

Application of spectroscopy for assessing linen treated with a crease recovery agent

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Introduction

Linen fabric has a tendency to crease easily and retain the creases, particularly in a dry state. Hence the development of a process to improve dry crease recovery, without impairing other fabric characteristics, has been a long-term goal for linen producers, but remains to be satisfactorily resolved.¹⁻⁴ Linen is woven from flax fibres, which are composed of approximately 80% cellulose with the remaining 20% being pectic substances, hemicellulose and lignin.⁵ One of the approaches to developing a crease recovery process has been to attempt to introduce cross-links between individual cellulose chains. A molecule that can achieve this cross-linkage is dimethylol urea (DMU).³ Linen fabrics treated with DMU can exhibit an improvement in crease recovery but often with an undesirable reduction in the fabrics resistance to abrasion.^{2,4}

The techniques for measuring abrasion resistance (AB) and crease recovery (CR) are performed using physical methods. These techniques are slow, destructive and provide no chemical bonding or structural information. They are also not suitable for rapid production line quality control monitoring.⁶

The possibilities of using infrared spectroscopy as techniques for assessing crease recovery angle, abrasion resistance and bonding changes for linen fabrics have been suggested by McCall *et al.* (2001).⁶ The suggestions were based on three different fabric pre-treatments, which were scoured, mercerised and bleached linens, and three DMU treatment rates. The techniques of near infrared (NIR) spectroscopy and Fourier transform infrared spectroscopy were used to produce spectral data which were compared to the physical data of CR, AB and percentage nitrogen (N) using PLS1 regression analysis producing an initial model.

The aims of this study are to attempt to validate this model by using it to predict CR, AB and N on a different set of DMU treated bleached linen. A further aim was to develop a new model using the combined data set. The technique of differential thermogravimetric analysis was also used, the results of which are not included in this report.

Materials and methods

The fabrics were plain weave linens of “blouse” weight (approximately 127 gm⁻²). The original calibration set comprised of scoured, mercerised and bleached linens treated with 5%, 2.5% DMU and water control.⁶

A new test set, comprising of bleached linens only, was prepared in the same way as the calibration set. Samples from the stock fabrics were carefully ruled out following single warp and weft yarns to 21.6×30.5 cm. The dimensions of the samples were selected to fit pin frames that allowed the drying of treated samples under constant tension. These samples were treated with 2%, 4%, 7%, 10% DMU, and water control. The reaction was catalysed using 25% magnesium chloride hexahydrate on the weight of DMU, and the treated fabrics cured at a temperature of between 140°C and 145°C.

These samples were then assessed for Crease Recovery angle (CR) according to British Standard method (BS 3086, 1972) using twelve replicates for each fabric treatment, and the assessment performed under standard conditions (20°C and 65% Relative Humidity).

Abrasion Resistance (AB) was assessed for each treatment using a Martindale Wear and Abrasion Tester Model 103 (J.H. Heal Co, Halifax, UK) according to British Standard No. 5690 (1979). Each treatment was replicated 12 times and the testing performed under standard conditions.

Elemental Analysis for percentage nitrogen (N) was also performed on the samples as detailed by McCall *et al* (2001).⁶ Three replicates for each treatment were analysed.

The FT-IR technique

The FT-IR spectra were obtained using a PerkinElmer Spectrum 1 Fourier transform infrared spectrometer equipped with a 2 mm diamond / ZnSe, single bounce Universal ATR accessory. The samples used were sub-samples taken from the stock treated linens. These sub-samples were cut using scissors to a particle size of about 0.1 mm. Three replicate spectra for each sample were obtained in the range 4000 cm^{-1} to 650 cm^{-1} wavenumber. Four scans were averaged for each spectrum at a resolution of 4.00 cm^{-1} wavenumber. Atmospheric correction was applied. The resultant FT-IR spectra of transmission against wavenumber were transformed to absorbance against wavenumber spectra, baseline corrected and transferred to the multivariate analysis software (Unscrambler version 7.0, Camo Trondheim, Norway) in JCAMP format. The resultant matrix size was 15×3351 , and this was reduced, by averaging the replicates, to a matrix size of 5×3351 . This data was differentiated using the Savitzky–Golay algorithm (first derivative, number of left side points = 4, number of right side points = 4, polynomial order = 2) and analysed by regression (PLS1) with full cross validation against, individually the CR, AB and N data.

The NIR technique:

NIR was performed on a Foss Model 6500, using WINISI 11 software for data capture. All scans were performed in the wavelength range 400–2500 nm on conditioned fabric (20°C and 65% humidity). 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. Averaging reduced the five replicates for each sample to one. The NIR spectra were imported into Unscrambler (Unscrambler version 7.0, Camo Trondheim, Norway) as a 5×1050 matrix, and transformed by derivatives and analysed as for the FT-IR data. Using the original calibration set, models were developed, using PLS1 regression, for FT-IR and NIR spectra relating individually to CR, AB and N. These models were then used to predict the performance of the fabrics from the new bleached only set.

Results

Both FT-IR and NIR gave excellent correlation for the determination of nitrogen, ($R^2 > 0.9$) performance, (Table 1). FT-IR resulted in a better R^2 (0.975) than the NIR technique (0.926). However NIR standard error for prediction (SEP) produced better performance ($SEP = 0.420$) than the FT-IR analysis ($SEP = 0.568$).

