derivatisation of alkaliswollen cellulose with carbon disulphide, extrusion of the dope and then regeneration of the fibres in an aqueous sodium sulphate or zinc sulphate solution (Bredereck and Hermanutz 2005; Cook 1984; Wilding 1995). The viscose process is characterised by high consumption of water and generation of by-products, which clearly have a significant environmental impact. The lyocell process involves the physical dissolution of the cellulose in N-methylmorpholine N-oxide (NMMO) solution, extrusion of the mixture and then regeneration of the fibres by a regenerating agent such as water or alcohols (Chanzy 1982; Kim et al. 1999; Chanzy et al. 1990; Fink et al. 2001; Woodings 1995), which removes the solvent without affecting the regenerated fibres. Unlike the viscose process, the lyocell process does not consume large quantities of water, generates no harmful by-products and allows recovery of over 99 % of the solvent for reuse.

The first demonstration of the possibility of regeneration of cellulosic fibres from cotton waste garments by the dissolution of the cotton waste garments in NMMO solution was by Firgo et al. (1997). The mechanical properties of the fibres regenerated from the cotton waste garments were demonstrated to be superior to the virgin cotton fibres. However, Firgo et al. did not investigate the effect of chemical finishes applied to the cotton garments on the dissolution process. One of the most common finishes applied in

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cellulosic garments is the easy-care finish dimethylol dihydroxyethylene urea (DMDHEU), which is applied to cellulosic fabrics in order to impart dimensional stability and anti-wrinkle performance. DMDHEU is applied to cellulose fabrics by a pad/dry/cure process whereby the ‘‘collapsed’’ cellulose chains are crosslinked, forming interchenic bonds that give memory to the garment in its flat crease-free form (Carty and Byrne 1987; Petersen 1968). The DMDHEU crosslinks by forming ether bonds with the cellulose polymer via the cellulose hydroxyl groups (Fig. 1). During application of the easy-care finishes, it is the hydroxyl groups of the amorphous fraction of the cellulose polymer that are modified, which implies that the application of easy-care finishes affects the accessibility of the cellulose material to various chemicals such as dyes and solvents (Haule et al. 2012).

The NMMO solution first interacts with cellulose molecules by water swelling the cellulose to enable easy penetration of the NMMO into the cellulose and allowing the subsequent interaction between the polar hydroxyl groups of the cellulose with the N–O of the NMMO (Johnson 1969). Based on the mechanisms of the interaction between the NMMO and cellulose, it is expected that the crosslinked cellulose might not dissolve in NMMO solution to the same extent as the DMDHEU-free cotton fabrics.

In the previous work by Haule et al. (2012) on the durability of the easy-care finish on cotton fabrics toward extended domestic laundering, it was demonstrated that the easy-care finishes are durable to domestic laundering for the entire lifecycle of the garment. This clearly implies that it will be necessary to remove the easy-care finishes from the garments in order to make possible the dissolution of the waste cotton garments in NMMO solution during the commercial production of the regenerated lyocell-type fibres.

Several investigations have previously been undertaken to determine the stability of the easy-care finishes and identify methods of removal from the fabrics (Abhyankar et al. 1985, 1986a, 1987). Abhyankar et al. (1985) reported the immersion of DMDHEU-treated cotton fabric in a solution of 23 % NaOH at the boil for 10 min and found that although the crease recovery angle (CRA) performance of the stripped fabric was reduced to that of the untreated fabric, there were still some traces of nitrogen assigned to DMDHEU remaining in the fabric. In addition, it was noted the stripped fabric did not dissolve in ethyl acetate solution. The DMDHEU removal was via deprotonation of the nitrogen in the urea component or the oxygen in the ether link (Abhyankar et al. 1986a, b).

The possible use of urea-phosphoric acid solutions to remove DMDHEU crosslinks in easy-care-finished cotton fabric has also been tested and recommended as a correcting treatment for errors occurring during the application of easy-care finishes (Jung et al. 1972, 1976, 1974; Segal and Timpa 1973). The advantage of urea phosphoric acid hydrolysis is that it is applied at relatively lower temperatures than alkaline hydrolysis. However, the stripping of easy-care finishes using urea phosphoric acid followed by alkali treatment left residual nitrogen in the cotton and an associated insolubility of the ethyl acetate solution even though the CRA performance of the cotton substrate was reduced to that of the untreated fabric (Abhyankar et al. 1987).

