Estimation of Nitrogen Content of Resin Finished Fabrics by Infrared Spectroscopy*

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Migration of resin during drying has been found to affect the balance of crease recovery and useful wear life of resin finished fabrics. To understand the phenomenon of resin migration better, fabrics have been crosslinked with DMDHEU by different processes and their physical properties have been studied. In this study, an attempt has been made to characterize the resin finished fabrics from their infrared spectra. The relationships obtained suggest that the nitrogen content of resin finished fabrics can be estimated easily and accurately from their infrared absorption spectra.

In resin finishing, uneven distribution of crosslinks within and around fibre surfaces affects adversely most of the important physical characteristics of the resin finished fabrics, namely crease recovery, tensile strength and wear life. Uneven distribution of resin is believed to arise mainly from the migration of crosslinking agents to the surface during drying after resin impregnation. To understand the phenomenon better, different crosslinking processes, different ways of removing excess water from impregnated fabrics and ways and means of restricting the crosslinks to the interior of the fabrics have been examined critically (Mehta, H. U. private communication). In the present study, the infrared spectroscopic data for DMDHEU treated fabrics have been examined thoroughly to find out whether infrared spectroscopy can be employed to quantitatively assess the resin content of fabrics finished by any process.

Experimental Procedure

Materials — Bleached 100% cotton poplin fabrics (39 s/39 s, 120/62) were employed.

Resin finishing processes — The following processes were employed to crosslink the fabric (Mehta, H. U. private communication):

1. Pad-dry-cure: Fabrics were padded with resin in a resin bath containing dimethylol dihydroxyethylene urea (DMDHEU) and a mixed catalyst [25% magnesium chloride hexahydrate and 10% catalyst DC (Indian Patent 114033) on the weight of solid resin]. The padded fabrics were squeezed to obtain 65-70% wet pick-up, dried at 100°C for 2 min and cured at 150°C for 2 min.

2. Pad-hydroextract-dry-cure: The fabrics padded with resin were hydroextracted to retain 45-50% imbibed liquor, dried at 100°C and cured at 150°C.

3. Pad-flame dry-cure: The resin padded fabrics were squeezed to obtain a wet pick-up of 70%, dried over a flame and cured at 100°C for 2 min.

4. Mild-cure: The fabrics were impregnated with liquor containing DMDHEU and a strongly acidic catalyst, such as hydrochloric acid, squeezed and cured at 60°C without intermediate drying.

5. Wet-cure: The fabrics were batched with DMDHEU and hydrochloric acid or a mixture of HCl and MgCl₂·6H₂O, washed and dried.

6. Core crosslinking: Fabrics crosslinked by the pad-dry-cure process were treated with dilute sulphuric acid dissolved in highly viscous polyvinyl alcohol. The concentration of the acid was varied to remove the surface resin to different extents. All the treated fabrics were given the usual process wash.

Infrared spectra — KBr pellet technique: The KBr spectrum was recorded following the method suggested by O'Connor et al. The untreated as well as the resin treated fabrics were cut in a Wiley mill so as to pass through a 20 mesh wire sieve. A weighed amount of the sample was ground with dry KBr powder and pressed into a disc. The amount of the sample was suitably adjusted in the case of the resin treated fabrics so as to have equal amount of cellulose in all the pellets. The infrared spectra of these samples were recorded with a Perkin Elmer Model 621 spectrophotometer. The differential spectra were obtained by keeping the KBr pellet of the untreated fabric in the reference beam of the spectrometer.

MIR technique — The multiple internal reflection spectra of untreated as well as different resin treated fabrics were obtained using a Wilks accessory (Model 9). A 52.5 x 10 x 1 mm, 45° KRS-5 crystal was used for all the samples.

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*Use of a company or product name by the department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.
The nitrogen content was determined by the Kjeldahl method.

Results
Comparisons of the conventional and differential spectra of untreated and crosslinked cottons are made in Figs. 1–3. Only the portion of the spectrum from 1800 to 1200 cm\(^{-1}\) is shown, because the prominent changes in the spectrum as a result of cross-linking take place in this region.

