

Analysis of a Crease-Resisting Finish on Linen Fabrics Using Fourier Transform Infrared Spectroscopy and Visible and Near-Infrared Spectroscopy

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ABSTRACT: A wide range of chemical reagents are capable of producing a satisfactory crease-resisting finish for cellulosic fabrics and are currently available on the market. However, these agents do not work as efficiently on linen relative to cotton or rayon. Untreated linen controls and samples treated with a *N*-methylol reagent were investigated for physical and chemical changes, and an attempt was made to quantify the crosslinking bonds formed and assess other changes in the treated fabrics using Fourier transform infrared spectroscopy (FTIR) and visible and near-infrared spectroscopy (NIR). The results were compared with nitrogen analysis data, crease-recovery angle measurements, and abrasion-resistance tests in an attempt to assess the effectiveness of the treatment relative to the responses of the instrumental techniques. This study shows correlations between the visible and NIR and FTIR spectra and the crease-recovery angle and abrasion resistance. The study also indicates that FTIR may be useful in assessing the crosslinking bonding changes associated with the dimethylol urea treatment of linen to achieve improved crease recovery. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1886–1896, 2001

Key words: linen; cellulose; crease-recovery; dimethylol urea; biofibers; crosslinking; infrared spectroscopy

INTRODUCTION

Perhaps the greatest single problem with linen fabric is its tendency to crease easily, particularly in the dry state. Hence, the development of a process which improves dry crease recovery, without impairing other performance characteristics, has been a long-term goal for finishers and reagent manufacturers, but still remains to be satisfactorily resolved.^{1–4} The characteristics of linen as a textile fabric depend on the flax fibers from which the yarn is spun and the fabric subsequently woven. A single flax fiber or ultimate fiber is composed primarily of cellulose (approx-

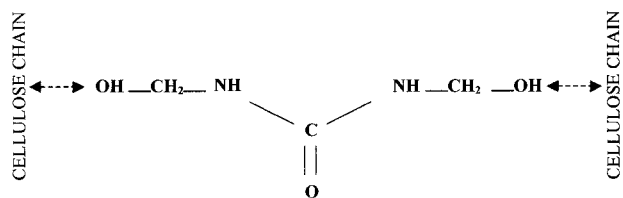
mately 80%) but also incorporates pectic substances, hemicellulose, and lignin.⁵

One of the approaches to improving crease recovery has been to introduce crosslinks between individual cellulose chains. A crosslinking molecule may be used to achieve this; one such molecule is dimethylol urea (DMU),³ which has proved effective with cotton and rayon. DMU has hydroxyl groups at both ends of the molecule; these groups can bond with available hydroxyl groups on cellulose chains, forming crosslinks between individual cellulose chains (Scheme 1). The reaction is a condensation reaction catalyzed by magnesium chloride hexahydrate and cured at about 140°C.

With linen, the treated fabric exhibits an improvement in crease recovery, but with a poorer performance when compared to cotton^{2,4} and a reduced resistance to abrasion. This apparent re-

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Scheme 1

duction in effectiveness of crosslinking treatment in linen, which also occurs with other reagents,⁴ appears to have several causative factors and is as yet not completely understood.

The techniques of measurement of the crease-recovery (CR) angle and resistance to abrasion (AB) of fabrics must be performed using physical testing, outlined below. These testing procedures are slow and give no chemical bonding or structural information; in addition, they are also unsuited to rapid production-line quality-control monitoring.

Modern instrumental techniques, such as Fourier transform infrared spectroscopy (FTIR) and visible near-infrared spectroscopy (Vis-NIR), have been shown to be sensitive to particular chemical bonds and to subtle changes in the bonding present in materials.⁶ As a result, the latter technique has become well established within the agrifood and polymer sectors.^{7–10} Therefore, the assessment of FTIR and or Vis-NIR as a potential replacement for specialized laboratory testing, detection, and identification of finishing¹⁰ and sizing compounds and estimation of the degree of mercerization in cotton¹¹ was a logical step. Discrimination of cellulosic fabrics (mainly of a cotton origin), on the basis of fabric type, dyeing, textile processing, and breaking force using diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and chemometrics, was demonstrated by Gilbert et al.^{12,13} FTIR was used effectively by Yang et al.¹⁴ in developing an understanding of the bonding changes associated with polycarboxylic acid treatment of cotton for CR and durable-press characteristics.¹⁵ However, evaluation and modeling for complex nonlinear physical parameters such as the CR angle and AB resistance for linen fabrics have had little attention.

The aim of this study was to detect the changes in CR and AB resistance in linen fabrics, which arise as a result of DMU treatment using FTIR and Vis-NIR. The spectral changes observed, with these instrumental techniques, were compared

with conventional physicochemical determination of the CR angle, AB resistance, and nitrogen content.

