

Mechanism of Crosslinking Tencel Woven Fabric for Superior Easy-Care Properties and Analysis Using Fluorescence Microscopy

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ABSTRACT: A crosslinking treatment to impart easy-care properties to Tencel fabric has been investigated, using dimethyloldihydroxyethylene urea (*Reaktant DH*) as crosslinking agent and magnesium chloride hexahydrate as catalyst. Nonconventional treatment techniques such as "flash curing," "moist curing," "pad-batch-cure," and "pad-dry-dry steam cure" are used to facilitate better penetration of crosslinking monomer into the fiber interior. Easy-care properties of Tencel fabrics using these techniques are evaluated and compared with those treated with resin monomer using conventional pad-dry-cure process. Analysis of treated fab-

ric using a fluorescent labeling technique and image analysis shows that nonconventional techniques significantly improve the penetration of crosslinking agent. The results further suggest that these techniques can be used to improve abrasion resistance and fabric handle of Tencel woven fabric. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2154–2161, 2006

Key words: microstructure; adsorption; crosslinking; curing of polymers; resins

INTRODUCTION

Tencel is a regenerated cellulosic fiber, which within a few years has already developed its own market profile. In addition to its characteristic physical properties and value in the textile and clothing industry, the manufacturing process offers a much greener, ecological alternative to traditional viscose and cotton.^{1–3}

Longitudinal fibrillation of Tencel induced by the introduction of wet abrasion or mechanical energy is a characteristic feature of the fiber. Fibrillation affects both the physical and esthetic properties of apparel fabrics making it more difficult to meet retail quality requirements and affects the serviceability of garments in use, particularly in respect to washing. The appearance of fibrils after domestic washing causes greying and creasing of fabrics^{4–7} and is generally considered to be objectionable. Many attempts have been made to control the propensity of Tencel to fibrillate by controlling production parameters during fiber formation^{8–12} as well as during fabric processing.^{5–7,10,13} It has been found that resins used for textile finishing, particularly those used to control crease

resistance can be a practical method of controlling this problem.

From initial investigations, it has been found that reducing the degree of fibrillation by crosslinking resins gives a parallel reduction in dry abrasion resistance. Possible contributing factors are the degradation caused by the acid catalyst, and the restriction of stress distribution within the fibers due to their rigid crosslinking by monomeric resins.^{14,15} Pad-dry-cure procedures to impart easy-care properties to other cellulosic fabrics have shown that rayon loses little or no tensile strength and suffers no acid damage under the same conditions, where cotton not only loses strength but sometimes suffers irreversible acid damage. Nuessle, Fineman, and Heiges employed 10% (dissolved solids) of highly efficient cyclic urea formaldehyde, together with either ammonium chloride or an amine hydrochloride catalyst, at a cure of 10 min at 149°C. On the removal of resin with organic amine catalyst, the loss was recoverable, indicating no acid damage, but with ammonium chloride the loss was partially recoverable.¹⁵ This is because cotton tensile strength is dependant upon a high degree of polymerization of the molecular chains, hence, breaking of chains by acid hydrolysis results in strength loss. In viscose rayon, by contrast, the fiber strength is dependent on the orientation and intertangling of chains during the drawing process, thus acid hydrolysis is less likely and less destructive if it does occur. The

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deterioration in the physical properties of viscose rayon fabrics on treatment with resin is due to altered stress-strain characteristics of the fibers;^{15,16} it is noted that the main change resulting from resin finishing is an increase in the elastic recovery, an increase in modulus, but a decrease in fiber extensibility. Both cotton and viscose rayon demonstrate reduced fiber extensibility as a result of resin treatment, which is alone responsible for the loss in abrasion resistance.¹⁷

Numerous studies of chemical modification of cellulosic fabrics have been conducted for the purpose of improving strength and abrasion resistance. Varying degrees of success have been achieved with variations in processes, but it is understood that conventional pad-dry-cure processes do not result in significant morphological changes in the fibers, mainly because of poor penetration of the resin monomer into the fiber structure; the success of nonconventional processes highly depends on the diffusion of the resin monomer into the fiber interior and the covalent crosslinking or anchoring of resin to the fibers.¹⁶ The objective of this preliminary study is to investigate the efficacy of nonconventional resin treatment techniques to facilitate satisfactory penetration and to investigate the effect of these treatments on fabric performance properties.