A comparison of the spectrum of the untreated cellulose (Fig. 1A) with the spectra of the resin treated sample (Figs. 1B and 1C) reveals three additional prominent bands in the spectra of the treated fabrics. Of these, the one at 1700 cm\(^{-1}\) is the most intense band. This band is assigned to the C=O stretching of DMDHEU. The weak band at 1235 cm\(^{-1}\) is assigned to OH deformation and/or CH\(_2\) wagging. On the other hand, the band at about 1470 cm\(^{-1}\) due to CN stretching overlaps the band at 1470 cm\(^{-1}\) due to OH in-plane bending of the unmodified cellulose. It is clear from Fig. 1 that at low add-ons, it is difficult to locate the position of the carbonyl band at 1700 cm\(^{-1}\), and hence, unambiguous identification of the resin becomes difficult. Consequently, for identification as well as quantitative evaluation of the actual resin content, especially at low add-ons, other methods have to be employed. One of the methods employed was to resolve the overlapping bands with the help of a computer.

The conventional IR spectra and the peaks resolved by the computer are presented in Fig. 2. The carbonyl band at 1700 cm\(^{-1}\) and the ratio of the intensity of the band at 1470 cm\(^{-1}\) to that at 1420 cm\(^{-1}\) due to CH\(_2\) bending, help to identify the resin. Further, the computer may be instructed to give the differential spectrum, which is characteristic of the resin alone. Alternatively, the differential spectrum may be directly obtained by placing a KBr pellet containing an equal amount of the untreated cellulose in the reference
beam, as first suggested by McCall et al.\(^2\). The conventional and difference spectra at low as well as high add-ons are presented in Fig. 3. Even at low add-ons, the resin can be identified.

### Discussion

According to Beer-Lambert Law, the absorbance \((A)\) of an infrared band due to a sample of thickness \(b\) and concentration \(c\) is given by

\[
A = \log \frac{I_0}{I} = abc
\]

In this relation, \(I_0\) is the incident intensity; \(I\), the intensity that will pass through the sample; and \(a\), the absorptivity of the band under consideration, is the absorption constant characteristic of the sample.

In the case of resin treated fabrics, the intensity of the bands characteristic of the resin itself, namely the C=O stretching band at 1700 cm\(^{-1}\) and the CN stretching band at 1470 cm\(^{-1}\), can be expected to be governed by the above relationship. Fig. 4 shows the plot of the absorbance of the carbonyl band at 1700 cm\(^{-1}\) as a function of the percentage nitrogen content for a number of fabrics resin treated by different processes. The relationship is linear, with a high degree of correlation. The peak intensity (background corrected transmittance) of the carbonyl stretching band is plotted against the percentage nitrogen content in Fig. 5. In this case, the relationship is curvilinear, with a high degree of correlation.

It has been suggested that the integrated absorption intensity, which is a better measure of the total resin content than the absorbance, should be plotted to partially account for the effect of finite slit width\(^4\), differences in particle size\(^5\), etc. However, even the plot of the total area under the carbonyl stretching band obtained from the linear transmittance versus wave number plots, as a function of nitrogen content, is linear over the entire range (Fig. 6).

To partly account for the variations in scattering arising from the differences in particle size in the KBr pellet, the absorbance of the carbonyl band is compared with that of an internal standard. Fig. 7 shows the relationship between the ratio of the absorbance of the carbonyl band at 1700 cm\(^{-1}\) and that of the CH\(_2\) stretching band at 2900 cm\(^{-1}\), which is taken as the internal standard, and the percentage nitrogen content. This relationship is linear, with a high degree of correlation. Even the ratio of the transmittances of the carbonyl stretching band and CH\(_2\) stretching band at 2900 cm\(^{-1}\) is linearly related to the percentage nitrogen content (Fig. 8). For routine rapid estimation of nitrogen contents of the resin treated fabrics, the approximate relationships involving the peak intensity and ratio of transmittances are more useful, since they involve less calculation, in general. The prediction accuracies of all the four relationships are compared in Table 1, which gives the nitrogen values directly read from the relationships shown in Figs. 4, 5, 7 and 8 as well as the percentage nitrogen values determined by the Kjeldahl method for a set of fabrics resin treated by the pad-dry-cure, skin crosslinking as well as core crosslinking techniques\(^6\). The agreement between the predicted and experimentally determined nitrogen values is satisfactory. Also, the prediction accuracy of the approximate relationships is as high as that of the rigorous relationships. Hence, these approximate relationships, though less sound theoretically, can be employed.
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Fig. 7 — Ratio of the absorbance of the carbonyl band at 1700 cm\(^{-1}\) and the \(\text{CH}_2\) stretching band at 2900 cm\(^{-1}\) vs bound resin content