EXPERIMENTAL

The fabrics utilized were proprietary blouse-weight pure linen of plain-weave construction, supplied in an undyed state by John Hannah Ltd. (Ballymena, Northern Ireland). Of identical origin, the three differed only in their preparative treatment: scoured only (S), scoured and bleached (B), and scoured but mercerized (M). Briefly, mercerization is a process involving treatment with a high concentration of sodium hydroxide at low temperature¹⁶ which can enhance specific properties of linen.¹⁷

Twelve subsamples from each of the three stock linen specimens were ruled parallel to the weft and warp directions to measure approximately 21.6×30.5 cm for S and B and 23.6×30.5 cm for M linen to allow for $\sim 8.5\%$ weft shrinkage in the mercerized fabric. These were then conditioned in a controlled environment [65% relative humidity (RH) and 20°C] for at least 12 h before being weighed and the percentage uptake of distilled water determined and noted. The subsamples were then mounted onto pin frames to prevent shrinkage and to maintain the original dimensions during subsequent drying.

Three treatments with four replicates for each were performed on each linen type, at a nominal 5 and 2.5% DMU (Sigma, Poole, Dorset, UK) catalyzed with 25% magnesium chloride hexahydrate (Sigma) on the weight of DMU and, finally, a distilled water control. The solutions were applied by a laboratory-scale padding mangle (Ernst Benz AG, Zurich), weighed for uptake, and dried (approximately 35°C for at least 20 min), before being cured in an oven at $140\text{--}145^\circ\text{C}$ for 4 min. All samples were subsequently afterwashed at 60°C for 5 min, using an aqueous solution of 5 g L^{-1} sodium carbonate decahydrate and 0.4 g L^{-1} sodium dodecyl sulfate, to remove any unreacted DMU and catalyst, then rinsed in running water for about 10 min. The water-treated controls were also washed in this way for consistency. All the samples were finally dried on pin frames prior to storing, for a minimum of 2 weeks, at 65% RH and 20°C until required for testing.

The range of techniques employed to assess the fabrics was as follows—Vis-NIR, FTIR, CR angle,

AB determination, and elemental analyses for nitrogen (N):

Vis-NIR: This was performed on a Foss visible-near infrared system, Model 6500, using WINISI 11 software for data capture. All scans were performed in the range 400–2500 nm on conditioned fabric (20°C and 65% RH). Using one complete sample sheet per treatment, these sample sheets were folded to give five replicates of each treatment, with each replicate being scanned 64 times.

FTIR: This was performed on a Biorad FTS 185 Fourier transform infrared system equipped with a Digilab diffuse reflectance accessory (DRIFT) and an MCT detector, using KBr as a background. Three discs approximately 7 mm in diameter were cut, using scissors, from each of the nine different samples of linen (i.e., S, B, and M linen, each treated with 5% DMU, 2.5% DMU, and water). Each sample disc was scanned 16 times and the spectra averaged.

The NIR and FTIR spectra were imported into Unscrambler (Unscrambler version 7.0, Camo Trondheim, Norway)¹⁸ as 27×1050 and 27×3474 matrices, respectively, and transformed by derivatives using the Savitzky–Golay algorithm (using first derivative, number of left-side points = 4, number of right-side points = 4, and polynomial order = 2). Calibrations for both were developed using partial least-squares (PLS1) regression. Due to the limited number of samples in this study, validations of the calibration equations were estimated by full cross-validation, using the same sample sets as used for calibration.

Physical Assessment

CR angles were determined according to the British Standard method (BS 3086) under standard conditions. Twelve replicates from each of the three treatments and from each of the three fabrics (total sample set $n = 108$) were measured using a CR angle meter (Shirley combined creasing and stiffness tester, Shirley Developments Ltd., Didsbury, UK). The CR angles obtained were recorded as a percentage of 180° and the mean values were determined.

AB resistance was determined under standard conditions (20°C and 65% RH), using a Martindale wear and an AB tester, (J. H. Heal Co, Halifax, UK) with 12 kPa pressure.¹ Four replicates could be accommodated for each AB run on this instrument, and the end point was determined by periodic visual inspection of the fabric yarns for the first abrasive brake in the yarn of the fabric.

Each sample was tested using 12 replicates and the mean number of rubs per treatment was calculated. The total sample set, n , was once again $12 \times 3 \times 3 = 108$.

Elemental Analysis

The fabric samples were analyzed for the percentage nitrogen (N) by pyrolysis gas chromatography. The samples were finely cut using a pair of serrated scissors, and between 5 and 10 mg of each sample was carefully weighed in tinfoil capsules and enclosed by folding over the tinfoil. The capsule pellets were then loaded into an auto sampler carousel of an elemental analyzer (Carlo Erba NA 1500 Series 2, Milan, Italy). The resultant gases such as nitrogen dioxide were measured as the percentage nitrogen (N). Each sample was analyzed in triplicate, giving a total sample set of $n = 27$.

The fabric samples were also qualitatively analyzed for the presence of elements of atomic number greater than 10 using an energy-dispersive X-ray (EDX) elemental microanalysis system (Link Exl, Oxford Instruments, High Wycombe, Bucks., UK) attached to a scanning electron microscope (SEM; JEOL, JSM 35CF, Tokyo Japan). Subsamples of approximate size 4×7 mm were cut from each fabric sample and attached to aluminum SEM specimen support stubs using double-sided conductive tape. These subsamples were then carbon-coated and transferred to the SEM for EDX analysis.