EXPERIMENTAL

The nonconventional techniques used in this study were "pad-batch-cure," "flash cure," "moist cure," and "pad-dry-dry steam" processes.¹⁸ The treatment parameters of catalyst type, concentration of resin and catalyst, and drying and curing conditions were kept constant throughout the study to observe the effect of each process on fabric performance. The physical properties of treated fabric of dry crease recovery angle, abrasion resistance, and fabric appearance after domestic washes were evaluated. A fluorescent labeling technique¹⁹ and image analysis were performed to locate the resin in the treated samples and also to confirm the changes in fiber structure.

Materials

The white and dyed 100% Tencel 3/1 twill fabrics of 30 × 30/44 × 35 quality, obtained from Lenzing Ltd., were used throughout this study; the fabrics had been singed and desized. Reaktant DH, the crosslinking agent, was obtained from TextilColor AG Ltd. Reaktant DH, dimethyloldihydroxyethylene urea, the dissolved solid content was 41%. All other chemicals were of general laboratory grade supplied by Aldrich.

Fabric treatments

The fabric samples were scoured and neutralized before use and treated in an aqueous bath containing

50 g dm⁻³ Reaktant DH and 10 g dm⁻³ catalyst (magnesium chloride hexahydrate). The following five different treatment processes were used:

Pad-dry-cure (PDC) process

The fabric samples (30 × 42 cm²) were impregnated in the pad bath containing resin and catalyst for 10 min. The samples were padded through the squeeze rollers at a pressure of 15 kg cm⁻² to obtain 80–85% pick-up, then dried in Werner Mathis stenter for 3 min at 130°C, and finally cured for 3 min at 160°C.

Pad-batch-cure (PBC) process

This process is similar to PDC process, except that after padding, samples were fixed by being individually sealed in polyethylene sheet and placed at a specific temperature for a specific time. Three different conditions were used; one sample was kept at room temperature for 24 h, another sample kept in an oven at 65°C for 30 min, and one more sample kept in an oven at 85°C for 15 min. After this fixation step samples were dried and cured as described in PDC process.

Flash cure (FC) process

The flash cure process is identical to PDC process, except that the drying and curing were performed in one step. The fabric samples were padded using the same padding conditions and then were cured at 160°C for 3 min.

Moist cure (MC) process

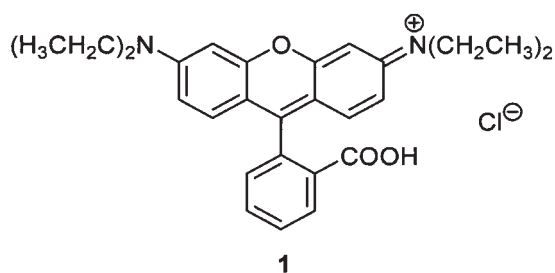
In this process, fabric samples were cured in a moist, partially swollen state. The fabric samples were padded with resin liquor and subsequently dried at 130°C for 1 min to residual moisture of 6–12%. Because no crosslinker or strong acidic catalyst was added, after being batched for 24 h at room temperature, the fabric samples were cured at 160°C for 3 min.

Pad-dry-dry steam (PDDS) process

Pad-dry-dry steam process is also identical to PDC process except that a steam and hot air mixture was used for curing. At 160°C curing temperature, steam content was 125 g m⁻³ and moisture content was 26%. Two fabric samples were prepared; one sample was padded, dried, and dry steamed, the other was padded, batched for 24 h at room temperature and then dried and dry steamed.

Fabric evaluation and analysis

Fluorescent labeling was used to obtain information concerning the location of resin in the treated samples. The fabric samples were dyed with $10^{-3}M$ Rhodamine B (C.I. Basic Violet 10; 1) solution for 1 h at room temperature, twice washed in a pH 9.3 buffer solution (NH_4Cl/NH_3) for 20 min, then dried at room temperature for at least 24 h. The resin-embedded fabric samples were prepared using JB-4 embedding kit; the embedding resin was based on glycolmethacrylate (GMA). The cured blocks of resin embedded samples were trimmed and $4\text{-}\mu\text{m}$ sections were cut using a base sledge microtome with a wedge knife. Four sections of each fabric sample were mounted on slides and studied using an Olympus BX51 optical microscope with mercury burner lamp, monochromatic Rhodamine/Texas red filter, and a digital Evolution MP Color camera at 545–580 nm excitation. The images were captured using Image Pro Plus version 4.5. Subsequently, the percentage of resin penetrated into the fabric interior was determined by performing image analysis of captured images using the same Image Pro Plus analyzing system. Because of the differences in fabric thickness, thickness of the resin layer, and thickness of the fabric, samples were measured at eight different places and presented as % of each sample thickness.