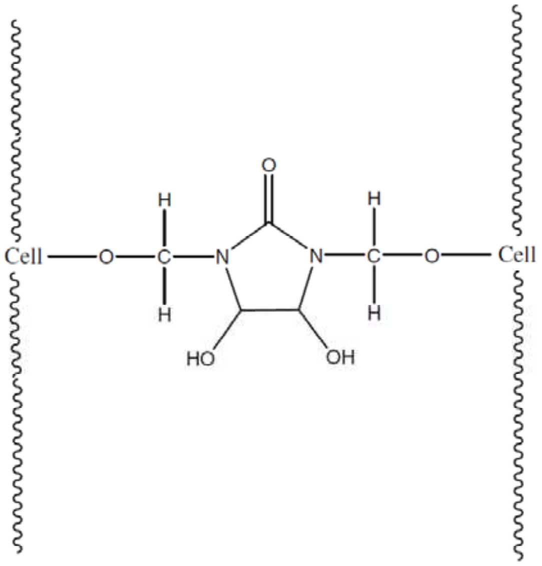

Fig. 1 Di-ether crosslinking between DMDHEU and cellulose polymers (Carty and Byrne 1987); cell = cellulose

It has been reported that the stability of easy-care finishes to hydrolysis is dependent on both chemical and physical equilibrium conditions (Kamath et al. 1985). Under strongly acidic conditions, the hydrolysis of the DMDHEU is mainly by scission of the ether bond, and this alone can hydrolyse up to 75 % of the ether bonds in cellulose-DMDHEU crosslinks. Under alkaline conditions, the hydrolysis is favoured by scission of the C–N bond, and this could remove up to 25 %of the crosslinks. This suggests that for a complete stripping of the DMDHEU easy-care finish from crosslinked cellulose, both acidic and alkaline conditions are essential.

This article investigated the removal of the DMDHEU easy-care finish from cotton fabric under alkaline and acidic conditions and optimises the stripping conditions. The stripping process would be a vital stage for the purification of cotton-based waste cellulose and increasing the cellulose yield and solubility in the production of the regenerated cellulosic fibres. The effectiveness of the stripping process was determined using surface and bulk analyses, CRA performance analysis and microscopic quantification using the fibres’ solubility in cupriethlylenediamine (CED) and NMMO solutions, respectively. The cellulose yield after the solubilisation process was further characterised by determining the viscosity average degree of polymerisation (DPv) of the purified cellulose.

Experimental

Materials

Scoured, bleached, 100 % plain woven cotton fabric, 152 g/m2, was supplied by Phoenix Calico, Manchester, UK. Wood pulp, unused indigo-dyed denim fabric and indigo-dyed waste denim jeans were supplied by Lenzing-Austria. Dimethylol dihydroxyethylene urea (DMDHEU) (Fixapret CP New) was supplied by Dystar, UK. Magnesium chloride, sodium hydroxide, sulphuric acid and glycerol were supplied by Fisher Scientific, UK. Propyl gallate (98 %), hydroxylamine sulphate (99 %) and 4-methylmorpholine-N-oxide (NMMO) solution, 50 % aqueous solution, were supplied by Acros Organics, UK. Cupriethylenediamine solution (1 M) was supplied by Merck, UK.

Application of DMDHEU easy-care finish to cotton

Aqueous solutions of DMDHEU, 100 and 140 g/l, and magnesium chloride, 20 and 28 g/l, respectively, were padded onto the cotton fabric at 80 %wet pick up. The padded fabrics were oven dried for 2.5 min at 100 ºC with subsequent curing for 4 min at 150 ºC. The cured fabrics were rinsed in warm water to remove any finish residue and then air dried for further tests. Parts of the untreated and DMDHEU treated cotton fabrics were repeat laundered 509 in a Wascator FOM 71 MP washing machine using the cotton wash programme, 5A. The washing was performed with 12.5 g of ECE non-phosphate detergent and after washing the fabrics were air dried.

Alkali and acid treatments of cotton fabrics

Both control and easy-care finished cottons were stripped in sodium hydroxide solution following the methods described in the literature (Abhyankar et al. 1985, 1986a, 1987) with minor modifications. A solution of 23 % w/w sodium hydroxide was cooled to 23 ºC and then divided into two portions each in a 250-ml beaker. The cotton fabrics were soaked in one of the sodium hydroxide solutions for 30 min while the remaining solution was heated to boil. After the fabric had soaked for 30 min in the cold sodium hydroxide solution, the fabrics were transferred to the boiling sodium hydroxide solution and boiled for increasing time periods. The liquor-to-goods ratio was 10:1. The stripped fabrics were rinsed in hot water, neutralised in 0.5 ml/l acetic acid for 10 min, warm rinsed and then air dried.

For the acid stripping treatment, both control and easy-care finished cotton fabrics were soaked in a 10 ml/l concentrated H2SO4 acid solution for at least 2 h at room temperature. The solution temperature was then raised to 60 ºC and the fabrics treated for increasing time periods. The fabric was then removed from the acid solution and divided into two portions. One portion of the fabric was warm rinsed and then neutralised in 0.5 ml/l NaOH for 10 min, warm rinsed and then air dried. The second portion of the fabric was transferred into the boiling 23 % w/w NaOH for 10 min and then subsequently warm rinsed in water, neutralised in 0.5 ml/l acetic acid for 10 min, warm rinsed and air dried.

Crease recovery angle (CRA) analysis

The crease recovery of the fabrics was determined using the British Standard test method-BS EN 22313:1992 (British Standards 1992). At least ten replicates were performed and the mean reported.

