

Evaluation of the Mechanical Properties of Lyocell Textile Materials Crosslinked with 2,4-Diacrylamidobenzenesulfonic Acid Under Swollen and Nonswollen Conditions

Roger Ibbett,¹ Yan Su,¹ Hunter Renfrew,¹ Duncan Phillips,¹ Jim Taylor²

¹Christian Doppler Laboratory for Fibre and Textile Chemistry in Cellulosics, University of Manchester, School of Materials, Manchester M601QD, United Kingdom

²Lenzing Aktiengesellschaft, 4860 Lenzing, Austria

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ABSTRACT: Lyocell fabrics were treated with 2,4-diacrylbenzenesulfonic acid (DABS) crosslinking agent under wet and dry reaction conditions, and also for comparison with a conventional dimethyloldihydroxyethylene urea (DMDHEU) agent, reacted under dry conditions. All treatments with DABS led to an improvement in wet and also dry fabric abrasion resistance, measured using the Martindale test, whereas treatment with DMDHEU reduced dry abrasion resistance. A model based on the kinetic strength theory of Zhurkov was used to interpret results, where dry-state abrasion is reduced through stress concentration at the rigid DMDHEU crosslinks, which does not occur with the larger flexible DABS crosslinks. Tensile testing of treated lyocell fabrics revealed that breaking strength initially increased at

low levels of DABS fixation, but fell at similar levels of DMDHEU fixation. The effect with DABS is due to an increase in the effective molecular weight, which can outweigh the development of stress concentration due to crosslinking. The Zhurkov model was also used to interpret the wet-state abrasion resistance of lyocell fabrics. From this it is concluded that water swelling leads to an increase in stress concentration within fiber structure because of the loss of lateral interfibrillar connectivity, which is reestablished by both DMDHEU and DABS crosslinking. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2116–2127, 2009

Key words: crosslinking; fatigue analysis; fibers; mechanical properties; microstructure

INTRODUCTION

Lyocell is the generic name for the regenerated cellulose fiber manufactured by the *N*-methylmorpholine-*N*-oxide direct dissolution route.^{1,2} Lyocell fiber has a crystalline fibrillar structure,³ which exhibits high accessibility to water and aqueous agents and therefore has excellent dyeing performance.^{4,5,6} However, the access of water into the fibrillar morphology leads to a significant weakening of lateral connectivity between cellulose domains,⁷ so the fiber is sensitive toward wet-state abrasion, which causes axial splitting and peeling, eventually leading to breakage.⁸ From a technical and consumer perspective, this abrasive effect is referred to as surface fibrillation, which is most pronounced on the filaments that work free from the fabric surface, because of the action of pilling.^{9,10} Fibrillated pills have greater optical reflectivity than the surrounding fabric and are highly visible and unsightly to the eye.

Fabric processing methods have been developed where surface fibrillation is controlled to give a uniform lightly frosted appearance [Tencel Technical Service, San Francisco, CA; Tencel Research and Technology, Acordis Fibres (Holdings) Coventry, UK].^{11,12} However, for other applications, a clean fabric appearance is required, which can be achieved by crosslinking treatments.^{13,14} Crosslinking can be carried out using *N*-methylol type easy-care resins, such as dimethyloldihydroxyethylene urea (DMDHEU) (I) in Figure 1, which are reacted by a pad-bake method during the fabric finishing process.¹⁵ Alternatively, specialized agents with functional groups based on reactive dye chemistry can be fixed when the fiber is in the swollen (wet) state, which leads to significant advantages in fiber performance.¹⁶ For example, lyocell treated with 1,3,5-triacryloylhexahydro-2,4,6-triazine (TAHT) (II) under wet alkaline conditions has excellent dyeability, with mechanical properties that are close to those of the untreated fiber.¹⁷ In contrast, lyocell treated with DMDHEU under baking conditions has seriously reduced dyeability and suffers a deterioration of both tensile strength and more importantly in dry abrasion resistance.^{18,19} However, easy-care resins are inexpensive and are extremely beneficial as treatments for improving the crease recovery

Correspondence to: R. Ibbett (roger.ibbett@nottingham.ac.uk).

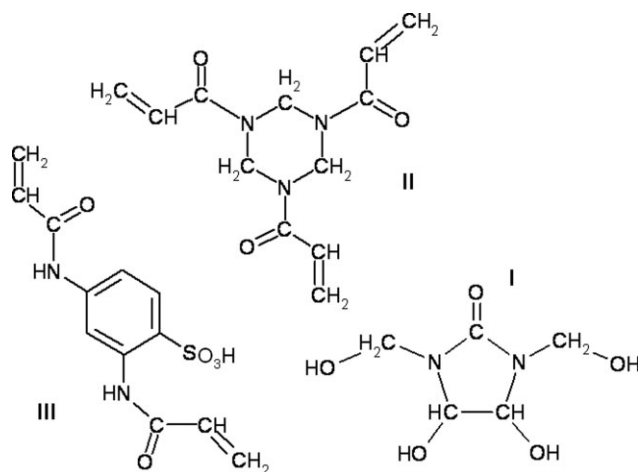


Figure 1 Molecular structure of crosslinkers for cellulosic fibers. I: dimethyloldihydroxyethylene urea (DMDHEU); II: 1,3,5-triacryloylhexahydro-2,4,6-triazine (TAHT); III: 2,4-diacrylamidobenzenesulfonic acid (DABS).

and wrinkle resistance of cellulosic textiles. Also, the more specialized wet-state crosslinking agents may be difficult to apply in a dye-house environment, either due to their lack of stability and poor water solubility or potential health and safety issues. Of further consideration is that traditional DMDHEU resins and also some wet-state reacted agents will break down to liberate formaldehyde, which results in further health and environmental concerns.²⁰ Improved *N*-methylol resins have been developed that do not release formaldehyde, but these are more expensive and also have lower fixation efficiency.

A new agent, 2,4-diacrylamidobenzenesulfonic acid (DABS) (III), has been evaluated as an online crosslinking agent for lyocell.²¹ The compound has good water solubility, offering no opportunity for formaldehyde release, with reactive groups that are suitable for reaction with cellulose under wet alkaline conditions. Previous studies have shown that treatment of lyocell with DABS in the swollen state can be carried out with high fixation efficiency, giving rise to a fiber with excellent resistance to fibrillation in neutral or high pH environments.²² The work reported here represents a continuation of these studies, exploring the influence of crosslinking by DABS on the mechanical properties of lyocell woven textiles, in particular, fabric strength, abrasion resistance, and crease recovery. The agent has also been successfully applied using a dry-baking method, which has allowed a direct comparison of the properties of textiles crosslinked under swelling and nonswelling conditions. Comparative measurements have been carried out on textiles treated under baking conditions with conventional DMDHEU resins, which has provided an insight into the effect of crosslinker molecular architecture on fiber and textile properties. The interpretation of results has been aided by a new adaptation of an

existing kinetic strength theory, which accounts for polymer bond breakage under fatigue conditions.^{23,24} This theoretical model has been used in this study to describe the development of local stress concentration due to crosslink ties and also due to interfibrillar swelling of lyocell fiber by water.