Prior to testing, all fabric samples were conditioned at 50% RH and 20°C . The percentage of resin solids on the fabric was determined by determining the bone-dry weight of fabric before and after resin application. The $10 \times 10\text{ cm}^2$ fabric samples were placed in clean weighing bottles and conditioned for 48 h. The conditioned samples were placed in a drying oven at $(105 \pm 5)^\circ\text{C}$ for 18 h. After 18 h, the samples were placed immediately inside a desiccator containing silica gel and allowed to cool for an hour. The cooled samples were then weighed by means of the same electronic balance. The % solid add-on was determined by using eq. (1):

$$\% \text{ Solid Add-on} = [(W_1 - W_0)/W_0] \times 100\% + (a)\% \quad (1)$$

where W_1 is the bone-dry weight of the fabric after resin finishing, W_0 is the bone-dry weight of the fabric

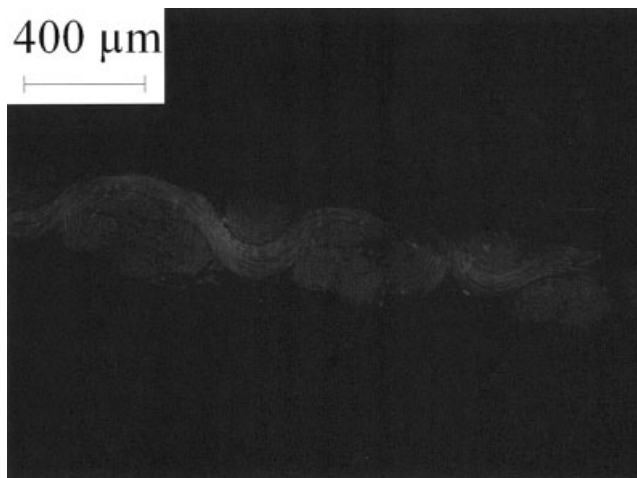


Figure 1 Typical optical microscopic image of untreated Tencel fabric sample, Exposure time 55 ms, magnification $40\times$.

before resin finishing (control sample), and (a) is the correction factor. Some small loss of the fibers occurred during padding of fabric; therefore a correction factor was used to determine the actual solid add-on on the bone-dried fabric.

The easy-care properties of unwashed and 5-times-washed treated samples were evaluated using standard procedures including dry crease recovery angle (DCRA; BS EN ISO 2213) and Martindale abrasion resistance (BS EN ISO 12947-2) using standard worsted abradant fabric and constant pressure of 9 kPa.

The treated samples were washed using standard procedure BS EN ISO 15487 at 40°C for 100 min with an additional load of 1 kg. After washing, fabric samples were tumble dried for 15–20 min to achieve a reduction in moisture level up to 15–20% and then air-dried.

RESULTS AND DISCUSSION

Diffusion of monomer

On nontreated Tencel fabric, the Rhodamine B did not dye intensively, but was able to penetrate the surface and weak fluorescence is seen through the cross section (Fig. 1). It was expected that the treatment conditions provided by PBC, MC, and PDDS processes would facilitate better penetration of monomer into the fabric interior with respect to the PDC and FC processes. Figures 2 and 3 show the cross sections of resin-treated fabric samples using the PDC and FC process. The presence of resin on the surface of fabric is clearly visible indicating that treatment conditions provided by PDC and FC processes are not effective in facilitating the penetration of resin throughout the fabric thickness. Using PDC process, the penetration of resin was 11% of the sample thickness, furthermore,