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 double-sided tape. Monochromatic Al Ka X-rays (1486.69 eV) with a power of 150 W were used to irradiate the sample and a wide scan spectrum was recorded with pass energy of 160 eV from which the surface composition (C, O and N) was determined. High-resolution carbon (1s) and nitrogen (1s) spectra were recorded with pass energy of 40 eV. The binding energy (BE) values were calculated relative to carbon (1s) photoelectron at 285.0 eV. Charge compensation for the samples was achieved using a 4–7-eV beam at a flood current of approximately 0.1 mA, with an electrically ground 90 % transmission nickel mesh screen. Data analysis was performed using CASA XPS software (Walton et al. 2010).

Elemental bulk analysis

Elemental analyses were performed by using a Carlo Erba Instruments EA1108 Elemental Analyser. The error associated with the measurement is ±0.04 %.

Light microscopy analysis

Light microscopy analyses were performed using a Leica CTR 6000 microscope.

Solubility in CED solution

The dissolution of cotton fabrics in CED solution was performed as per the British Standard test method-BS ISO 5351:2010 (British Standards 2010). The cotton fabrics, waste denims and wood pulp were completely disintegrated into fibres by means of cutting with scissors and then dried at room temperature to a constant mass. The weights of the dried sample were chosen such that the product of cellulose concentration in the solution and limiting viscosity of the solution were 3.0 ± 0.1. The dried fibre samples were then introduced into a 60-ml plastic bottle with 25 ml of distilled water and 10 pieces of clean copper wire, each 3 mm diameter and 20 mm long. After 30 min of agitation on a mechanical shaker 25 ml of 1 M CED solution was added and the bottle compressed in order to remove any air, which would cause oxidation of the cellulose. The bottle was closed and the solution agitated on the mechanical shaker for another 30 min.

After the 30 min of agitation the solubility of the cellulose in the CED solution was determined by viewing a drop of solution on a glass slide using a Leica

CTR 6000 optical microscope. The rest of the solution was then filtered onto pre-weighed Whatman Glass microfiber-GF/C filter paper, which was then oven dried for 4 h at 102 °C and then cooled in a desiccator containing phosphorus pentoxide for a further 2 h. Finally the cooled filter paper was weighed and the percentage of cellulose dissolved in CED solution was calculated as per Eq. 1:

$$S=\frac{X-(w-f)}{X}\times 100\% \tag{1}$$

where s is the solubility in %, x is the oven dry (OD) weight of the sample before dissolution in g, and w and f are the OD weights in g of the filter paper after and before filtration, respectively. Only samples that 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 limiting viscosity and DPv of 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 using Rheotek capillary viscometers (as described by the British standard test method, BS ISO 5351:2010) (British Standards 2010). The viscometer was calibrated by recording the efflux time (s) for distilled water, 65 % glycerol solution and 0.5 M CED solution and then used to determine the efflux time of the test solution. Both calibration and testing were performed at 25 °C.

The viscosity ratio was calculated from the viscometer constants and the determined efflux time. For the known viscosity ratio and cellulose concentration in the solution, the limiting viscosity was calculated using the British Standard test method table in BS ISO 5351:2010. From the calculated limiting viscosity, the DPv of the cellulose was calculated using the Marianne Marx-Figini equation for limiting viscosity (Marx-Figini and Figini 1995). The DPv reported was the mean for three replicates.

Dissolution of cellulose in NMMO

The solubility of the treated and untreated cotton fabrics was determined as per the literature method (Chanzy et al. 1990) with some minor modifications. The solubility tests of the specimen in NMMO solution were established by adding 14 g of 50 % w/w NMMO solution into a 200-ml spherical flask followed by 80 mg of n-propyl gallate antioxidant and then stirred until all the antioxidant had 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 by water at 100 °C and connected to a 15-mmHg 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 a silicone oil bath at 130 °C for 20 min in order to make a free-flowing solution. The solution was sampled on a glass slide and observed on a Leica CTR 6000 polarising light microscope in order to determine the cellulose solubility.

Results and discussion

The application of DMDHEU to cotton fabric at increasing concentration levels similarly increased the CRA performance recovery angle of the easy-care finished fabric (Table 1). Subsequent treatment of the DMDHEU-treated cotton fabrics with 23 % NaOH resulted in a decrease in the CRA value as the crosslinking bonds between the cellulosic polymer chains were hydrolysed. Beneficially the CRA performance of the fabrics after 5 min of alkali treatment was reduced to the level of the DMDHEU-free cotton fabric. Similarly, the surface nitrogen, which was assigned to the chemically bound DMDHEU in the XP spectrum (Fig. 2) decreased, but not to the levels observed in the untreated cotton fabric. In addition, the bulk elemental analysis of the alkali-treated cotton also showed that the nitrogen content did not decrease to zero even with extended alkali treatment time (Fig. 3), probably because of some cellulosic chain modifications being less accessible to the alkali.