EXPERIMENTAL

Agents

DABS acid agent was synthesized as reported in a previous publication.²¹ Two commercial dimethyloldihydroxyethylene urea products (DMDHEU) were used, Fixapret CP, which is a regular grade, and Fixapret ECO, which is a low-formaldehyde grade containing a polyethylene-glycol auxiliary (BASF PLC, Cheadle Hulme, UK). Other agents such as sodium hydroxide (solid), urea, sodium chloride, and magnesium chloride hexahydrate were of standard laboratory grade (Fisher Scientific UK Ltd., Loughborough, UK).

Lyocell fabric

A plain-weave lyocell fabric was obtained from Lenzing AG, Austria. This was manufactured from 30 tex yarn, with a specific fabric weight of 190 g/m². The fabric was desized and singed and then dyed with a monofunctional reactive dye (CI reactive Blue 19) using a pad-steam process. This coloration step was required to allow the easier visual assessment of fibrillation during laundering. A neutral 40 g/L dye solution was first applied to the fabric using a laboratory pad-mangle, at 75% w/w pickup. The fabric was stenter-dried at 110°C for 1 min, and then padded again using a mixed solution of 250 g/L NaCl together with 20 mL/l NaOH (32.5% w/w solution), at a pickup of 100% w/w. The padded fabric was steamed for 45 s in a laboratory steamer, rinsed, neutralized to pH 5–6 using dilute acetic acid, boil-washed, and then given a final cold rinse. The dyed fabric was allowed to dry in air.

Exhaust treatment with 2,4-diacrylbenzenesulfonic acid

Separate 20 g pieces of the dyed fabric were exhaust-treated with a range of solutions of DABS at 1, 2, 4, 6, and 8% w/w of agent on a fabric weight basis, at a liquor-to-fabric ratio of 20 : 1, at 95°C. Fabric and solutions were rotated in steel tubes using a laboratory dyeing machine (Mathis AG, Zurich, Switzerland). Sodium chloride was added at the start of treatment (for 1% w/w DABS, 20 g/L NaCl; for 2% w/w DABS, 40 g/L NaCl; for 4, 6, 8% w/w DABS, 60 g/L NaCl). After 60 min, the tubes were removed and sodium carbonate alkali was added (for 1% w/w DABS, 5 g/L Na₂CO₃; for 2% w/w DABS, 10 g/L Na₂CO₃; for, 6 and 8% w/w DABS, 15 g/L Na₂CO₃). The fixation

stage of treatment was continued for a further 60 min, followed by a series of cold rinses. The fabric samples were then allowed to dry in the air. Finally, a blank fabric treatment was carried out using 60 g/L NaCl, with 6% w/w DABS and 15 g/L Na₂CO₃.

Alkaline bake treatment with 2,4-diacrylbenzenesulfonic acid

Separate 20 g pieces of the dyed fabric were padded with a range of solutions containing different concentrations of DABS, CO(NH₂)₂, and Na₂CO₃ (100 g/L urea and 10 g/L Na₂CO₃ for <20 g/L DABS, 150 g/L CO(NH₂)₂ and 15 g/L Na₂CO₃ for 20–50 g/L DABS, and 200 g/L CO(NH₂)₂ and 20 g/L Na₂CO₃ for >50 g/L DABS). Treatment solutions were applied to the fabrics using a laboratory pad-mangle to give a pickup of 80% w/w. The padded fabrics were dried on a stenter for 1 min at 110°C, and then baked in the stenter at 180°C for 1 min. The baked fabrics were given a series of cold rinses, using defined volumes of liquor, and then allowed to dry in the air. A blank fabric treatment was carried out using 200 g/L urea and 20 g/L sodium carbonate only. In an additional experiment, a set of fabric samples was treated using pad liquors made up with the same range of DABS and sodium carbonate pad concentrations, but with a constant urea concentration of 150 g/L.

Acid-bake treatments using dimethyloldihydroxyethylene urea

The two commercial resin formulations, Fixapret CP and Fixapret ECO, were dissolved as supplied at a range of concentrations with magnesium chloride hexahydrate catalyst. The solutions were made up as follows: 10 g/L resin with 7 g/L catalyst, 20 g/L resin with 7 g/L catalyst, 40 g/L resin with 8 g/L catalyst, 60 g/L resin with 12 g/L catalyst, 80 g/L resin with 16 g/L catalyst. The solutions were padded onto 20 g pieces of lyocell fabrics to give an 80% w/w pickup. The fabrics were first dried using a pilot-scale stenter, with a transit time of 5 min at 110°C, and then cured on the same stenter for 3 min at 180°C. No washing or further treatment was carried out prior to mechanical testing. A blank fabric treatment was carried out using 12 g/L of magnesium chloride catalyst only.

Measurement of agent fixation

Samples of the initial and final DABS exhaust treatment baths were collected for measurement by UV spectrophotometry. The absorbances of the solutions were recorded at a wavelength of 250 nm, after suitable dilution, with the solution concentrations determined from a Beer's law calibration. The residual bath concentration was proportional to the amount of unfixated agent, with the initial bath concentration pro-

portional to the amount of agent applied. The total amount of agent fixed on the fabrics (X % w/w) was determined from the knowledge of the initial (I) and residual (R) concentrations (in grams/liter), the bath volume (V) (in liters) and fabric weight ((W) in grams), according to eq. (1). The fixation efficiency (F %) was calculated similarly according to eq. (2).

$$\% X (\text{exhaust}) = \frac{(I - R) \times V}{W \times 10} \quad (1)$$

$$\% F (\text{exhaust}) = \frac{(I - R)}{I} \quad (2)$$

The UV absorbances of the wash liquors from the DABS pad-bake treatment were also measured by spectrophotometry, with concentrations calculated as previously from the Beer's law plot. The amount of washed-off agent (O) (in grams) was calculated from the concentrations of each of the separate wash liquor volumes, with amounts in each volume (in grams) added together to give the total. The amount of applied agent (A) (in grams) was calculated from the values for the initial fabric pickup (P) (liters) and the initial pad-liquor concentration (grams/liter). The difference between the amount of agent applied and washed-off was used to calculate the amount of agent fixed on fabric (X % w/w) and the fixation efficiency (F %), according to eqs. (3) and (4).

$$\% X (\text{pad-bake}) = \frac{(A - O) \times 100}{W} \quad (3)$$

$$\% F (\text{pad-bake}) = \frac{(A - O) \times 100}{A} \quad (4)$$

The amounts of DMDHEU agents fixed on fabrics (X %) were calculated from the known agent pad-liquor concentration (L) (grams/liter), fabric pickup (P) (liters), fabric weight (W) (grams), and fixation efficiencies (F %), according to eq. (5). The fixation efficiencies of these two products were determined by separate experiment, with treated fabrics washed and dried and the amount of fixed agent determined by elemental nitrogen analysis, assuming a molecular structure (I). This gave a value of 90% efficiency, which was used for all subsequent calculations. The concentrations of active agent in the commercial formulations were found by gravimetric and NMR analysis to be 64 wt % for Fixapret CP and 55 wt % for Fixapret ECO.

$$\% X (\text{resin pad-bake}) = \frac{P \times L \times \% F}{W} \quad (5)$$

Dry and wet abrasion resistance

Fabrics were tested according to the BS/ISO/EN 1294-7: 1999 standard (Martindale instrument). The

number of rubs resulting in two broken threads was recorded for all fabric samples. The same end-point protocol was applied for wet-state measurements, using a modification of the standard test, with the lower abrasive fabric pad saturated with distilled water. The pad was rewetted at intervals during testing, with again the number of rubs recorded for two broken threads.