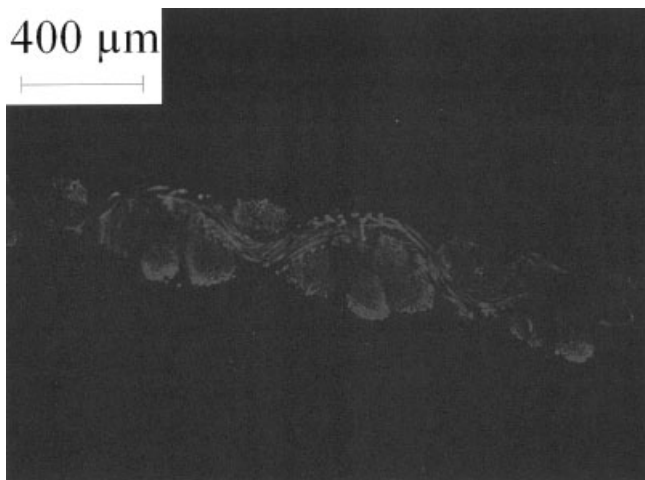


Figure 2 Typical optical microscopic image of resin-finished fabric sample using PDC process, exposure time 55 ms, magnification 40×.

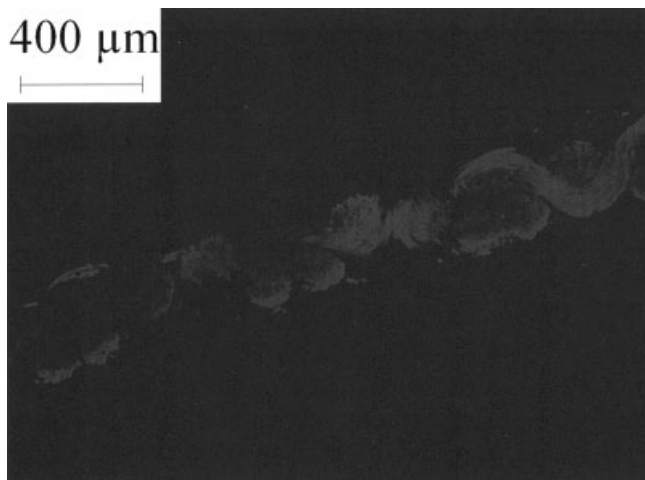


Figure 4 Typical optical microscopic image of resin-finished fabric sample using room temperature, 24 h PBC process, Exposure time 55 ms, magnification 40×.

resin distribution was not uniform. In the FC process, performing drying and curing in one step reduced the diffusion time, the rate of crosslinking was greater than the rate of diffusion, thus resin penetration was only 7.8% of the sample thickness

The microscopic images of the PBC processes (Figs. 4 to 6) show that the diffusion time given to the resin monomer before drying is important to achieve maximum diffusion of resin, however, temperature is important to achieve uniform distribution of crosslinks. Using the PBC process, in which samples are batched for 24 h at room temperature, the distribution of resin is not uniform, the migration of resin can be clearly seen; at some points resin had penetrated through the cross section of fabric, while at others the penetration was only 16% of the thickness of the treated sample.

The samples that were batched at 65°C for 30 min and at 85°C for 15 min form a significant uniform resin layer on the fabric surface. Using the 65°C, 30 min PBC process resin penetration was 10%; however, using the 85°C, 15 min PBC process, resin penetration was slightly higher: 12% of sample thickness.

Figure 7 shows the cross section of MC-treated fabric sample in which the penetration of resin is 100%. It is also observed that the fibers have a fuller structure than other differently treated fabrics. With this process, the diffusion and crosslinking process can be completely separated. Monomers diffused into the fiber interior during 24 h batching process and crosslinking occurred during the subsequent curing process. This greater extent of diffusion of resin mono-

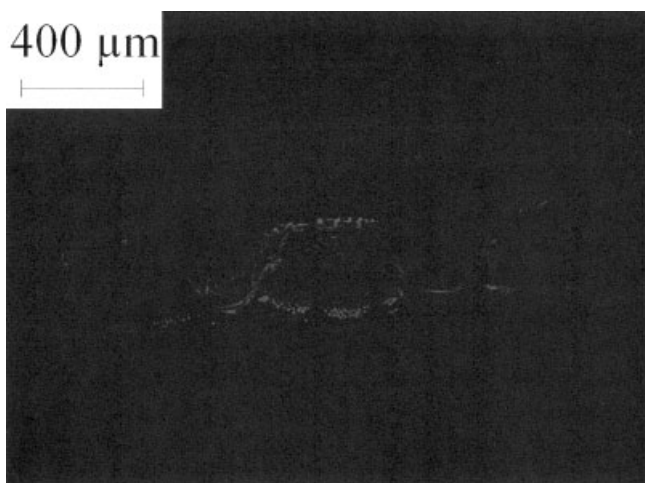


Figure 3 Typical optical microscopic image of resin-finished fabric sample using FC process, exposure time 55 ms, magnification 40×.