Subsequent solubilisation studies of the alkali treated DMDHEU-treated cotton fabrics in CED solution indicated only 70 % of the fibres dissolved in the solution (Fig. 4), suggesting that some crosslinking was still present in the modified cotton. Light microscopy inspection of the solutions of cellulose in CED solution and NMMO solution after the alkali stripping processes confirmed the presence of fibres in the test solution. In contrast, the untreated DMDHEU free cotton fabrics completely dissolved in CED and NMMO solutions, respectively, with no undissolved fibres observed.

The presence of residual surface and bulk nitrogen and lack of solubility of the fibres in CED and NMMO solutions after the stripping process imply that the alkali treatment conditions were not totally effective. Indeed, the inability of the NaOH solutions to remove all the bound nitrogen and hence produce incomplete dissolution of the alkali-treated fabrics in CED solution has been previously reported (Abhyankar et al. 1985, 1986a, 1987). The inability to remove all of the nitrogen assigned to DMDHEU is due to the nature of the interaction between the easy-care finish and the cotton cellulose. The presence of surface and bulk nitrogen assigned to the chemically bound DMDHEU after the alkaline stripping of the cotton fabric treated with the DMDHEU easy-care finish was due to the partial scission of the C–N bonds, which leaves the DMDHEU mono-functionally bonded to the cellulose. In such a situation, the CRA performance of the cotton fabric will be reduced (Table 1), but with the easy-care finish persisting as indicated by the nitrogen detected by the XPS and bulk elemental analysis (Figs. 2, 3).

The reduced solubility of the alkali-hydrolysed DMDHEU-treated cotton fabric in CED solution (Fig.

4) was due to the cellulose hydroxyl groups in the amorphous fraction ineffectively hydrogen bonding with the solvent. With the alkaline-stripped cotton fabric, the residual mono-functionally bound DMDHEU and the unhydrolysed crosslinks leave the cellulose with reduced ability to form hydrogen bonds with the CED solution. This suggests that a method that applies both acidic and alkaline conditions may be useful for the total hydrolysis of the DMDHEU crosslinks from the easy-care-treated cotton fabric.

Examination of the bulk elemental analyses of the untreated and DMDHEU-treated cotton fabrics before the chemical stripping treatments of 10 ml/l H2SO4 at 60 ºC, with varying exposure times, followed by 23 % NaOH solution at 100 ºC for 10 min, indicated the bulk nitrogen content of the untreated cotton fabric was zero and the DMDHEU finished cotton fabrics had a bulk nitrogen content of 1.2 and 1.4 % for the 100 and 140 g/l DMDHEU-finished fabrics, respectively, Fig. 5. However after 30 min of hydrolysis in the acid/alkali solutions, the bulk nitrogen content for the hydrolysed DMDHEU-treated fabric was reduced to zero (Fig. 5),

Table 1 Effect of treatment time on the CRA performance of DMDHEU-finished cotton fabrics treated in 23 % NaOH solution at 100 ºC

Treatment time (min)	CRA performance (W + F)°		
	Untreated	100 g/L DMDHEU	140 g/l DMDHEU
0	150	247	249
1	156	162	214
2	154	150	192
5	150	154	165
30	141	148	170

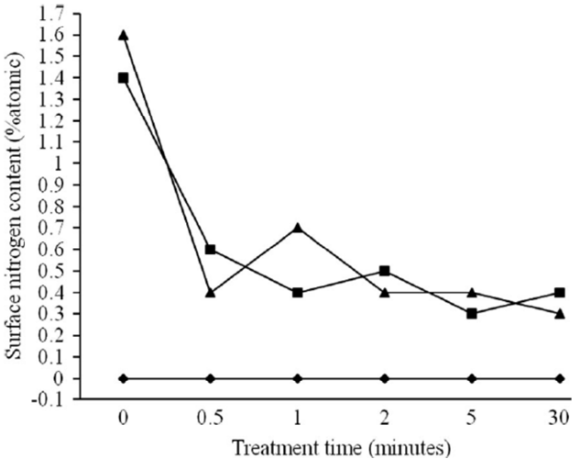

Fig. 2 Effect of treatment time on the removal of surface nitrogen assigned to DMDHEU for DMDHEU-treated cotton fabrics stripped in 23 %sodium hydroxide at boil and increasing time; diamond DMDHEU free, square 100 g/l DMDHEU and triangle 140 g/l DMDHEU cotton fabrics

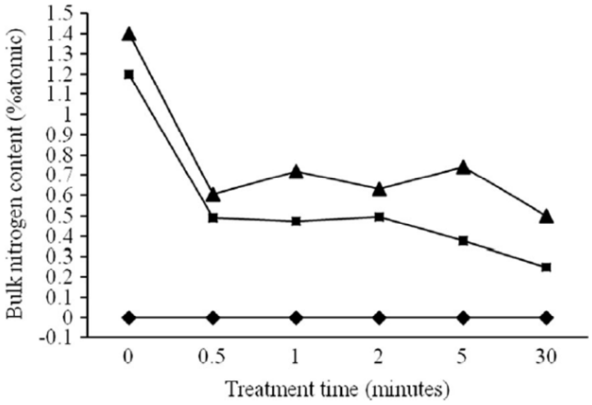

Fig. 3 Effect of treatment time on the removal of bulk nitrogen assigned to DMDHEU for DMDHEU-treated cotton fabrics stripped in 23 % NaOH at boil and increasing time; diamond DMDHEU free, square 100 g/l DMDHEU and triangle 140 g/l DMDHEU-treated cotton fabrics