With reference to the individual values for the test samples, FT-IR predicting nitrogen gave lower deviation figures than NIR. FT-IR predicted nitrogen values closer to the measured values than the NIR predictions. Both NIR and FT-IR did not predict well at the lowest nitrogen levels, corresponding to the results for the water treated fabric. FT-IR over estimated about five times and NIR under estimated and predicted a negative value.

Table 1. Prediction using regression model of percentage nitrogen in bleached linen treated as noted. SEP = standard error in prediction, DMU = dimethylol urea.

	N (%)	FT-IR $SEP = 0.568$ $R^2 = 0.975$	NIR $SEP = 0.420$ $R^2 = 0.926$
Treatment	Measured	Predicted	Deviation
Water	0.08	0.475	-0.708
2% DMU	0.430	0.713	0.359
4% DMU	1.127	1.207	0.520
7% DMU	1.867	1.454	0.794
10% DMU	2.610	1.631	1.513

Crease recovery angle prediction (Table 2) using FT-IR produced a SEP value of 5 with an excellent correlation performance ($R^2 > 0.9$). However the NIR performance was poorer with a SEP result of 16 and provided a moderate correlation ($R^2 = 0.825$).

With reference to the individual sample performances (Table 2) the FT-IR technique yielded lower deviations than the NIR technique. FT-IR over estimated whilst NIR mostly under estimated and returned a notably poor figure for the water treated fabric (lowest nitrogen).

Table 2. Prediction using regression model of crease recovery angle (CR) in bleached linen treated as noted. SEP = standard error in prediction, DMU = dimethylol urea

	CR (degrees)	FT-IR $SEP = 5$ $R^2 = 0.949$	NIR $SEP = 16$ $R^2 = 0.825$
Treatment	Measured	Predicted	Deviation
Water	24	39	1
2% DMU	36	46	36
4% DMU	53	63	40
7% DMU	60	73	48
10% DMU	54	77	73

Table 3. Prediction using regression model of abrasion resistance (AB) in bleached linen treated as noted. *SEP* = standard error in prediction, DMU = dimethylol urea.

	AB (rubs)	FT-IR <i>SEP</i> = 813 $R^2 = 0.971$	NIR <i>SEP</i> = 2023 $R^2 = 0.800$
Treatment	Measured	Predicted	Deviation
Water	6533	6226	8218
2% DMU	7650	6315	6700
4% DMU	1558	2412	9695
7% DMU	967	157	14180
10% DMU	650	74	11960

The results for predicting abrasion resistance are summarised in Table 3. Once again FT-IR gave lower standard error in prediction ($SEP = 813$) than the NIR technique ($SEP = 2023$). FT-IR produced an excellent result for correlation ($R^2 = 0.971$) whilst NIR only delivered a moderate performance ($R^2 = 0.8$). With reference to the individual treatments, FT-IR under predicted with high deviations notably at the high DMU application rates. NIR over predicted and returned very high deviations for all application rates.

The new test sample set was combined with the original calibration set and a new model was developed using PLS1 regression with full cross-validation. The statistics from this new model are summarised in Table 4.

Table 4. Statistics from the new models to determine N, CR and AB using FT-IR and NIR. These models were developed using the combined data sets. *SEC* = standard errors in calibration and *SECV* = is the standard errors in cross validation.

$n = 14$	<i>SEC</i>	R^2 calibration	<i>SECV</i>	R^2 validation
FT-IR vs N	0.1275	0.986	0.2755	0.932
FT-IR vs CR	2.39	0.987	5.83	0.924
FT-IR vs AB	2711	0.922	3811	0.841
NIR vs N	0.1068	0.990	0.2452	0.948
NIR vs CR	6.98	0.884	11.65	0.662
NIR vs AB	3094	0.893	5150	0.675

With particular reference to the cross validation statistics (Table 4), the FT-IR technique produced excellent validation correlation performance (R^2 greater than 0.9) for N and CR, but only moderate performance in relation to AB ($R^2 = 0.841$). The NIR technique yielded the best validation correlation performance for N ($R^2 = 0.948$) and the lowest standard error in cross validation at 0.2452. However the NIR correlation performance for CR and AB were both poor at 0.662 and 0.675 respectively. Also, for CR and AB, the FT-IR technique returned lower standard errors in cross validation than the NIR technique.

Discussion

In relation to the determination of crease recovery angle and abrasion resistance the FT-IR technique appears to be the more accurate of the two techniques used. However in relation to nitrogen determination the NIR technique was the most accurate.

Neither crease recovery or abrasion resistances are amenable to elementary explanations. Crease-recovery performance is principally dependent on degree of chemical cross-linking and should correlate with specific bonding changes, confined to localised regions of the IR spectrum. However, some contribution from the fabric construction is inevitable, as this influences abrasion resistance and to a limited extent, the un-creasing 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, whilst conversely, resistance to flat abrasion depends primarily on the purely physical criteria of mass/m² and cover (the degree of evenness of yarn spacing).⁶

The model reported above represents only an initial starting point for the development of a good predictive model. This report suggests that given enough samples with different treatments such a model is feasible. The non-destructive nature of infrared spectroscopy coupled with its potentially high speed of analysis could make IR analysis useful for CR and AB applications.

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