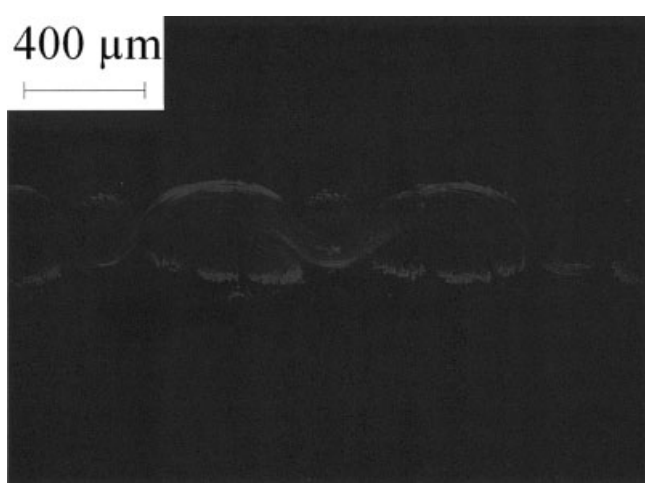


Figure 5 Typical optical microscopic image of resin-finished fabric sample using 65°C, 30 min PBC process, exposure time 55 ms, magnification 40×.

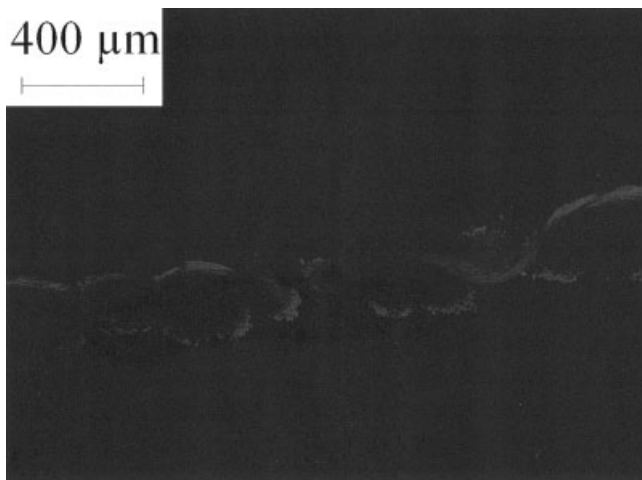


Figure 6 Typical optical microscopic image of resin-finished fabric sample using 85°C, 15 min PBC process, exposure time 55 ms, magnification 40×.

mer has also given the fabric uniform distribution and soft handle.

Considering PDDS-treated samples, the penetration of resin was 12%, which is higher than PDC-treated samples (Fig. 8), but it was also observed that the fibers in the resin layer had fuller structure than did the fibers in the fabric interior. This suggests that dry steaming not only gives better penetration of resin monomer but also helps monomer to diffuse into the fiber interior. However batching for 24 h had given better penetration of resin monomer than subsequent drying–dry steaming (Fig. 9). Again better diffusion of resin had given the fabric softer handle.

Effect of different curing processes on easy-care properties

Table I shows the effect of different curing processes on DCRA values of fabric. The fabric samples treated

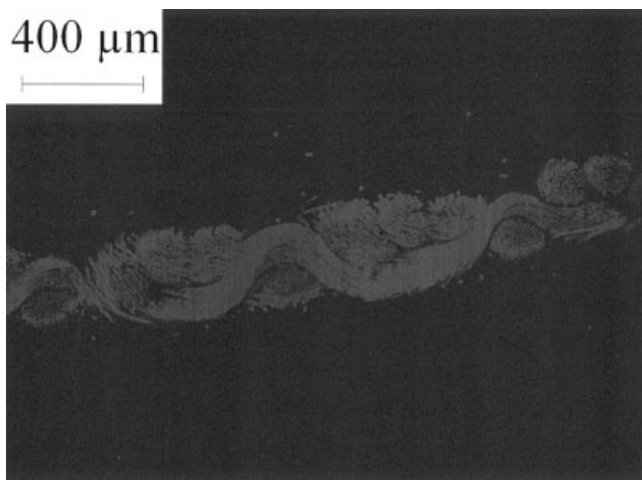


Figure 7 Typical optical microscopic image of resin-finished fabric sample using MC process, exposure time 55 ms, magnification 40×.