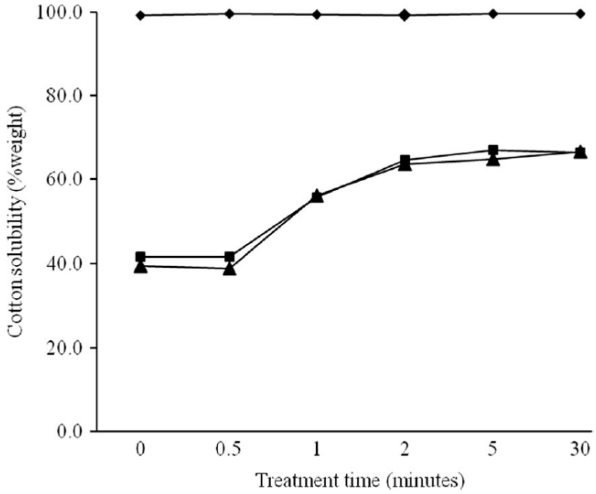

Fig. 4 Effect of aqueous sodium hydroxide treatment time on the CED solubility of DMDHEU-treated cotton fabrics stripped in 23 %NaOH solution at boil; diamond DMDHEU free, square 100 g/l DMDHEU and triangle 140 g/l DMDHEU-treated cotton fabrics

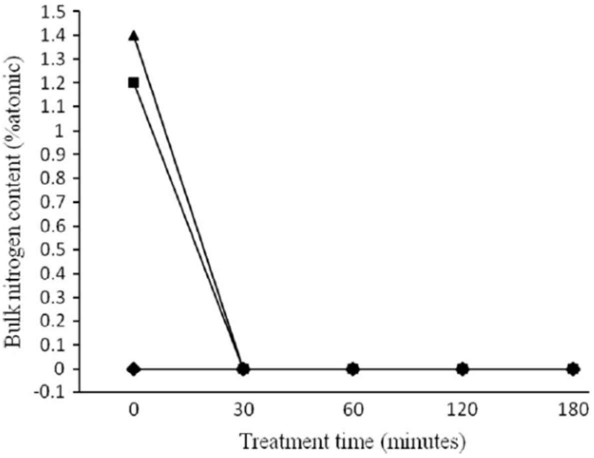

Fig. 5 Effect of stripping time on the bulk nitrogen content of DMDHEU-treated cotton fabrics stripped in 10 ml/l H_2SO_4 at 60 ºC at increasing time and then 23 % NaOH at boil for 10 min; diamond DMDHEU free, square 100 g/l DMDHEU and triangle 140 g/l DMDHEU-treated cotton fabrics

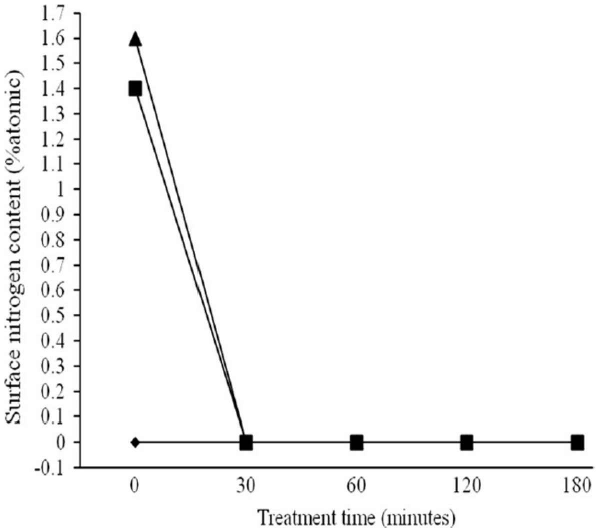

Fig. 6 Effect of stripping time on the surface XP nitrogen content of DMDHEU-treated cotton fabrics stripped in 10 ml/l H_2SO_4 at 60 ºC and increasing time and then 23 % NaOH at boil for 10 min; diamond DMDHEU free, square 100 g/l DMDHEU and triangle 140 g/l DMDHEU-treated cotton fabrics