RESULTS

Fabric Parameters

Table I shows descriptive statistics for the full sample set (namely, scoured, bleached and mercerized fabrics, in untreated state and after treatment with DMU at two concentrations), for CR angle, AB resistance, and percentage nitrogen values. All parameters showed a wide range of values, as indicated by the maximums and minimums.

The effect of DMU treatment of the fabrics (Table II) resulted in a significant ($P < 0.001$) increase in the percentage nitrogen content in all three test fabric samples compared to untreated controls, leading to a significant ($P < 0.001$) improvement in CR. Of the three materials, bleached fabric contained, significantly ($P < 0.001$), the highest nitrogen and exhibited the highest percentage CR

Table I Descriptive Statistics for the Full Test Fabric Sample Set, for CR Angle, AB, and Nitrogen Content (N)

Parameters	<i>n</i>	Min	Max	Mean	SEM
CR %	108	16.6	65.4	41	0.966
AB (rubs)	108	400	30,500	9143	791
N %	27	0.03	1.272	0.608	0.0085

SEM, standard error mean, *n*, number of samples tested for each parameter.

(60.8% with the 5% DMU treatment). Similar effects on scoured linen were significantly reduced and followed by mercerized fabric samples, for both the nitrogen content and the CR angle. However, the fabric resistance to AB was significantly ($P < 0.001$) reduced in bleached linen compared to the other two test fabrics, which showed an initial increase in resistance to AB at 2.5% DMU, followed by a decline at the 5% DMU application rate. AB was observed to vary significantly ($P < 0.001$) between the three test fabrics, with the bleached samples

showing the poorest resistance to AB (600 rubs for the 5% DMU treatment), once again followed by the scoured fabric and, finally, the mercerized linen.

The true concentration of DMU absorbed by each fabric sample was determined from the individual uptake measurements. The additional nitrogen present in the cured afterwashed samples was calculated from the analysis data, permitting estimation of the degree of fixation for each batch (Table III). EDX analysis spectra obtained from the subsamples of the fabrics (not

Table II Effect of DMU Treatment on Bleached, Scoured, and Mercerized Fabric Samples for Changes in CR, AB, and Nitrogen Content (N)

Treatment	Bleached	Scoured	Mercerized
CR (%)			
Control	25.5	22.4	20.8
2.5% DMU	49.2	44.4	35.1
5% DMU	60.8	58.3	51.9
SEM			
Fabric = 0.557***			
DMU = 0.557***			
Fabric × DMU = 0.966***			
Abrasion (rubs)			
Control	6135	7838	18,444
2.5% DMU	3712	10,292	23,393
5% DMU	600	1471	10,402
SEM			
Fabric = 144.3***			
DMU = 144.3***			
Fabric × DMU = 790.6***			
Nitrogen (%)			
Control	0.0084	0.056	0.033
2.5% DMU	0.562	0.595	0.557
5% DMU	1.224	1.2467	1.1273
SEM			
Fabric = 0.005***			
DMU = 0.005***			
Fabric × DMU = 0.009***			

SEM, standard error of means; ***, $P < 0.001$.

Table III Comparison of Nitrogen Present in the Three Fabrics Treated with DMU at Nominal 2.5 and 5.0% on the Weight of the Fabric (OWF) and Degree of Nitrogen Fixation (DOF)

Nominal OWF	Bleached			Scoured			Mercerized		
	N (%)	DMU	DOF	N (%)	DMU	DOF	N (%)	DMU	DOF
2.5%	0.48	2.63	0.78	0.54	2.57	0.89	0.52	2.37	0.94
5.0%	1.14	5.19	0.93	1.19	5.19	0.98	1.09	4.86	0.96

N, total added nitrogen as determined by elemental analysis of treated fabric; DMU, true concentration in fabric calculated from reactant concentration and measured uptake; DOF, proportion of nitrogen chemically fixed in the fabric.

presented) showed that there are no elements detected above the atomic number 10.

fabric only for clarity, of typical FTIR spectra (Fig. 1), and typical NIR spectra (Fig. 2).

Infrared Spectroscopy

The infrared spectroscopy results are presented below with examples given, from the bleached

FTIR

Calibration statistics for CR, AB resistance, and nitrogen content, using the full FTIR spectral

Table IV Calibration Statistics for the FTIR Spectra (Full or Eight Segments) and Their Relationship to CR, AB, and Nitrogen Content(N) for All Fabric Samples (27) After Mathematical Treatment (144) of the Spectra