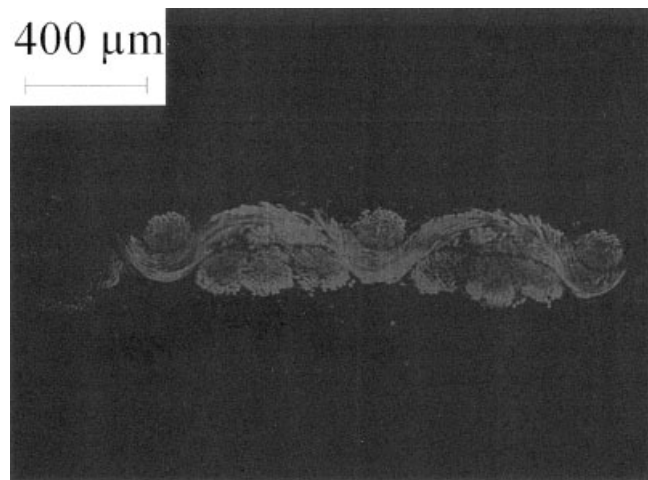


Figure 8 Typical optical microscopic image of resin-finished fabric sample using PDDS process, exposure time 55 ms, magnification 40×.

using PDC process had better DCRA values compared with those treated using MC and PDS processes, which, in turn, were better than those treated using the FC and PBC processes. The DCRA values of FC and PBC processes are even less than the DCRA values of original Tencel fabric. The better DCRA values of PDC samples are due to the formation of a more extensive and stronger hydrogen bonding system established at the junction points because of high temperature crosslinking. The combination of normal hydrogen bonds, heat-generated hydrogen bonds, and resin entanglements provides an elastic network, which imparts recovery from creasing.^{15,20,21}

In PBC and FC samples resin is deposited as surface resin at the fabric surface and at or near the fiber surface in case of PBC samples. This surface resin

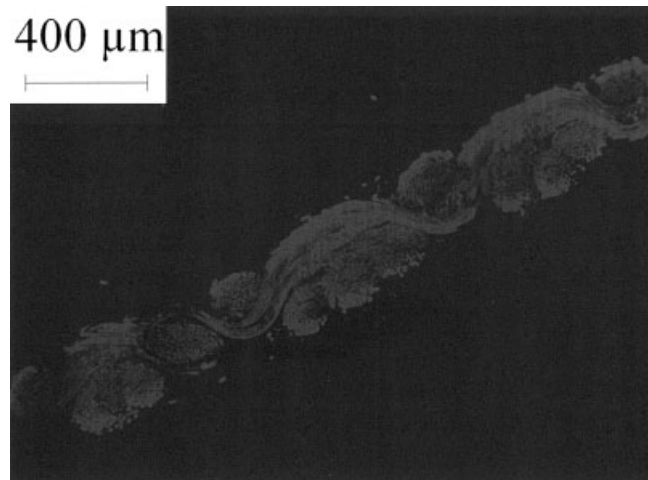


Figure 9 Typical optical microscopic image of resin-finished fabric sample using pad-batch (24 h)-dry-dry steam process, exposure time 55 ms, magnification 40×.

TABLE I
Effect of Various Treatments on the Mechanical Properties of Tencel Fabric