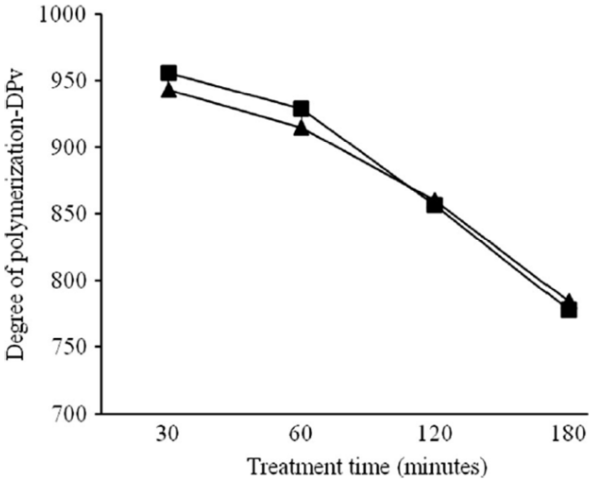

Fig. 7 Effect of stripping time on the DPv of the square 100 g/l DMDHEU and triangle 140 g/l DMDHEU-treated cotton fabrics stripped in 10 mL/l H_2SO_4 at 60 ºC and increasing time then in 23 % NaOH at boil for 10 min

indicating the combination acid/alkali treatment was more effective than the alkali treatment alone in removing the DMDHEU from the cellulose.

Application of the sulphuric acid to the 100 and 140 g/l DMDHEU-finished cotton fabrics over increasing time periods followed by 10 min in the sodium hydroxide solution indicated there was an effective removal of all surface (XP) atomic nitrogen after 30 min (Fig. 6). The total hydrolysis of the crosslinked DMDHEU in the cotton fabrics under sequential acid/alkali conditions was due to the complementary contribution of the acidic condition in the hydrolysis of the ether links. Similarly the effect of acid/alkali treatment on the solubility of 100 and 140 g/l DMDHEU-treated cotton fabrics in CED and NMMO solutions was to allow 100 % dissolution, as confirmed by the light microscopy visual inspection. The ability of the CED and NMMO solutions to dissolve the acid/alkali pre-treated cotton fabrics treated with the DMDHEU easy-care finish was due to the increased accessibility of the cellulose hydroxyl groups in the amorphous fraction.

Table 2 DPv of cellulosic material from different fibre sources

Source of cellulosic material	Degree of polymerization (DPv)
Wood pulp	1,000
Scoured, bleached and 50× washed cotton fabric	3,900
Scoured, bleached, DMDHEU-treated and then acid/alkali-treated cotton fabric	700
Indigo-dyed waste denim fabric	1,900
Indigo-dyed denim fabric	4,200

The effect of acid/alkali hydrolysis on the cotton fabric treated with the DMDHEU easy-care finish was to reduce the limiting viscosity and the degree of polymerisation of the cotton cellulose as the treatment time increased (Fig. 7). The reduction in the degree of polymerisation was due to the degradation of cellulose polymer by scission of the glycosidic linkages between the pyranose rings of the amorphous fraction regions (Ibbett et al. 2008). The breaking of the glycosidic linkages resulted in a loss of molecular weight and hence the degree of polymerisation of the cellulose.

The cellulose degradation during the chemical stripping of cotton fabrics treated with easy-care finishes may be undesirable in some applications, since the limiting viscosity and degree of polymerisation of the cellulose affect the rheology of the spinning solution, which is important for the structural formation and final properties of the regenerated fibres (Fink et al. 2001; Navard and Haudin 1980). A higher degree of polymerisation would result in a reduced interaction between the cellulose and the solvent, aggregation of cellulose chains in the solution and increased relaxation times (Fink et al. 2001). One of the possible ways to control the rheology of the spinning dope is either by changing the cellulose concentration in the solution or changing the degree of polymerisation of the cellulose. It has been reported that reducing the cellulose concentration in the solution would adversely affect the mechanical properties and fibrillation of the fibre (Braverman et al. 1990). Moreover, dissolution at a lower cellulose concentration would also deleteriously affect the productivity of the fibre spinning plant because the plant's mass output rate would be reduced. Hence, the degree of polymerisation or limiting viscosity of the waste cotton garments will be very important for the dissolution and quality of spinning of the fibres.

Comparison of the degree of polymerisation of cellulose from different fibrous sources and treatment history indicated that the degree of polymerisation of the acid/alkali-treated cotton fabric was the lowest observed (Table 2), while the scoured, bleached and repeatedly washed cotton fabric and indigo-dyed fabric exhibited the highest DPv values, 3,900–4,200, because of the least degradation of the cellulose polymer. A typical lyocell process requires a wood pulp feedstock with a DPv of 600–1,000; thus, the lower DPv of the chemically stripped fabric falls within the optimum DPv range suitable for the fibre making process. The dispersity of the degree of polymerisation of the acid/alkali-treated cotton suggests that the stripped waste cotton may be mixed with wood pulp in order to obtain the desired degree of polymerisation for the fibre-making process. Since both stripped waste garments and wood pulp are homogeneous polymers, the desired degree of polymerisation for the mixture of wood pulp and waste garment pulp may be achieved by following the rules of mixtures of homogeneous polymers.