Fabric strength

Fabrics were tested according to the BS/ISO/EN 13934:1991 standard (strip-ravel method), with preconditioning and measurements carried out at 20°C and 65% RH. Test strips were cut using 200 mm × 60 mm template, which were then unraveled to 50 mm in the width direction. The specimens were clamped lengthwise in the jaws of an Instron 5546 materials tester, at a gauge length of 100 mm. Testing was performed at an extension rate of 100 mm/min, with the breaking load recorded in Newtons. The average results of four measurements were recorded for both warp and weft directions for each fabric.

Fabric crease recovery

This test was carried out according to the BS/EN 22313 : 1992 standard, with preconditioning and measurement at 20°C at 65% RH. Fabric strips of 40 mm × 15 mm were folded lengthwise and pressed with a standard 10 N weight, maintained for 5 min. After pressing, the test strips were mounted in an inclinometer device, and the angle of recovery of the crease was determined after 5, 15, 30, and 60 min. The average results from six measurements were recorded for both warp and weft directions for each fabric.

Fabric wash appearance

A repeated laundering test was carried out on 25 cm × 25 cm pieces of all fabrics, according to the AATCC124 protocol, using a domestic washing machine (BOSCH, WFB 2000, Bosch UK Ltd, Milton Keynes, UK). The cycle comprised a wash at 60°C for 30 min, at 1 g/L concentration of the standard 1993 : AATCC124 reference detergent. This was followed by a rinse for 40 min and an 8-min final spin at 650 rpm. A 50 : 50 poly-cotton fabric ballast of 1.75 kg was employed. The fabrics were tumble-dried at 60°C for 20 min. Laundering was repeated for 1, 5, 10, and 15 cycles. The visual appearance of the fabrics was compared against the standard AATCC reliefs, to give an easy-care rating between 1 and 5 (1 = very wrinkled, 5 = smooth).

Representative samples of the fabrics were examined using a scanning electron microscope (Hitachi SM-300 system, Hitachi UK Ltd, Maidenhead, UK).

Specimens were gold-coated, with measurements performed at 5 kV accelerating voltage. Images of the fabric surface were collected at 300× magnification to give an indication of the extent of surface fibrillation and pilling. Ranking was carried out according to whether fibrillation was absent, slight, mild, or severe.

RESULTS

The amounts of resin or crosslinker fixed on the fabrics and the respective fixation efficiencies are summarized in Table I. The exhaust technique for application for the DABS agent is less efficient than the pad-bake technique, as the high liquor ratio increases the opportunity for hydrolysis rather than the desirable alcoholysis reaction with cellulose. From previous studies, the DABS agent is known to have low affinity for cellulose so the concentration of unfixed molecules will be the same in the bath and in the internal fiber volume.²² It is only the fixation reaction itself that enables the build up of agent on the fiber, with a chance that one or other of the acrylamido groups will be hydrolyzed before this fixation occurs. Under pad-bake conditions, the majority of the moisture is removed from the fiber before the fixation reaction is initiated, greatly increasing the opportunity for alcoholysis over hydrolysis. The role of urea is partly that of a plasticising agent, promoting sufficient molecular mobility for reaction to take place. The data in Table I show that the reaction efficiency actually improved at higher levels of DABS application, which was considered to be due to the increasing amount of urea used in the pad formulation. When the urea concentration was maintained at a constant level, it was found that fixation efficiency reduced slightly with increasing agent application. Most importantly, from a structural perspective, it can be assumed that the pad-bake reaction with DABS occurs in the nonswollen state, in contrast with the swelled state of the fiber under exhaust reaction conditions.

The reaction of the fiber with the DMDHEU agents was performed under similar nonswollen conditions to those used for the pad-bake reaction with DABS, although this was with a metal salt acid catalyst, without urea. The magnesium chloride salt was present as the hexahydrate, which may remain partially hydrated even under baking conditions, and therefore may assist with the plasticization of the polymer structure. The Fixapret ECO product contains a minor proportion of polyethylene oxide in the formulation, which is designed to react with any residual *N*-methylol group and so reduce the risk of liberation of formaldehyde during laundering. The additional mobility achieved in the presence of the polyol may possibly increase the effectiveness of the fixation

TABLE I
Chemical Compositions and Fixation Data for Lyocell Fabric Treated with
Different Crosslinking Agents

Reagent application	Reagent conditions				
DABS exhaust					
Applied weight on fiber (% w/w)	1	2	4	6	8
Amount fixed (% w/w)	0.47	0.90	1.62	2.52	3.2 (est)
Fixation efficiency (%)	47	45	41	42	40 (est)
DABS pad-bake (variable urea)					
Agent pad concentration (g/L)	10	20	40	60	80
Urea pad concentration (g/L)	100	150	150	200	200
Amount fixed (% w/w)	0.52	1.15	2.24	3.72	4.4 (est)
Fixation efficiency (%)	67	76	75	85	75 (est)
DABS pad-bake (constant urea)					
Agent pad concentration (g/L)	10		40	60	
Urea pad concentration (g/L)	150		150	150	
Amount fixed (% w/w)	0.61		2.32	3.44	
Fixation efficiency (%)	78		78	74	
Fixapret CP pad-bake (90% efficiency)					
Pad concentration (g/L)	10	20	40	60	80
Estimated amount fixed (% w/w)	0.46	0.92	1.84	2.76	3.69
Fixapret ECO pad-bake (90% efficiency)					
Pad concentration (g/L)	10	20	40	60	80
Estimated amount fixed (% w/w)	0.40	0.79	1.58	2.38	3.17

reaction, although this may be counteracted by the reaction of some of the methylol groups with the polyol rather than cellulose. The net effect of the polyol on fixation efficiency was expected to be minimal.