Curing processes	Resin solids add-on (%)	Recovery in warp direction		Recovery in weft direction		DCRA (degree)		Abrasion resistance (no of cycles)
		1 min	5 min	1 min	5 min	1 min	5 min	
Original		82.5	91.5	90.3	99.2	172.8 ± 4.4	190.7 ± 4.2	10250
PDC	1.54	97.3	107.3	104.7	113.7	202 ± 5.3	221 ± 5.1	5480
PBC (24 h)	1.76	76.8	85.5	83	93.2	159.8 ± 5.3	178.7 ± 4.9	9567
PBC (65°C)	1.61	75.5	85.2	79	89.5	154.5 ± 7.0	174.7 ± 7.1	9000
PBC (85°C)	1.55	82.8	92.5	83	95.5	165.8 ± 6.7	188 ± 6.8	11433
FC	1.63	79.3	90.3	79.5	91.5	158.8 ± 6.6	181.8 ± 6.2	10567
MC	1.73	83.2	96.3	99.2	107.5	182.4 ± 6.1	203.8 ± 5.4	14000
PD-Dry steam	1.11	89.5	99.2	90.2	101.7	179.7 ± 5.8	200.9 ± 5.6	7433
PBD-Dry steam	1.23	88.7	99.5	90.5	100	179.2 ± 5.5	199.5 ± 5	9600

welded the fibers together inside the yarns and produced a stiff three-dimensional structure. The resin links are inextensible, so when dry fabric was creased, highly localized stresses were produced in the strain areas; the nonrecoverable strain in these areas accounts for the poor dry crease recovery. These processes enhanced the abrasion resistance due to deposition of surface resin but failed to aid crease recovery.

The performance results of MC and PDDS samples show the importance of diffusibility of resin into the fiber interior. Diffusion of resin into the fiber interior has improved the DCRA values and also the abrasion resistance values are better than the abrasion resistance value of conventionally cured (PDC) sample. Notably the MC process gave the fabric a significantly increased abrasion resistance; this suggests that MC may have resulted in a significant modification of fiber structure, probably because of the greater extent of penetration and diffusion of resin monomer into the fabric interior.

Effect of domestic washing

The easy-care properties of differently treated samples after five domestic washes are shown in Table II. The

DCRA values of five-times-washed fabric samples increased in all cases, except for PDDS-cured samples, which were unchanged (Fig. 10). Comparison of abrasion resistance before and after five domestic washes (Fig. 11) shows that abrasion resistance of PDC-treated samples significantly increased. The abrasion resistance of PBC-, MC-, and PBDs-treated samples slightly decreased, while abrasion resistance values of PDS and FC remained almost the same.

It was observed that, apart from minimizing the formation of fibrils during domestic washing, resin finish also leads to dehairing of fabric. The brittle fibrils and hairs break off easily during laundering, leaving fabric surface clean and smooth; this gives the advantage of pill-free fabric, but also causes significant loss in abrasion resistance.

The visual analysis of differently treated fabric samples shows that all resin-treated samples have clean, pill-free surface, except FC-treated samples. Deposition of resin on the surface did not prevent fabric fibrillation; appearance of mild fibrillation caused entanglement of hairs on the surface, causing light scattering and an associated visually paler appearance.

TABLE II
Effect of Five Domestic Washes on Mechanical Properties of Various Treated Tencel Fabric

Curing processes	Recovery in warp direction		Recovery in weft direction		DCRA (degree)		Abrasion resistance (no of cycles)
	1 min	5 min	1 min	5 min	1 min	5 min	
PDC	111.2	121.8	105.7	115.3	216.9 ± 5.3	237.1 ± 4.6	11000
PBC (24 h)	92.8	105	93.8	104.2	186.6 ± 6.0	209.2 ± 5.9	7500
PBC (65°C)	92.7	103.7	92.7	104.8	185.4 ± 4.5	208.5 ± 4.2	6433
PBC (85°C)	84.7	95.8	87.5	99.2	172.2 ± 5.5	195 ± 5.2	7500
FC	82.3	93.5	93.8	105	176.1 ± 9.0	198.5 ± 8.8	11133
MC	90	101.3	98.7	109.2	188.7 ± 7.3	210.5 ± 6.6	9833
PD-Dry steam	79.7	92.2	89.3	101.2	169 ± 8.7	193.4 ± 8.6	7420
PBD-Dry steam	85.7	98	89.3	102.3	175 ± 7.5	200.3 ± 7.2	8110

Appearance of fibrillation also accounts for the unchanged abrasion resistance of the fabric sample.

CONCLUSIONS

This work has resulted in significant findings about the mechanism of easy-care finishing and imparted properties of Tencel woven fabric. The critical feature of Tencel fabric crosslinked by pad-batch process at 65°C and 85°C is the uniform distribution of crosslinks throughout the fabric surface as compared with PDC process. Unwashed samples have better abrasion resistance (in comparison with PDC-treated samples) presumably because of the deposition of surface resin, but dehairing caused by the presence of the resin furnishes a 30% reduction in abrasion resistance after domestic washing.