Parameter	SEC	r^2 Calibration	SECV	r^2 Cross-validation
AB				
653–3996 cm^{-1}	254	0.9994	5068	0.7406
653–1000 cm^{-1}	4002	0.8416	3198	0.9021
1000–1400 cm^{-1}	3419	0.8872	4320	0.8132
1400–1800 cm^{-1}	1340	0.9835	3389	0.8896
1800–2200 cm^{-1}	3323	0.8938	4648	0.7788
2200–2600 cm^{-1}	3180	0.9032	5826	0.6340
2600–3000 cm^{-1}	474	0.9979	4261	0.8187
3000–3400 cm^{-1}	2959	0.9168	5481	0.6781
3400–3996 cm^{-1}	2716	0.9304	5071	0.7294
CR				
653–3996 cm^{-1}	1.443	0.9953	5.593	0.9471
653–1000 cm^{-1}	3.789	0.9672	7.850	0.8519
1000–1400 cm^{-1}	4.221	0.9591	9.838	0.7517
1400–1800 cm^{-1}	3.600	0.9704	4.764	0.9480
1800–2200 cm^{-1}	4.386	0.9558	10.474	0.7135
2200–2600 cm^{-1}	13.567	0.4151	17.362	-0.2134
2600–3000 cm^{-1}	3.360	0.9743	13.418	0.4492
3000–3400 cm^{-1}	13.908	0.3608	16.305	-0.0828
3400–3996 cm^{-1}	13.523	0.4215	15.467	0.1334
Nitrogen				
653–3996 cm^{-1}	0.0516	0.9941	0.1984	0.9268
653–1000 cm^{-1}	0.1449	0.9527	0.2886	0.7990
1000–1400 cm^{-1}	0.1486	0.9502	0.3406	0.7007
1400–1800 cm^{-1}	0.0697	0.9893	0.1344	0.9596
1800–2200 cm^{-1}	0.1553	0.9455	0.3707	0.6312
2200–2600 cm^{-1}	0.4115	0.5053	0.6200	-0.4656
2600–3000 cm^{-1}	0.0274	0.9983	0.4416	0.4022
3000–3400 cm^{-1}	0.3822	0.5982	0.6566	-0.4786
3400–3996 cm^{-1}	0.4036	0.5327	0.5820	-0.2492

SEC, standard error of calibration; SECV, standard error of cross-validation.

range, are presented in Table IV. Initially, the regression analysis was carried out using the data set from the entire spectrum (653–3996 cm^{-1}) in steps of 1 cm^{-1} , resulting in a 27×3474 matrix, this yielded excellent ($r^2 > 0.99$) calibrations for all three test parameters. Very good cross-validation performances were obtained for the CR angle and nitrogen content CR ($r^2 = 0.947$) and N ($r^2 = 0.927$) (Table IV), however, the r^2 cross-validation value for AB resistance was only moderate at 0.741.

The spectral data set was then divided into eight segments of approximately 400 cm^{-1} wavenumber. Partial least-squares regression analysis was then performed on each of these segments separately, comparing each one in turn with the AB, CR, and N. The results are summarized in Table IV. For AB, the three important spectral regions are revealed, 653–1000 cm^{-1} (r^2 calibration and cross-validation equals to 0.842 and 0.902, respectively), 1400–1800 cm^{-1} (r^2 calibration and cross-validation equal to 0.983 and 0.890, respectively), and 2600–3000 cm^{-1} (r^2 calibration and cross-validation equal to 0.998 and 0.819, respectively). For the CR angle, two important spectral regions were revealed: 653–1000 cm^{-1} (r^2 calibration and cross-validation equal to 0.967 and 0.852, respectively) and 1400–1800 cm^{-1} (r^2 calibration and cross-validation equal to 0.970 and 0.948, respectively). For nitrogen, only one important spectral region was revealed, 1400–1800 cm^{-1} (r^2 calibration and cross-validation equal to 0.989 and 0.960, respectively). The standard error of calibration (SEC) and the standard error of cross-validation (SECV) were also lower for these segments with the exception of AB in the 653–1000 cm^{-1} region where the SEC was high at 4002.

Inspection of the spectra [Fig. 1(a)] revealed that the single peak present in the spectrum for the untreated controls, centered at about 1550 cm^{-1} , was replaced by two peaks in the DMU-treated material at 1498.8 and 1591.4 cm^{-1} , respectively. The minor differences in heights of the peaks obtained from all treatments were caused by the physical geometry of the samples relative to the spectrometer and were not an effect of the treatments. To minimize these variations, the spectra were range-normalized, which involves scaling all samples to a common range. Using the same spectra from the bleached fabric presented in Figure 1(a) and applying range-normalization to the spectra [Fig. 1(b)] improved the visual appearance of the spectra and eased their interpretation. Plotting the absorbance, instead of the

reflectance, against the wavenumber [Fig. 1(c)] revealed that the DMU treatment had given rise to a single new peak at 1557 cm^{-1} , increasing in height with an increased level of DMU. A peak at about 1634 cm^{-1} in the water-treated spectra was slightly shifted toward the higher wavenumbers at about 1651 cm^{-1} in the spectra obtained from the DMU-treated fabric. Good correlation was also observed for FTIR versus CR in the 653–1000- cm^{-1} segment, where no obvious visual difference was observed between the spectra, except for small changes in the gradients.