Figure 2 show the trends in dry Martindale abrasion resistance of lyocell fabric for all treatments. From these results it is seen that the number of rubs to failure decreases with DMDHEU fixation for both Fixapret CP and ECO products. This behavior is well documented in the literature and is considered partly to be due to the embrittlement of the fiber, caused by insertion of rigid crosslinks, making the polymer structure less resistant to fatigue processes.¹⁹ In addition, the acid catalytic conditions are known to increase the risk of hydrolytic scission of the polymer glycosidic bonds, which would degrade the overall mechanical properties of the fiber.²⁵ The tensile properties of the fabric samples baked with only the magnesium chloride catalyst were found to be unchanged from the untreated fabric, so it is concluded that this second chain-scission mechanism is not significant for this study. However, in contrast with DMDHEU, the number of rubs to failure of DABS-treated fabrics increased with fixation level for both pad-bake and exhaust application methods. The upward trend is similar for both methods, regardless of whether fixation is in the swelled or nonswelled condition. For this crosslinker, it seems that embrittlement has not taken place and that the insertion of new covalent bonds between the polymer chains has increased the resistance of the structure to fatigue processes. Random glycosidic bond

scission is also less likely under alkaline fixation conditions.

The wet-state Martindale abrasion resistance of the lyocell fabrics is shown in Figure 3. The fibrillar morphology of lyocell is prone to axial splitting and breakdown in the swollen state, so the untreated fiber survived a very low number of revolutions before failure. The insertion of crosslinks reduces the tendency for splitting as covalent bonds reinforce the lateral interfibrillar connectivity. This mechanism is effective with both DMDHEU and DABS agents, with Figure 3 showing that a significant increase in rubs-to-failure occurs with increasing agent fixation. From this data,

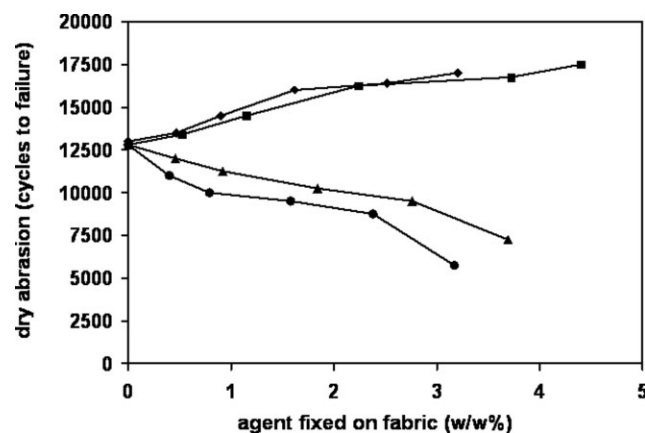


Figure 2 Dry abrasion performance of lyocell woven fabrics following different crosslinking treatments (standard Martindale test). DABS-exhaust (◆), DABS-bake (■), Fixapret CP (▲), and Fixapret ECO (●).

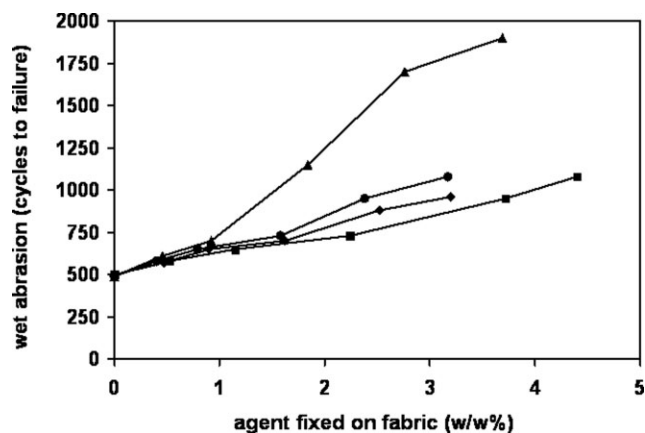


Figure 3 Wet abrasion performance of lyocell-woven fabrics following different crosslinking treatments (modified Martindale test). DABS-exhaust (◆), DABS-bake (■), Fixapret CP (▲), and Fixapret ECO (●).

it appears that DABS applied under either exhaust or pad-bake conditions is less effective than Fixapret CP and to a lesser extent than Fixapret ECO. This may be an indication that the number of active crosslinks is lower for bifunctional DABS when compared with tetrafunctional DMDHEU. In the wet state, the accessible polymer chains have increased mobility due to water plasticization, which increases the yield or creep tendency of the fiber structure. Such yield phenomena would suppress embrittlement resulting from the insertion of DMDHEU crosslinks, which is therefore only evident in the dry state.

The dry tensile strength of the fabrics following the different treatments is shown in Figure 4. For both DMDHEU products, it was found that the strength reduced with increasing fixation, consistent with the downward trend in dry abrasion performance. Again this may be due to the increase in fiber brittleness caused by the insertion of crosslinks. The tensile properties of both the DABS-treated fabrics were similar, although the trend with fixation level was more complex than found with DMDHEU. A significant increase in strength was seen at the lowest fixation level, from around 10.5 kN/m, for the untreated blank, to 12.5 kN/m with around 0.5% DABS agent on fiber. This could be a function of the increase in effective molecular weight of the cellulose polymer. At higher levels of fixation, the tensile strength reduced slightly for both exhaust and pad-bake treatments, but was still greater than that of the untreated fabric. This may be the result of the onset of embrittlement, as the polymer yield behavior is modified. This downturn is not apparent from the dry abrasion data, although it might also be expected at even higher levels of DABS fixation.

The dry crease recovery of the different fabrics depends on the recovery time allowed before measurement of the crease angle, as shown in Figure 5.

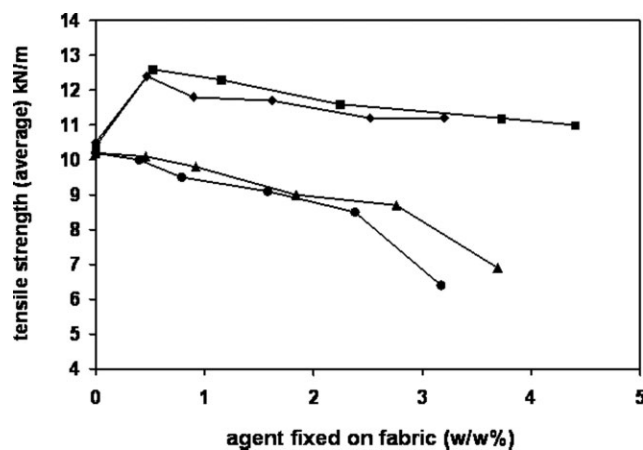


Figure 4 Average conditioned dry tensile strength of lyocell-woven fabrics following different crosslinking treatments (combined warp and weft). DABS-exhaust (◆), DABS-bake (■), Fixapret CP (▲), and Fixapret ECO (●).

The behavior of all treated fabrics followed a saturation type profile, reaching a constant value at around 50–60 min. The performance of the two DABS-treated fabrics was slightly higher, with an ultimate recovery of 114° when compared with around 110°–112° for the DMDHEU-treated fabrics. The insertion of covalent crosslinks between polymer chains reduces the extent of permanent yield under these bending conditions, leading to more complete recovery. Both crosslinker types appear to operate effectively with a similar performance also found for DABS applied by either exhaust or pad-bake method. The data in Figure 6 for the DABS reagents showed that the greatest relative enhancement was experienced at low levels of fixation.