Though flash-cured samples have slightly better DCRA values than PBC samples and better abrasion resistance values compared with PBC, PDC, and PD-Dry steamed-treated samples, fabric appearance after domestic washes is compromised because of fibrillation.

From the properties of the fabric samples shown in Tables I and II, it can be concluded that the MC process provides the most superior performance overall in comparison with other differently treated samples. This process yields a high level of diffusion of resin monomer into the fiber interior in conjunction with a high abrasion resistance value and soft handle. After five domestic washes, the abrasion resistance has decreased by 30%, but is still higher than the

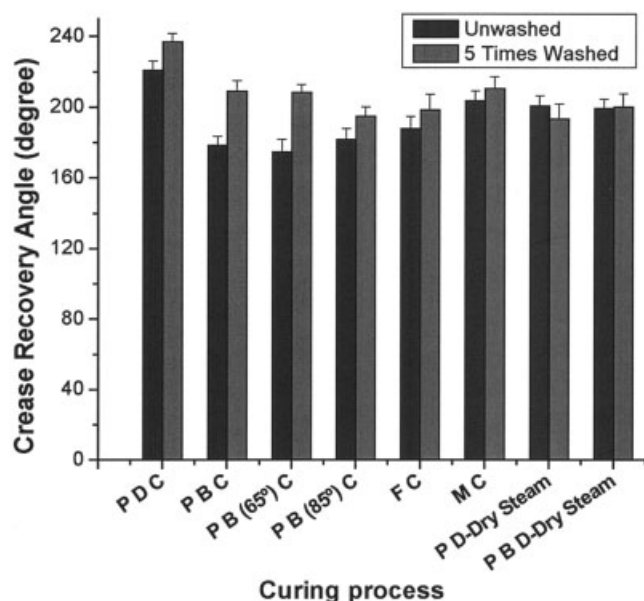


Figure 10 Crease recovery angle values (degree) of unwashed and five-times-washed; differently treated fabric samples.

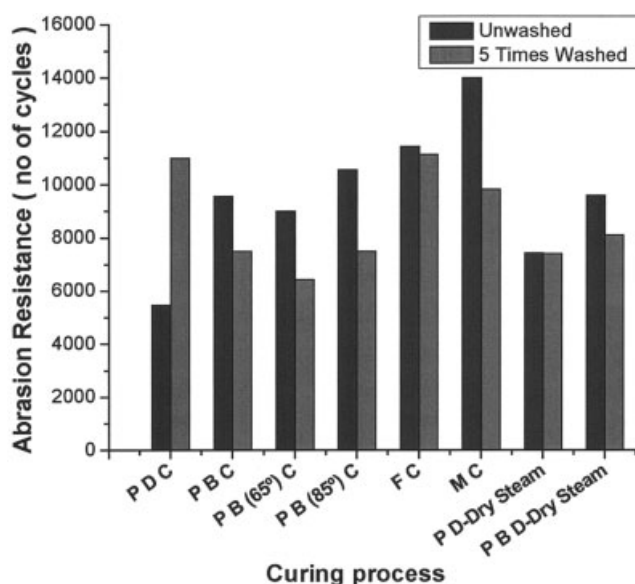


Figure 11 Abrasion resistance values (no. of cycles) of unwashed and five-times-washed; differently treated fabric samples.

abrasion resistance values of other differently treated samples. The DCRA values of MC samples are less than the DCRA values of PDC-treated samples, but are better than untreated, PBC-, FC-, and dry-steamed samples.

From a continuous processing perspective, dry-steam curing is an attractive option; better abrasion resistance values are obtained with respect to fabric treated with a conventional PDC process because fibers were crosslinked in a partially swollen state, but the treatment is not as effective as MC. The DCRA values are also not as high as obtained in PDC processes, which could be because the steam curing time is too short. Furthermore, laundering does not have any adverse effects on performance properties. A 160°C curing temperature and 3 min curing time has been used to compare this process with other nonconventional processes, but optimization of experimental parameters such as moisture content, curing time, and temperature can further improve performance properties of fabric, however, this is beyond the scope of the research discussed here because of its comparative nature, but this work is ongoing.

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