Fig. 8 — Plot of the ratio of the transmittance of the carbonyl band at 1700 cm\(^{-1}\) to that of the \(\text{CH}_2\) stretching band at 2900 cm\(^{-1}\) against nitrogen content

Fig. 9 — Plot of the transmittance of the CN stretching band at 1470 cm\(^{-1}\) vs nitrogen content

Fig. 10 — Ratio of the intensity of the CN stretching band at 1470 cm\(^{-1}\) to that of the \(\text{CH}_2\) bending band at 1420 cm\(^{-1}\) as a function of nitrogen content

Table 1 — Estimated and Experimentally Determined Nitrogen Contents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrogen content, %</th>
<th>Kjeldahl Peak intensity of 1700 cm(^{-1}) band</th>
<th>(\text{A}_{1700})</th>
<th>(\text{T}_{1700})</th>
<th>(\text{A}_{2900})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pad-dry-cure</td>
<td></td>
<td></td>
<td>0.24</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>do</td>
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<td>0.57</td>
<td>0.57</td>
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<td>do</td>
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<td>0.86</td>
<td>0.88</td>
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<tr>
<td>do</td>
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<td></td>
<td>1.10</td>
<td>1.08</td>
<td>1.16</td>
</tr>
<tr>
<td>Core crosslinked, ethanol rinsing</td>
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<td></td>
<td>0.39</td>
<td>0.36</td>
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<tr>
<td>do</td>
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<td>1.01</td>
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<tr>
<td>do</td>
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<td></td>
<td>1.33</td>
<td>1.36</td>
<td>1.40</td>
</tr>
<tr>
<td>Core crosslinked, (\text{NH}_3) treatment</td>
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<td>0.36</td>
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<td>0.34</td>
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<td>do</td>
<td>0.96</td>
<td></td>
<td>0.94</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Skin crosslinked</td>
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<td>1.42</td>
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</tr>
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</tr>
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<td>1.15</td>
<td>1.16</td>
<td>1.28</td>
</tr>
</tbody>
</table>

1470 cm\(^{-1}\) as obtained from the computer resolved spectrum to that of the \(\text{CH}_2\) bending band at 1420 cm\(^{-1}\), an internal standard, is seen to be linearly related to the percentage nitrogen content (Fig. 10).

The relationship between the \(\text{C=O}\) stretching band intensity (transmittance) obtained from the multiple internal reflection spectra and the nitrogen content is shown in Fig. 11. Though the relationship is linear, there is a considerable amount of scatter, arising from the differences in the distribution of resin near the surface of the fabrics treated by different processes. From the trend of the points lying below the regression line (the points representing the core crosslinked and the pad-hydroextract-cure samples) it appears that the hydroextraction of the resin padded fabrics instead of squeezing and drying, as in the conventional pad-dry-cure process, leads to less resin migration. However, this observation has to be confirmed by other studies.

Thus, several relationships are obtained, which are highly correlated even when the data for fabrics treated with DMDHEU by different processes are pooled together. Any one of the relationships obtained above

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can be employed to estimate the nitrogen content. Further, only a small region of the entire spectrum has to be scanned, and hence, the time required for resin estimation by the IR technique is small in comparison to that required in the Kjeldahl method.

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References