The performance of the fabrics during laundering is summarized in Table II, comparing samples that were fixed with approximately the same level of

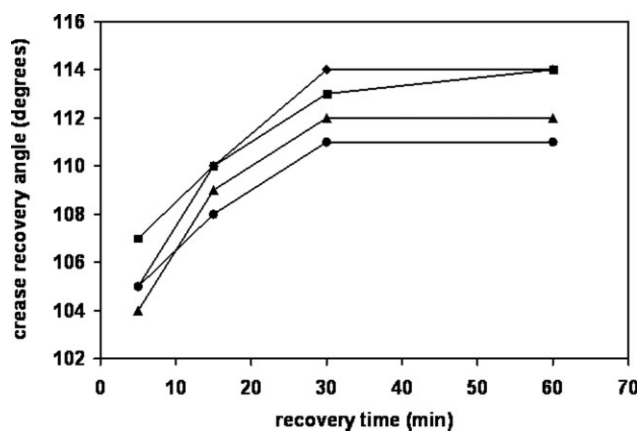


Figure 5 Average dry crease recovery angle of lyocell-woven fabrics following different crosslinking treatments (combined warp and weft) (data for all agents at ~2.5% fixation on fiber). DABS-exhaust (◆), DABS-bake (■), Fixapret CP (▲), and Fixapret ECO (●).

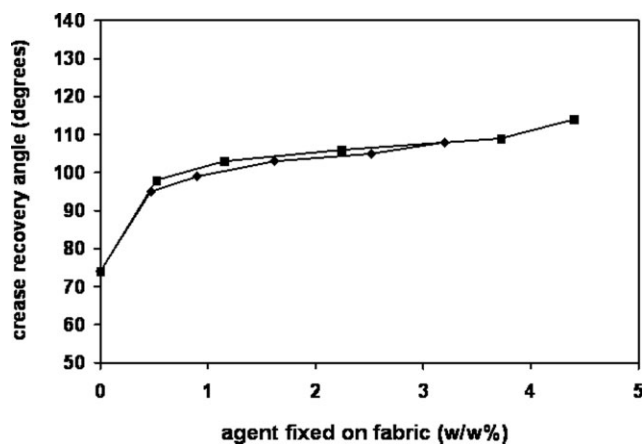


Figure 6 Average dry crease recovery of lyocell-woven fabrics following different levels of crosslinking treatment (combined warp and weft) (crease recovery after 5 min). DABS-exhaust (◆) and DABS-bake (■).

crosslinking agent. The DMDHEU-treated fabrics had slightly higher performance, both in terms of wrinkle rating and the appearance of surface fibrillation, although this became apparent only after increasing the numbers of wash cycles. Previous studies²¹ have demonstrated that both the DMDHEU and DABS crosslinks are stable under these laundering conditions so the deterioration in fabric appearance is presumed to be the result of purely mechanical action. The breakdown of the fiber structure resulting in surface fibrillation will probably have its origins in the same fatigue processes causing wet abrasion in the Martindale test. The development of wrinkling may be due to progressive fiber yield during each laundry cycle, leading to a measurable permanent distortion of the fabric construction.

DISCUSSION

Many crosslinking agents have been evaluated as treatments for the suppression of wet-state fibrillation of lyocell.^{13,14} The sensitivity of lyocell fiber to surface

abrasion is understood to be a characteristic of its fibrillar-crystalline structure,^{26,27} where cellulosic fibers with less organized morphologies such as viscose are resistant to this form of degradation. Cross-linking chemicals are delivered from aqueous solution and therefore have access to longitudinal interfibrillar spaces of lyocell, which are formed as a result of water uptake. The incorporation of covalent ties across the elementary fibrils is therefore believed to be responsible for the increase in toughness of the structure toward abrasive mechanical action. However, there is limited information on exact nature of fatigue failure of lyocell under such conditions or how fiber breakdown differs in the swollen and non-swollen state.^{8,10}

The tenacity of lyocell fiber is not significantly reduced by the uptake of water, being ~ 40 cN/tex in the nonswollen (dry) and ~ 35 cN/tex in the swollen (wet) state.^{7,28} From this it can be argued that the ultimate tensile breakdown of the structure requires the actual rupture of longitudinal polymer chains. These mechanically sensitive chains will exist in the non-crystalline regions surrounding the individual crystallites, as illustrated in Figure 7c. The modulus of the fibre in the swollen state is significantly reduced compared to the nonswollen state, from around 1200 to 250 cN/tex, which is consistent with the disruption of interchain hydrogen bonds in these noncrystalline regions, which are accessible to water.^{2,27} Local molecular flexibility is increased through plasticization, but despite the additional opportunities for slippage, the ultimate strength depends on the covalent continuity of these polymer chains in the fiber direction.²⁹ The chain segments between crystallites will have a distribution of lengths but all will eventually become taught and will undergo rupture beyond their strain limit.³⁰ In contrast, cyclic abrasive mechanical action involves deformations that are lower than the ultimate fiber strength limit, but which eventually also lead to full-scale failure.^{31,32} Flexing and shearing deformations are likely to be dominant, acting in part

TABLE II
Appearance of Crosslinked Lyocell Fabrics Following Standardized Domestic Laundering

Agent		Untreated	Fixapret CP	Fixapret ECO	DABS exhaust	DABS pad-bake
% w/w fixed			2.5	2.5	2.5	2.3
Wash cycles						
1	Wrinkle rating	3	4-5	4-5	4-5	4-5
5		2-3	4	4	4	4
10		1-2	3.5-4	3.5-4	3	3
15		1	3	3	2	2
1	Fibrillation appearance	None	None	None	None	None
5		Slight	None	None	None	None
10		Moderate	Very slight	Very slight	Slight	Slight
15		Severe	Slight	Slight	Moderate	Moderate

AATCC Rating: 5 = smooth, 1 = badly wrinkled; fibrillation appearance from visual inspection and from SEM images of fabric surface.

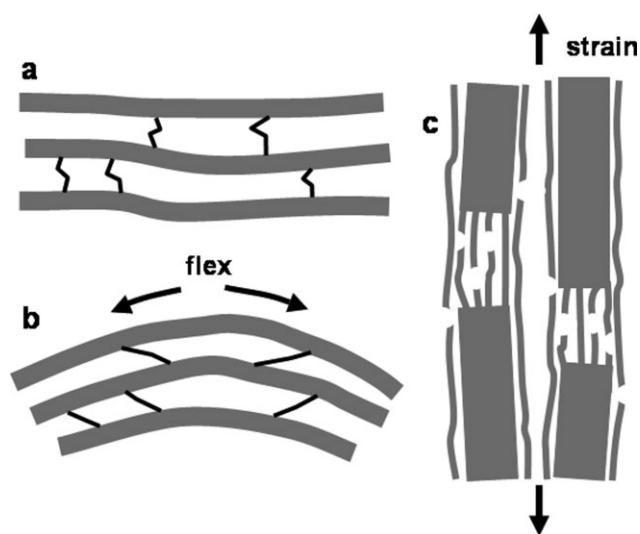


Figure 7 Schematic of deformation experienced by cross-linked lyocell fibrillar structures resulting from flexural action, (a) relaxed, (b) strained. Also, (c) schematic of rupture of longitudinal polymer chains between fibrillar crystalline domains due to tensile strain.

against the lateral noncovalent bonds within fibrils and also between fibrillar regions. The abrasion resistance of lyocell will therefore be strongly influenced by the disruption of lateral interchain hydrogen bonding in the swollen condition.