The regression analysis of the full FTIR spectra versus CR, AB, and N revealed that by the second principal component 91, 87, and 85% of the variances, respectively, were explained. Inspection of the loading plots [Fig. 3(a,c,e)] emphasized the observations of which regions of the spectra were important relative to the particular physical measurements. Both CR and N loading plots revealed that the highest positive loadings occurred at about 1697 cm^{-1} and the greatest negative loadings at about 1524 cm^{-1} . The AB loading plot [Fig. 3(a)] revealed the highest positive value occurring at 1071 cm^{-1} and the lowest negative loading at 1693 cm^{-1} .

Visible and NIR

Calibration statistics for CR, AB resistance, and nitrogen content using the full Vis-NIR spectral range are presented in Table V. Initially, the regression analysis was carried out using the data set from the entire spectrum (400–2498 nm in 2 nm steps, resulting in a 27×1050 matrix). This gave excellent r^2 calibration values (>0.95) for CR, AB, and N. Similarly, good cross-validation performances ($r^2 > 0.9$) were obtained for the three parameters.

The spectral data were then subdivided into five segments of approximately 400 nm wavelength. Regression analysis was then performed on each of these segments separately, comparing each one, in turn, with AB, CR, and N. The results (Table V) revealed a very uniform response across all segments; r^2 calibrations > 0.93 and r^2 cross-validation > 0.8 .

For AB, the r^2 values for calibration and cross-validation were highest (0.990 and 0.939, respectively) in the 1998–2498-nm segment and this region was also associated with the lowest SEC and SECV values. CR revealed the highest r^2 calibration value (0.991) in the visible segment (400–798 nm), which also gives the lowest SEC value (1.97), however, the highest r^2 cross-validation