Microscopic visual inspection of the CED and NMMO solutions containing the dissolved indigo dyed waste denim jeans indicated there was complete solubilisation of the fibre specimens in the solvents and accordingly the fibre was compatible with the lyocell process. The degree of polymerisation of the indigo dyed waste denim jeans was about 1,900 and the decrease in DPv reflected the nature of the subsequent wash/wear lifetime. However, while the DPv was still relatively high provided the fibre was pre-mixed with wood pulp, this waste cellulose source could still be utilised in lyocell production.

Conclusions

The effectiveness of alkali and sequential sulphuric acid/NaOH hydrolysis of DMDHEU easy-care finish in cotton fabric was investigated using CRA performance, surface XPS analysis, elemental bulk analysis, degree of polymerisation and fibre solubility in CED solution and NMMO solutions. Sodium hydroxide treatment alone could reduce the CRA performance of the DMDHEU-finished cotton fabric to the untreated level; however, the surface XPS and bulk elemental analysis still revealed the presence of chemically bound nitrogen associated with the DMDHEU on the cotton fabric. The solubility tests revealed that at most 70 % of the alkali-stripped cotton fabric dissolved in the CED solution and this was due to inability of the alkali alone to effect total hydrolysis of the crosslinks.

In contrast, the easy-care crosslinker was successfully removed from the cotton cellulose by sequential application of acid and alkali solution to the DMDHEU- finished cotton fabrics, as indicated by XPS, bulk elemental analysis and fibre solubility tests. The acid/alkali treated cotton could then be completely dissolved in both the CED and NMMO solutions and used to regenerate cellulosic fibres. Following acid/alkali stripping, the cellulose DPv decreased but nevertheless the final degree of polymerisation of the cotton cellulose was comparable to that of the standard wood pulp used for lyocell production and potentially a blend of reclaimed cellulose pulp and virgin wood pulp could provide the commercial feedstock for lyocell production.

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References

Abhyankar PN, Beck KR, Ladisch CM, Rowland SP (1985) A new and effective method for removing DMDHEU crosslinks from cotton 1. Text Res J 55(7):444–448. doi:10.1177/004051758505500708

Abhyankar PN, Beck KR, Ladisch CM, Frick JG (1986a) Effect of different catalysts on the DMDHEU-cotton cellulose reaction. Text Res J 56(9):551–555. doi:10.1177/004051758605600904

Abhyankar PN, Beck KR, Ladisch CM, Rowland SP (1986b) Reply to ‘‘comments on ‘a new and effective method for removing DMDHEU crosslinks from cotton’’’. Text Res J 56(6):401–403. doi:10.1177/004051758605600611

Abhyankar PN, Beck KR, Ladisch CM, Bertoniere NR (1987) Stability of DMDHEU and alkylated crosslinking finishes towards acidic and alkaline hydrolysis. Text Res J 57(7):395–400. doi:10.1177/004051758705700704

Baden S, Barber C (2005) The impact of second-hand clothing trade on developing countries. Oxfam, Oxford. http://policypractice.oxfam.org.uk/publications/the-impact-ofthe-secondhand-clothing-trade-ondeveloping-countries-112464

Ball DL, Hance MH (1994) Process for recycling denim waste. United States Patent 5 369 861, 6 December Bianchi C, Birtwistle G (2012) Consumer clothing disposal behaviour: a comparative study. Int J Consum Stud 36(3):335–341. doi:10.1111/j.1470-6431.2011.01011.x

Birtwistle G, Moore CM (2007) Fashion clothing-where does it all end up? Int J Retail Distrib Manag 35(3):210–216. doi:10.1108/09590550710735068

Braverman LP, Romanov VV, Lunina OB, Belasheva TP, Finger GG (1990) Rheological properties of concentrated cellulose solutions in N-methylmorpholine-N-oxide. Fibre Chem 22(6):397–400. doi:10.1007/bf00632892

Bredereck K, Hermanutz F (2005) Man-made cellulosics. Rev Prog Colour Relat Top 35(1):59–75. doi:10.1111/j.1478-4408.2005.tb00160.x

British Standards (1992) Textile fabrics-determination of the recovery from creasing of a horizontally folded specimen by measuring the angle of recovery BS EN 22313. 1992 edn, British Standards Online

British Standards (2010) Pulps-determination of limiting viscosity number in cupriethylenediamine (CED) solution BS ISO 5351. 2010 edn, British Standards Online

Bromley J, Dunstan R (1978) Textile reclamation in Britain: some recent impacts on a traditional industry. Conserv Recycl 2(3–4):211–218. doi:10.1016/0361-3658(78)90014-0

Campman AR, Barbod H (1970) Apparatus for shredding fibers and fabrics. United States Patent 3,491,956, 27 January

Carty P, Byrne MS (1987) Chemical finishing of natural fibres. The chemical and mechanical finishing of textile materials, 2nd edn. Newcastle Upon Tyne Polytechnic Products Ltd, Newcastle, pp 32–49

Chanzy H (1982) Cellulose-amine oxide systems. Carbohydr Polym 2(4):229–231. doi:10.1016/0144-8617(82)90021-2

Chanzy H, Paillet M, Hagege R (1990) Spinning of cellulose from N-methyl morpholine N-oxide in the presence of additives. Polymer 31(3):400–405. doi:10.1016/0032-3861(90)90376-A