The breakdown of fibers or other polymer materials due to fatigue processes has been interpreted from the basis of classical fracture mechanics, following crack growth and the energy balance associated with the dissipation of stress.³³ Zhurkov has extended these ideas with the development of a kinetic or rate theory for material failure, which was applied to interpret the fatigue performance of fibers under creep conditions with different magnitudes of constant tensile stress.^{23,34} The resulting model is based on an Arrhenius type expression,²³ shown as eq. (6), which contains a term accounting for the activation energy of covalent bond rupture (U_0). The theory assumes that the polymer bonds have a natural vibration time constant (τ_0), which acts as a reference for all time-dependent behaviors. The probability of an individual bond breakage depends on the chance of its vibration beyond the critical length required for rupture. The rate of bond breakage is increased, or alternatively the lifetime of the bond is reduced, as the absolute temperature (T) of the material is increased, where R is the gas constant. The theory also recognizes that the probability of bond rupture will increase if the material is subjected to an external stress (σ) as the superimposed vibrational excursions will then have a greater chance of stretching the bond beyond its limit. The actual stress experienced at the molecular level by the polymer bonds is dependent on the material structure, which is accounted by an

additional parameter (γ). The term ($\sigma\gamma$) has the effect of lowering the Arrhenius activation energy barrier and so reducing the time to failure under a fatigue regime.

$$\tau = \tau_0 \exp[(U_0 - \sigma\gamma)/RT] \quad (6)$$

$$\tau = \tau_0 \exp[(U_0 - \sigma\{\gamma + \lambda[X]\})/RT] \quad (7)$$

The kinetic model has been very useful for interpreting the creep type behavior of bulk polymers and fibers. Variable temperature and variable stress experiments have provided data that can be used to establish the unstressed activation energy (U_0), which is consistent with that expected for the rupture of covalent bonds by thermal degradation.³⁵ Zhurkov suggested a value of 150 kJ/mol for cellulosic rayon fibers, which should be applicable to other cellulosic materials.³⁵ The parameter (γ), which is derived from variable stress experiments, has special significance from a materials perspective. Although described as an activation volume, it also represents the extent to which the external stress is concentrated due to geometrical or structural heterogeneities, such as variations in the lengths of polymer chain segments.^{28,29,31,36} Stress concentration is a central feature of fracture theory, which explains how natural defects result in the development of microcracks, which act as stress intensifiers within the material. For this study, the parameter (γ) will be referred to in these terms and will be given physical meaning as a fiber stress factor.

The kinetic approach to materials failure should be equally applicable for the interpretation of cyclic fatigue processes, with the experiment timescale (τ) representing the number of cycles between a low and high stress condition.^{24,32} In the Martindale fabric test configuration, this equates to the number of rubs or oscillations of the test piece over the abrasive pad, where yarns and constituent filaments will be subjected to a regime having some similarity to a biaxial flexural deformation.³⁷ The number of rubs to failure is recorded when a yarn suffers a complete lateral break, which must therefore result in the rupture of all longitudinal polymer chains. It can therefore be argued that the activation energy (U_0) required for eq. (6) must be equivalent to that in the tensile experiments, as described by Zhurkov.³⁵ The progress to failure in the Martindale test will depend on the magnitude of the applied stress, which is a result of the weight applied in the test and the frictional characteristics of the fabric surfaces. In a dry test it may be argued that the applied stress cycle will be the same for all samples from identical fabric stock and will be reduced by a constant amount in a wet test due to the lubricating influence of water.

During an abrasion cycle, the filaments at the fabric face may be displaced laterally by distance

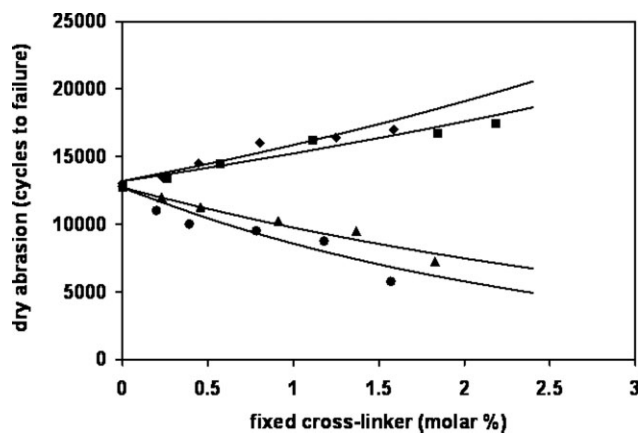


Figure 8 Kinetic model for relationship between cross-linker content and dry Martindale abrasion resistance (continuous lines), with experimental data for DABS-bake (■) and CP-bake (▲) treatments.

approximating to the yarn diameter. Then this will correspond to a radius of curvature for a plain weave fabric of around 1000 μm . The maximum tensile strain experienced by polymer chains at the surface of the filament may therefore be somewhere around the fiber yield point, of the order of 1%, when compared with a 12% breaking strain for lyocell fiber. From the dry tensile stress-strain curve, this would correspond to a stress around 12 cN/tex or 0.18 GPa. The average stress over the cycle is then ~ 0.09 GPa, for a dry-state test, with each cycle of ~ 1 s. If the external stress and temperature are constant, then the variations between the different treated fabric samples will depend only on the stress concentration factor (γ) and how the distribution of bond stresses is modified by the incorporation of crosslinks. A simple scheme can be envisaged, where crosslink ties are inserted between the longitudinal elementary fibrils, which therefore influence their flexural and shear response. In a dry experiment, the fibrils are also tied by a lateral hydrogen-bonding network, which starts to break down above the yield point. For a flexural deformation, illustrated in Figure 7, it can be seen that the additional crosslinks will stiffen the structure above the yield point and will introduce pathways where stress is concentrated through a reduced number of polymer chains. An additional crosslink stress factor (λ) is therefore introduced, in the assumption that the effect is proportional to the molar concentration of crosslinks $[X]$, according to a revised kinetic eq. (7).