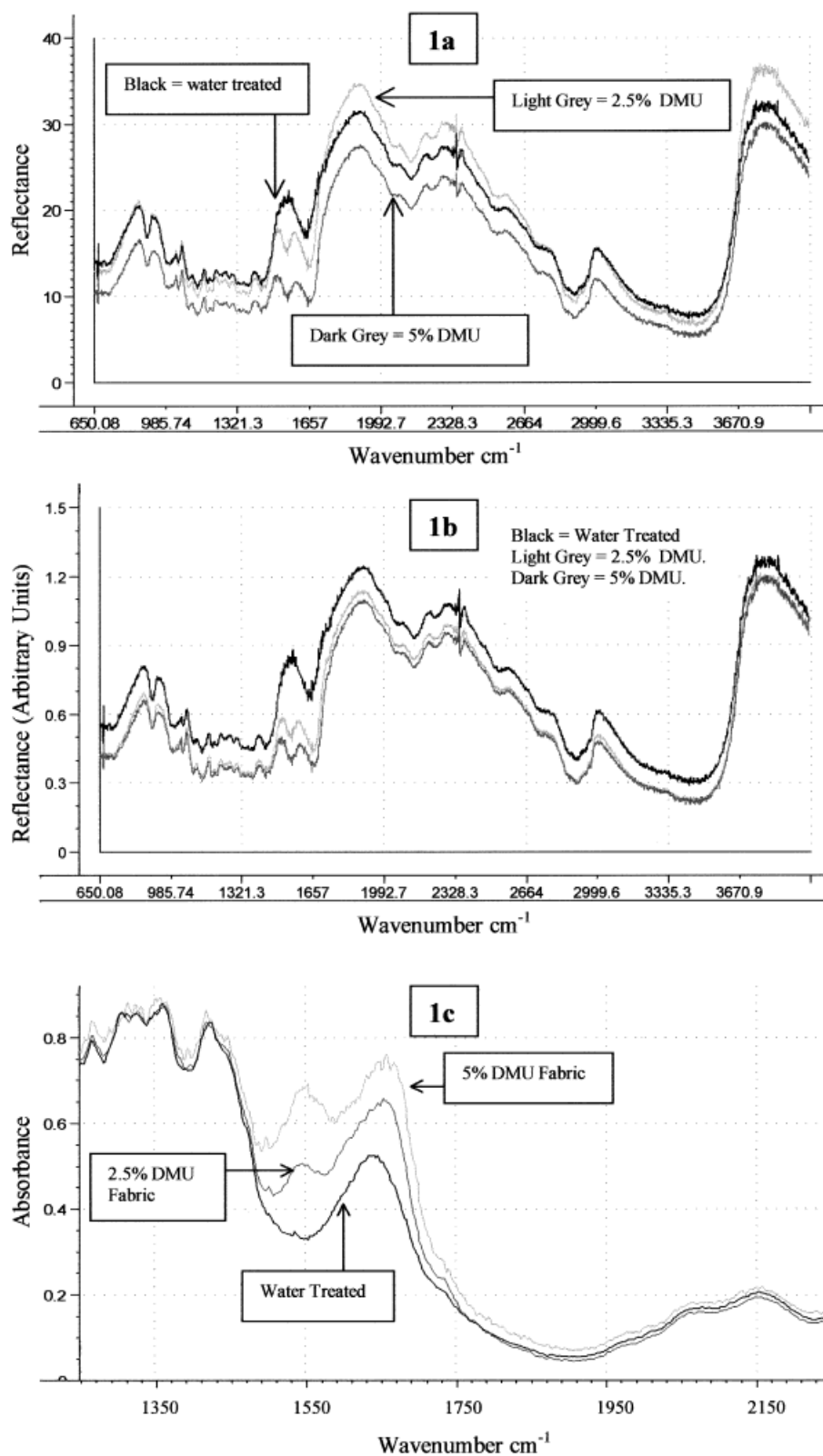


Figure 1 (a) Mean reflectance FTIR spectra for the bleached fabric samples showing differences between the three treatments at the 1550 cm^{-1} in water-treated (black = control) and two peaks at the 1499 and 1591 cm^{-1} in all the DMU-treated (light grey) 2.5% and (dark grey) 5% samples. (b) The same as (a) but with range normalization applied. (c) The active region of the absorbance FTIR spectra.

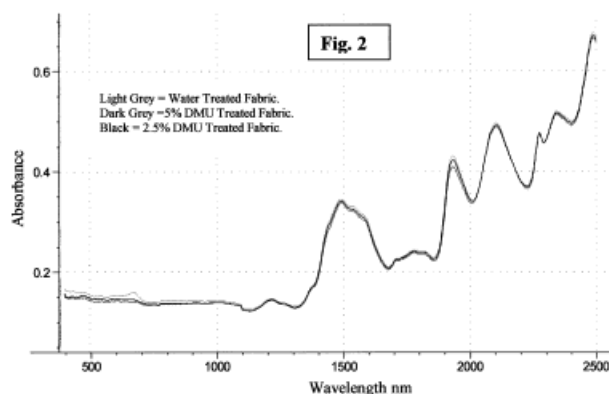


Figure 2 Mean visible and NIR spectra for bleached fabric samples showing the three treatments: (black) water-treated; (dark gray) 5% DMU-treated; (light gray) 2.5% DMU-treated.

tion value (0.967) and the lowest SECV (3.81) value occurred in the 1998–2498 nm segment. The nitrogen data revealed the highest r^2 calibration value (0.992) and the lowest SEC value (0.058) associated with the 781–1198 nm segment. For cross-validation, the highest r^2 value (0.983) and the lowest SECV value (0.087) occurred in the 1998–2498 nm segment.

Visual examination of the Vis-NIR spectra of all the samples revealed slight differences between treatments in the 400–800, 1400–1600, 1900–2000, and 2300–2498 nm spectral regions (Fig. 2). The regression analysis of the full Vis-NIR spectra versus CR, AB, and N revealed that, by the second principal component, 94, 75, and 92% of the variances, respectively, were explained. Inspection of the loading plots [Fig. 3(b,d,f)] emphasized the spectral regions of importance, relative to the particular physical measurements. AB resistance give high positive loadings at about 1430 and 1904 nm, with CR and N both giving large negative values at about 1404 and 1900 nm.

DISCUSSION

FTIR spectroscopy has been used successfully^{10,14,15} to investigate bonding changes associated with polycarboxylic acid treatments of cotton fabrics, as potential replacements for *n*-methylol reagents, because of high formaldehyde emission. No indication was given of any important effects occurring at the 1550 cm^{-1} wavenumber region. The apparent peak splitting in the reflectance against wavenumber plots near this wavenumber

appears to be confined to cellulose treated with DMU, although pure unbound DMU does not exhibit any spectral peaks in this region. Initially, FTIR spectra from the fabrics were acquired using the attenuated total reflectance (ATR) technique, but much better results were obtained using the DRIFT technique. This effect may be due to the difficulty in achieving good fabric samples to diamond contact using ATR. However, the two peaks in the reflectance against wavenumber plots, at about 1498 and 1591 cm^{-1} in all the DMU-treated fabrics, always replaced the single peaks at about 1550 cm^{-1} in the untreated fabrics, and this was still present, apparently undiminished, in samples of fabrics analyzed a year after treatment. Any possible crosslinks caused directly by magnesium chloride, included as a catalyst in the DMU treatments, did not occur since neither magnesium or chlorine peaks were present in the X-ray spectra of the treated fabric; the catalyst appears to be effectively removed during the washing.

It can be envisaged that a DMU molecule can interact with the cellulose chains in one of three ways: First, by the hydroxyl group forming a bond with a cellulose chain with the other hydroxyl group forming a bond with an adjacent cellulose chain, this mechanism would result in the desired crosslinks. Second, one of the hydroxyl groups of a DMU molecule could form a bond with a cellulose chain while the other hydroxyl group remains unattached. Finally, both DMU hydroxyl groups could possibly bond with different cellulose hydroxyl groups on the same chain. In the reflectance-against-wavenumber plots, the replacement of a single peak in the FTIR spectra of the untreated fabric by the two peaks, one at higher energy and one at lower energy in the treated fabric, may offer a technique for studying these reactions. Plotting the absorption against the wavenumber again revealed the same active area of the spectra, 1500–1700 cm^{-1} ; however, these plots can be interpreted, as the DMU treatment produced a new absorption peak at 1557 cm^{-1} which increased in absorption with added DMU. This is consistent with the NH bending vibration.