Cook JG (1984) Handbook of textile fibres: 1 Natural fibres. Merrow Publishing Co. Ltd, Durham

DEFRA (2006) Recycling of low grade clothing waste. Department for Environment, Food and Rural Affairs, London. http://www.oakdenehollins.co.uk/pdf/Recycle-Low-Grade-Clothing.pdf

DEFRA (2009) Maximising reuse and recycling of UK clothing and textiles. The Department for Environment, Food and Rural Affairs-UK, London. http://randd.defra.gov.uk/Document.aspx?Document=EV0421_8745_FRP.pdf

Fink HP, Weigel P, Purz HJ, Ganster J (2001) Structure formation of regenerated cellulose materials from NMMOsolutions. Prog Polym Sci 26(9):1473–1524. doi:10.1016/S0079-6700(01)00025-9

Firgo H, Eichinger D, Eibl M (1997) Process for the production of a cellulose moulded body 5,601,767, 11 Feb 1997

Haggblade S (1990) The flip side of fashion: used clothing exports to the third world. J Dev Stud 26(3):505–521. doi:10.1080/00220389008422167

Haule LV, Rigout M, Carr CM, Jones CC (2012) Surface and bulk chemical analysis of the durability of an easy care finish on cotton. Cellulose 19(3):1023–1030. doi:10.1007/s10570-012-9672-x

Hawley JM (2006a) Digging for diamonds: a conceptual framework for understanding reclaimed textile products. Cloth Text Res J 24(3):262–275. doi:10.1177/0887302x06294626

Hawley JM (2006b) Textile recycling: a system perspective. In: wang Y (ed) Recycling in textiles. Woodhead, Cambridge, pp 7–13

Hirsch GF, Woodside C (2002) System and method for reconstituting fibers from recyclable waste material. United States Patent 6378179, 30 April

Ibbett R, Domvoglou D, Phillips D (2008) The hydrolysis and recrystallisation of Lyocell and comparative cellulosic fibres in solutions of mineral acid. Cellulose 15(2):241–254. doi:10.1007/s10570-007-9157-5

Johnson DL (1969) Compounds dissolved in cyclic amine oxides. United States Patent 3,447,939, 6 March

Jung HZ, Benerito RR, Gonzales EJ, Berni RJ (1972) Ureaphosphoric acid hydrolysis of mercerized cotton modified with methylated methylolmelamine. Text Res J 42(8): 464–467. doi:10.1177/004051757204200805

Jung HZ, Benerito RR, Gonzales EJ, Berni RJ (1974) Ureaphosphoric acid hydrolysis of cotton modified with N-methylolated ethylene ureas. Text Res J 44(9):670–679. doi:10.1177/004051757404400906

Jung HZ, Berni RJ, Benerito RR (1976) Urea phosphoric acid as a quality-control reagent for the poly-set process. Text Res J 46(1):26–29. doi:10.1177/004051757604600104

Kamath YK, Weber RU, Hornby SB, Weigmann HD (1985) Factors controlling formaldehyde release from durable press cotton. Text Res J 55(9):519–529. doi:10.1177/004051758505500902

Kim SO, Shin WJ, Cho H, Kim BC, Chung IJ (1999) Rheological investigation on the anisotropic phase of cellulose—MMNO/H_2O solution system. Polymer 40(23): 6443–6450. doi:10.1016/S0032-3861(98)00852-0

Lebedev NA (1995) Use of natural and chemical fibre wastes in production of mixed yarns (a review). Fibre Chem 27(1):52–54. doi:10.1007/bf00551533

Marx-Figini M, Figini RV (1995) Studies on the mechanical degradation of cellulose. Angrew Makromol Chem 224(1):179–189. doi:10.1002/apmc.1995.052240118

Morel A (1984) Shredding machine for recycling textile fibers and method. United States Patent 4,484,377, 27 November

Navard P, Haudin J-M (1980) Rheololgy of mesomorphic solutions of cellulose. Br Polym J 12(4):174–178. doi:10.1002/pi.4980120408

Petersen H (1968) Reaction mechanisms, structure, and properties of methylol compounds in cross-linking cotton 1. Text Res J 38(2):156–176. doi:10.1177/004051756803800208

Segal L, Timpa JD (1973) Concerning the restoration by resin stripping of the tensile properties of cotton fabric finished with dimethylolethyleneurea. Text Res J 43(12):748–752. doi:10.1177/004051757304301211

Walton J, Wincott P, Fairley N, Carrick A (2010) Peak fitting with casa XPS a casa pocket book. Acolyte Science, Cheshire

Wilding MA (1995) The structure of fibres. In: Chris MC (ed) Chemistry of the textile industry [electronic resource]. 1st edn. Knovel e-Book, pp 1–45

Woodings CR (1995) The development of advanced cellulosic fibres. Int J Biol Macromol 17(6):305–309. doi:10.1016/0141-8130(96)81836-8