Figures 8 and 9 show the time (cycles) to failure from the revised model as a function of crosslink concentration, for DABS- and DMDHEU-treated lyocell fabrics, tested under dry and wet abrasion conditions. The fitted model parameters are summarized in Table III, with a value for τ_0 of 10^{-12} s taken from Zhurkov's work, for an organic polymer.²³ As can be seen, the

crosslink stress factor (λ) must be allowed negative values to account for an opposite stress-dilution effect, which is apparent for both exhaust and dry-bake treatment with DABS. For this crosslinking agent, the stress-dilution appears to be a function of its intrinsic molecular architecture rather than the state of fiber swelling during the fixation reaction. From Figure 1 it can be seen that on reaction with cellulose, the acrylamido groups of DABS will be longer and more flexible than the short *N*-methylene groups of DMDHEU (12 bonds when compared to 6 bonds between cellulose oxygens). So stress concentration may not occur during the bending deformation illustrated in Figure 7. The model activation energy (U_0) is unchanged by the agent concentration, as in this fatigue test the lateral crosslinks are not considered to have an independent contribution to the longitudinal strength of the material. Stress-dilution may therefore be due to a more uniform reinforcement by the flexible DABS crosslinks between the fibrillar domains, which will help dissipate the shear stresses that would otherwise lead to propagation of cracks. As will be discussed, the resistance to axial cracking may be critical in determining the toughness of lyocell fiber under a flexural or shear regime.

The external stress used in the model has been reduced to 0.04 GPa for the wet-state abrasion data, to account for the reduction in friction across the wet fabric surface. The model indicates that untreated lyocell fiber has a much higher positive fiber stress factor (γ) in the swollen condition, which must be associated with the delamination of fibrillar domains, due to the disruption of lateral hydrogen bonding. This means that cracks can progress with low resistance in the axial fiber direction, between these delaminated layers, which under flexural or shear action will allow the applied stress to seek out weak points over greater distances throughout the fiber. Figure 10 shows a

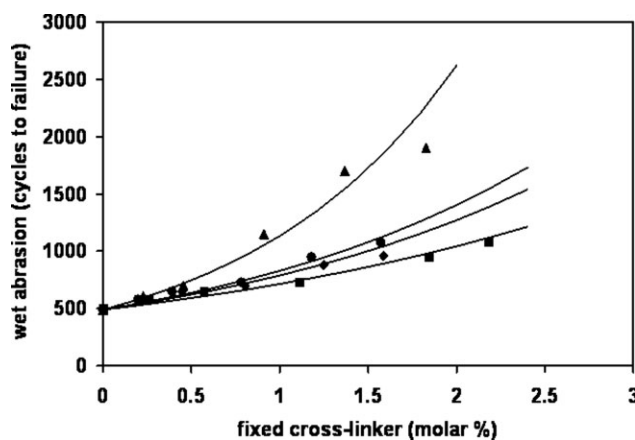


Figure 9 Kinetic model for relationship between cross-linker content and wet Martindale abrasion resistance (continuous lines), with experimental data for DABS-bake (■) and CP-bake (▲) treatments.

TABLE III
Kinetic Strength Model Parameters for Mechanical Performance of Plain Lyocell Fabric

Fabric treatment		Activation energy (U_0) (kJ/mol)	External stress (σ) (GPa)	Fiber stress concentration factor (γ) ($\times 10^{-4}$ m ³ /mol)	Crosslink stress factor (λ) ($\times 10^{-4}$ m ³ /mol)
DABS-exhaust	Dry Martindale abrasion	150	0.09	6.63	-5.0
DABS-bake					-3.8
CP-bake					7.2
ECO-bake					10.5
DABS-exhaust	Wet Martindale abrasion	150	0.04	16.9	-29
DABS-bake					-23
CP-bake					-54
ECO-bake					-31
			Breaking stress (uncross linked) (GPa)		
DABS-bake	Dry strength	150	0.62	1.07	0.9
DABS-exhaust				1.12	0.9
CP-bake				1.33	2.6
ECO-bake				1.33	2.7

schematic of this process, where stress is concentrated at localized defects in each separated fibrillar layer. Stress concentration is also experienced as the delaminated fibrillar layers are not able to act cooperatively with each other and will peel away individually from the fiber surface. Stress can be focused at each layer in turn, with no reinforcement from layers below. The insertion of lateral crosslinks will therefore be effective against these two modes of action, in reducing the propagation of axial cracks and also in reintroducing a measure of cooperative reinforcement between fibrillar layers. Consequently, the kinetic model predicts a large negative value for the crosslink stress factor (λ), for both DABS- and DMDHEU-treated fabrics experiencing wet-state abrasion. The apparent stress-dilution is assumed to be proportional to the number of links, which results in an increasing total exponent in eq. (9). Also, in the swollen state the hydrated polymer chains at fibrillar surfaces have increased flexibility, which is apparently sufficient to suppress the stress-concentration experienced in the dry-state due to the rigid crosslinks of DMDHEU.

The linear tensile strength of polymer materials can also be treated by the kinetic theory proposed by Zhurkov.³³ Equation (6) can be rewritten as a function of the ultimate breaking stress (σ_b) according to eq. (8). This indicates that the breaking stress will be dependent on the timescale of the stress-strain experiment, as dictated by the strain rate conditions used for fabric measurements.

$$\sigma_b = (U_0/\gamma)[1 - (RT/U_0) \ln(\tau/\tau_0)] \quad (8)$$

$$\sigma_b = \frac{U_0}{(\gamma + \lambda[X])} [1 - (RT/U_0) \ln(\tau/\tau_0)] \quad (9)$$

If it is assumed that tensile failure requires the rupture of load-bearing bonds then the activation energy

used for abrasive failure is also applicable, that is $U_0 = 150$ kJ/mol. The measured fabric strength includes contributions due to the geometrical influences of yarn twist and crimp, which will reduce the measured breaking stress and increase the extensibility. From the experimental force values, with a balanced yarn frequency and a fabric weight of 190 g/m², the measured strength in either weave direction is around 0.2 GPa for the initial non-crosslinked fabric. The actual

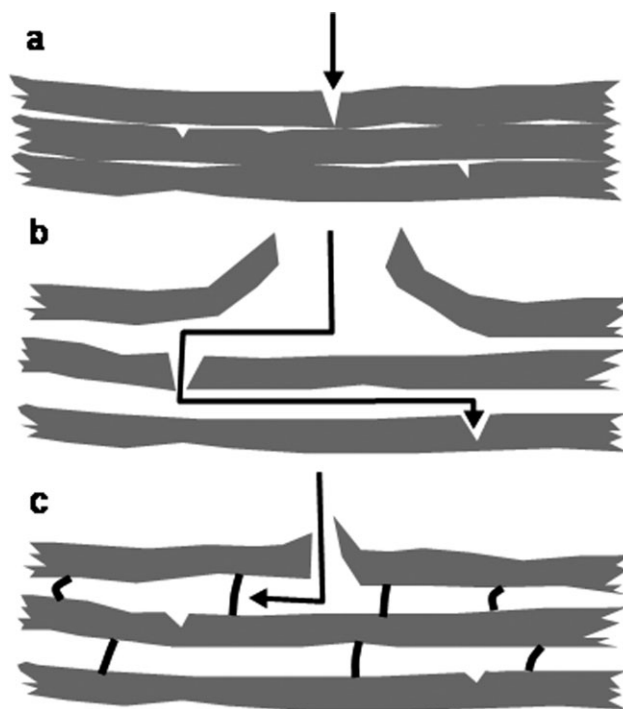


Figure 10 Schematic showing polymer chain breakage at lateral weak points in the fibrillar structure of lyocell under abrasive action. (a) dry state, (b) wet (swollen) state, (c) inhibition of axial transfer of stress due to lateral crosslinks.