DMU treatment significantly improves CR in linen relative to untreated linen. Increasing the concentration of DMU improves the CR performance at the expense of reduced resistance to AB. This effect has long been observed for all cellulose^{16,19,20}; however, the dramatic increase in AB resistance obtained at the 2.5% DMU application rate for the scoured and mercerized material illustrates a feature that appears to be peculiar to

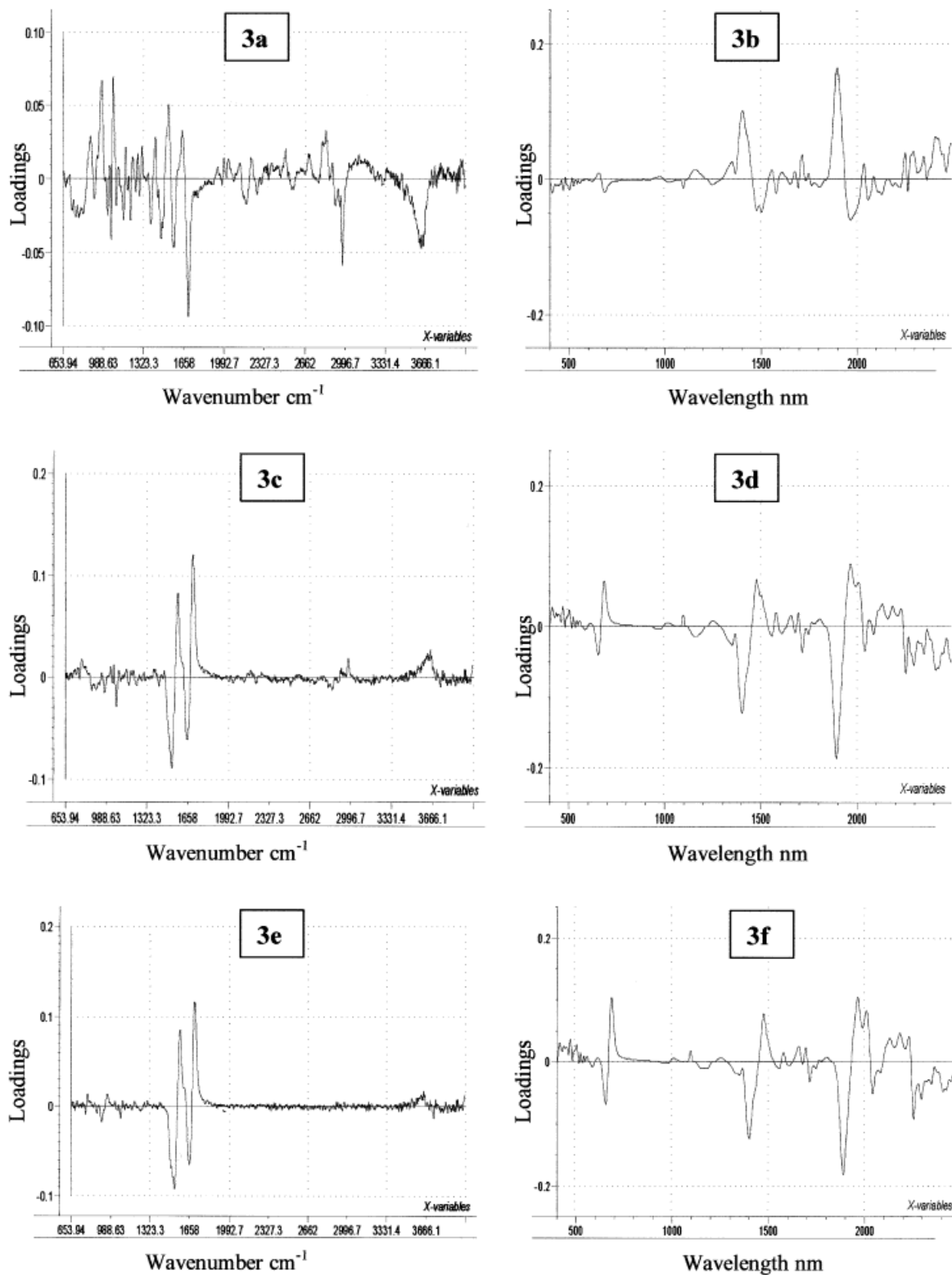


Figure 3 Loading plots: (a) FTIR versus AB; (b) NIR versus AB; (c) FTIR versus CR; (d) NIR versus CR; (e) FTIR versus nitrogen; (f) NIR versus nitrogen.

Table V Calibration Statistics for NIR Spectra (Full or Five Segments) and Their Relationship to CR, AB, and Nitrogen Content of All Fabrics Samples (27) and Mathematical Treatment (144) of the Spectra

Parameter	SEC	r^2 Calibration	SECV	r^2 Validation
AB				
400–2498 nm	2143	0.9831	3122	0.9691
400–798	1363	0.9829	4554	0.8050
798–1198	1278	0.9850	2921	0.9194
1198–1598	2660	0.9334	3326	0.8956
1598–1998	1761	0.9714	2820	0.9252
1998–2498	1062	0.9897	2567	0.9394
CR				
400–2498 nm	2.729	0.9573	3.683	0.9085
400–798	1.974	0.9912	4.210	0.9597
798–1198	2.792	0.9823	4.145	0.9558
1198–1598	3.100	0.9782	3.918	0.9651
1598–1998	3.339	0.9738	3.932	0.9648
1998–2498	3.201	0.9767	3.813	0.9668
Nitrogen				
400–2498	0.0595	0.9918	0.0911	0.9816
400–798	0.0647	0.9907	0.2165	0.9000
798–1198	0.0584	0.9925	0.0987	0.9784
1198–1598	0.0699	0.9892	0.0895	0.9823
1598–1998	0.0714	0.9887	0.0952	0.9800
1998–2498	0.0732	0.9881	0.0870	0.9832

SEC, standard error of calibration; SECV, standard error of cross-validation.

linen. The enhancement of AB resistance by a low concentration of the crosslinking agent was first observed some time ago,^{21,22} but it seems to have had little or no commercial exploitation. It must also be noted that bleaching the material appears to have a major detrimental effect on AB resistance, but, conversely, it gave the best substrate for CR.

Mercerization had a major effect on improving the AB resistance. Of the three fabrics, resistance to AB was in the order mercerized \gg scoured $>$ bleached, with the mercerized samples displaying highly significant performance gains. A consensus of previously published work suggests that mercerization generally yields only moderate improvements in AB resistance,⁴ but performance can be aided by the improved cover (the degree of evenness of yarn spacing), thickness, and weight/m² produced by this process which involves considerable weft shrinkage in linens. Resistance to AB is sensitive to the fabric construction and degree of shrinkage permitted, and as this was derived from work on both traditional yarn- and piece-bleached fabrics and samples from modern rove-bleached origins, it may be concluded that the specific construction employed in

the test fabric is near the optimum for the mercerization response.

Utilizing the entire FTIR spectral data set yielded excellent prediction. Subdividing the spectrum did not improve the correlation, however, it has succeeded in highlighting the most significant region, being 1400–1800 cm⁻¹, common to AB, CR, and N and illustrating that the best correlation values (>0.8) were confined to specific spectral regions. Inspection of the loading vectors confirmed the importance of this spectral region and emphasized the inverse relationship between AB and CR. Splitting the spectra into eight segments revealed, for AB resistance, three spectral regions, with the CR angle correlating well in two spectral regions, while nitrogen revealed good correlation in only one spectral region.

The NIR response gave an apparent relatively uniform response in correlation across all spectral regions and differences in spectral responses to the treatments were difficult to assess visually, only effectively being detected by statistical comparisons. The loading plots emphasized two important regions for AB around 1500 and around 1900 nm, and for CR and nitrogen content, three regions were apparent around 680, 1400, and 1900 nm.

These results suggest that both FTIR and NIR may be useful for rapid assessment of CR and AB resistance in DMU-treated linen and that FTIR may be useful in assessing the bonding changes that are taking place. The standard errors from the spectral techniques were high in comparison with the standard errors produced in the physical and chemical tests.

Neither CR or AB resistances are amenable to elementary explanations. CR performance is principally dependent on the degree of chemical crosslinking and should correlate with specific bonding changes, confined to localized regions of the IR spectrum. However, some contribution from the fabric construction is inevitable, as this influences AB resistance and, to a limited extent, the uncreasing capabilities. The relevant criteria may conflict, as some degree of movement for individual yarns is desirable for crease-shedding ability. An open construction is desirable, while, conversely, resistance to flat AB depends primarily on the purely physical criteria of mass/m² and cover (the degree of evenness of yarn spacing).²³ Complications may arise, however, if the cellulose chain-length values fall below about 1800, as AB resistance has been shown to correlate with the degree of polymerization (DP) over a wide range.²⁴ As a decrease in DP due to the bleaching process is accompanied by the presence of specific chemical end groups, spectral contributions from these may be of significance.

CONCLUSIONS

The results of this study suggest that both spectroscopic techniques would be effective for determining the CR and nitrogen content of fabrics treated with DMU or other nitrogenous crosslinking agents. NIR appears to be the most effective spectroscopic technique for determining AB resistance when assessed using statistical comparison. The most striking features of the FTIR spectra are the distinct changes in the 1500–1700 cm⁻¹ spectral region in all the DMU-treated linen samples in comparison with the water-treated fabrics—hence, a clear artifact of the DMU treatment. This phenomenon does not appear to have been noted in the published literature on cellulose crosslink investigations utilizing FTIR techniques. As the bulk of such data refers to the development of nonnitrogenous agents for cotton, we assign the effect to the presence of chemical bonds involving DMU in flax fibers.

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