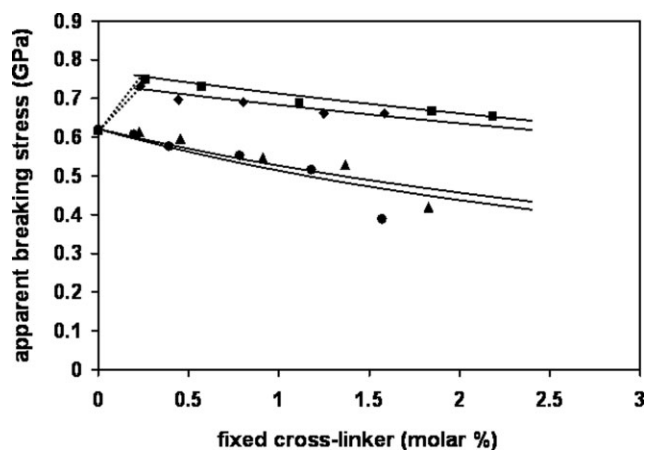


Figure 11 Dry tensile strength of lyocell-woven fabrics following different crosslinking treatments (warp + weft average). DABS-exhaust (◆), DABS-bake (■), Fixapret CP (▲), and Fixapret ECO (●).

breaking stress experienced by the fibers within the yarns can be found if the fibers in the untreated fabric are assumed to fail at their true tenacity limit, which is around 40 cN/tex or 0.62GPa, for untreated lyocell fiber. All measured fabric strength data was therefore multiplied by the ratio (0.62/0.2) prior to the modeling exercise.

Equation (8) can be modified to account for the effect of crosslinking, also with the introduction of a crosslink stress factor (λ), according to eq. (9). Both (λ) and the initial fiber stress factor (γ) can be adjusted to achieve a fit with the normalized experimental data, as displayed in Figure 11 and summarized in Table III. A failure timescale (τ) of 1 s has been applied, with (τ_0) as before at 10^{-12} s. The progressive reduction in strength with increasing levels of the DMDHEU-type crosslinkers is then modeled successfully with a positive value for (λ). However, the model does not fully describe the behavior of the DABS-treated fabrics, where a small but significant increase in breaking strength is seen at low crosslink concentrations. However, a slight reduction of the initial fiber stress-factor (γ) allows successful fitting of the later data points in Figure 11, also with a positive value for (λ). In both tensile and abrasion configurations, a positive value for (λ) is an indication that the insertion of crosslinks reduces the proportion of active load-bearing chains. However, from Table III, this effect in the tensile configuration is apparently not as severe as under abrasion conditions, as the larger strains involved may bring a greater fraction of the total polymer chains into play.

The initial improvement in tensile strength seen with the DABS crosslinker could be a manifestation of the increase in molecular weight and the reduction in number of inactive chain ends, with such effects reported for thermoplastic and elastomeric materi-

als.^{31,36,38} In a perfectly distributed network, the molecular weight will reach infinity at a 1 : 1 polymer to crosslinker mol ratio (for a bifunctional crosslinker). Lyocell has a typical weight-average degree of polymerization (P_w) of around 650,⁵ with a polydispersity (P_w/P_n), which is assumed for most processed cellulosic materials to be around 2.³⁹ This would give a number-average molecular weight (P_n) of 225, requiring 1/225 moles of crosslinker per chain or 0.44 mol % to achieve a complete network. The accessibility of the crosslinker may be only of the order of 30–50% of the total number of polymer hydroxyl groups, which is counterbalanced by the expected efficiency of creation of effective crosslinks, also maybe only 25% of total fixed agent. With these assumptions from Figure 4, it is not unreasonable to see a peak in the fabric breaking strength at less than 0.6 mol % DABS content.

At higher DABS contents, the effect of stress concentration becomes apparent in the strength data, with a positive value for (λ), around $0.9 \times 10^{-4} \text{ m}^3/\text{mol}$ required to successfully fit eq. (4). The molecular strains experienced in the tensile experiment are much greater than those encountered during abrasion, so it is plausible that even the longer flexible arms of the DABS crosslinks can become over extended under these conditions and so lead to stress concentration at higher levels of fixation. The improvement in dry-crease recovery seen with DABS treatment confirms that additional bond stressing takes place, following the deformations resulting from a tight fabric fold, which therefore leads to a greater recovery force. However at the molecular level, the induced stresses appears to be much more concentrated for the shorter, more rigid DMDHEU crosslinks, reflected in a higher model (λ) parameter from the strength data, around $2.7 \times 10^{-4} \text{ m}^3/\text{mol}$.

CONCLUSIONS

This work has shown that differences in molecular architecture of crosslinkers applied to lyocell fiber have a major influence on the resulting fabric performance. The DABS agent can be fixed under either wet-alkaline or dry baking conditions, with both treatments resulting in an improvement in wet and also dry fabric abrasion resistance. In contrast, treatment under dry baking conditions with conventional DMDHEU results in a reduction in the dry abrasion resistance because of the embrittlement of the fiber structure. A theory has been revisited that describes failure under a fatigue regime as a kinetic process, with progressive rupture of polymer chemical bonds. From this it can be shown that the activation energy for bond rupture is reduced by an external stress, and most importantly by the concentration of this stress at over-extended polymer tie chains. The distribution of tie lengths in the material can be modified by the

insertion of covalent links and in the case of a small rigid crosslinker such as DMDHEU this leads to concentration of stress at fewer bonds. These overstressed bonds are ruptured first, transferring load to neighboring bonds, which also progressively break, leading to failure of the material. Crosslinking with the longer flexible DABS molecule leads to a reduction in stress concentration, as the flexible ties enable the cellulose polymer chains to act cooperatively to support the stress. The influence of crosslinker architecture is also seen under a tensile testing regime, where stress concentration following treatment with the small rigid DMDHEU agent leads to a progressive reduction in breaking tenacity with increasing fixation. More complex behavior is seen with the longer flexible DABS agent, where an increase in tensile strength is seen at low levels of fixation, probably due to the increase in effective molecular weight. The strength of fabrics are reduced at higher levels of fixation, as the insertion of additional crosslinks causes stress concentration under the large-strain conditions of the tensile experiment. According to the kinetic strength model, lyocell experiences in a large increase in the fiber stress concentration parameter in the swollen condition in a wet-abrasion experiment. This is believed to be due to the breakdown of interfibrillar hydrogen bonding, causing a separation of fibrillar layers and increasing the ease of propagation of cracks along the fiber axis. Stresses can seek out lateral weak points in the structure over larger axial distances, which leads to progressive failure of independent fibrillar layers and the development of a breakage across the entire fiber.

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