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Spectroscopic studies of the ageing of cellulosic paper

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Abstract

Fourier transform infrared (FTIR) and near-infrared (NIR) spectroscopy have been used to characterise the ageing of cellulosic paper, with the long term aim of developing a technique to assess the condition of paper insulation in electrical transformers. There are differences in the spectra of new and aged materials from different sources, which provide the basis of a “fingerprint” method to categorise papers into different “families”. Measurements of the rate of development of a carbonyl band during ageing in air give an activation energy of 98 kJ/mol for cellulose oxidation. Applying chemometric methods to NIR spectra of aged cellulose gives a correlation of 0.994 between the spectra and time of ageing, with an error of prediction of 95 h for samples up to 3000 h of ageing. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Large electrical transformers are insulated with cellulose-based paper and mineral insulating oil, which also serves to cool the windings. The paper ages under the influence of heat, air and moisture and eventually loses all mechanical integrity, at which point the risk of failure due to damage to the insulation increase dramatically [1]. The cost of an unexpected transformer failure are primarily counted in terms of lost generation/ transmission capacity, which can be more than the cost of the unit itself. The power industry therefore needs tools to measure the aged condition of paper, preferably in situ, in order to determine when to service or replace key units. This paper reports the results of initial experiments to assess the use of infrared spectroscopy to monitor the ageing of cellulose.

Cellulose has been widely studied by Fourier transform infrared (FTIR), and many of the adsorption peaks can be assigned to specific bond vibrations [2]. The use of second derivative spectra sharpens the peaks and makes the assignment easier [3]. Much interest has centred on the effects of crystal structure and crystallinity on the intensity of the peaks, but there is little information in the literature about the effects of ageing of paper. However, the crystallinity might be expected to change, since the amorphous regions degrade more rapidly than the crystalline ones. In addition, oxidation during ageing generates carbonyl and carboxyl ligands in cellulose, which should be visible in the mid infrared, with overtones in the near-infrared (NIR).

Certain peak intensities are reported to change in opposite directions with changes in crystallinity and can therefore be ratioed and used as a crystallinity index. O’Connor et al. [4] used peaks at 690 and 1100 nm, which decrease and increase, respectively, with increasing crystallinity. Nelson and O’Connor [5] later showed that bands at 1430 and 900 cm^{-1} (CH_2 bending and C–O stretching, respectively) are particularly sensitive to changes in crystallinity. Basch et al. [6] used 4760 and 5190 cm^{-1} in the NIR spectrum. Fengel [7] has shown that peaks at 895, 985 and 1165 cm^{-1} increase with decreasing crystallinity, while 1280 and 1430 cm^{-1} bands decrease. The same author has used other peak intensity changes to follow the conversion from cellulose I to cellulose II. Tasker et al. [2] used 1430 and 2900 cm^{-1} to track these changes. Yousef et al. [8] used the ratio of line intensities at 1400 and 900 cm^{-1} to measure crystallinity changes during air ageing of paper in the temperature range 100–200°C. They treated samples for 1 h at eight temperatures between 80 and 220°C. The crystallinity decreased with increasing temperature up to 160°C, and then increased. Unfortunately, it is not clear whether the changes are a result of increased ageing or increased temperature, since only one measurement was made at each temperature.

More recently, NIR–FT Raman and NIR have been used for the non-destructive analysis of natural cotton [9,10], and for the discrimination between cotton cellulose fibres [11,12].

The aim of this study is to investigate the possibility of

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using a variety of vibrational spectroscopic techniques to monitor ageing of cellulose paper, with a view to eventually devising a method for assessing the ageing of cellulosic insulation in electrical power transformers. Both the near- and mid-infrared were used in reflectance mode, because this offers the possibility of eventually making in situ measurements using fibre optic probes. In addition to systemic studies of the effects of ageing, chemometric analysis of NIR spectra of paper insulating material from different sources is used to fingerprint materials types, in order, eventually, to enable the separation of differences in material from changes due to ageing. Some preliminary measurements were made on paper removed from a scrapped transformer, but most of the results reported here came from samples aged in the laboratory under controlled conditions.

2. Experimental

FTIR and NIR spectra of laboratory aged paper samples and insulation samples from a failed transformer were obtained by multiple reflectance techniques. For the NIR a Fosse Electric instrument (Model 6500 NIR spectrometer) was used with an ATR detector. The samples were cut into small strips (approximately $5 \times 20\ \mathrm{mm}^2$) and placed in standard sample cups. Spectra were recorded over the range 300–2500 nm, as the average of 32 scans and the sample was rotated to allow for orientation effects. Mid infrared spectra were measured using a Perkin–Elmer PE2000 FTIR and a single reflectance, high-pressure diamond-windowed ATR cell. All spectra were taken with an average of at least 20 scans.

For FTIR analyses in the carbonyl region of 1600–1700 nm, the samples were dried and exposed to a controlled D_2O atmosphere to replace free H_2O in the paper, which absorbs in the same region, with D_2O.

Effects of ageing on crystallinity were investigated by plotting critical peak ratios against ageing time and changes in the availability of the hydroxyl groups with ageing were measured using rates of derivatisation with trifluoroacetic anhydride (TFAA) and X-ray photoelectron spectroscopy (XPS) to measure fluorine concentrations in the paper.

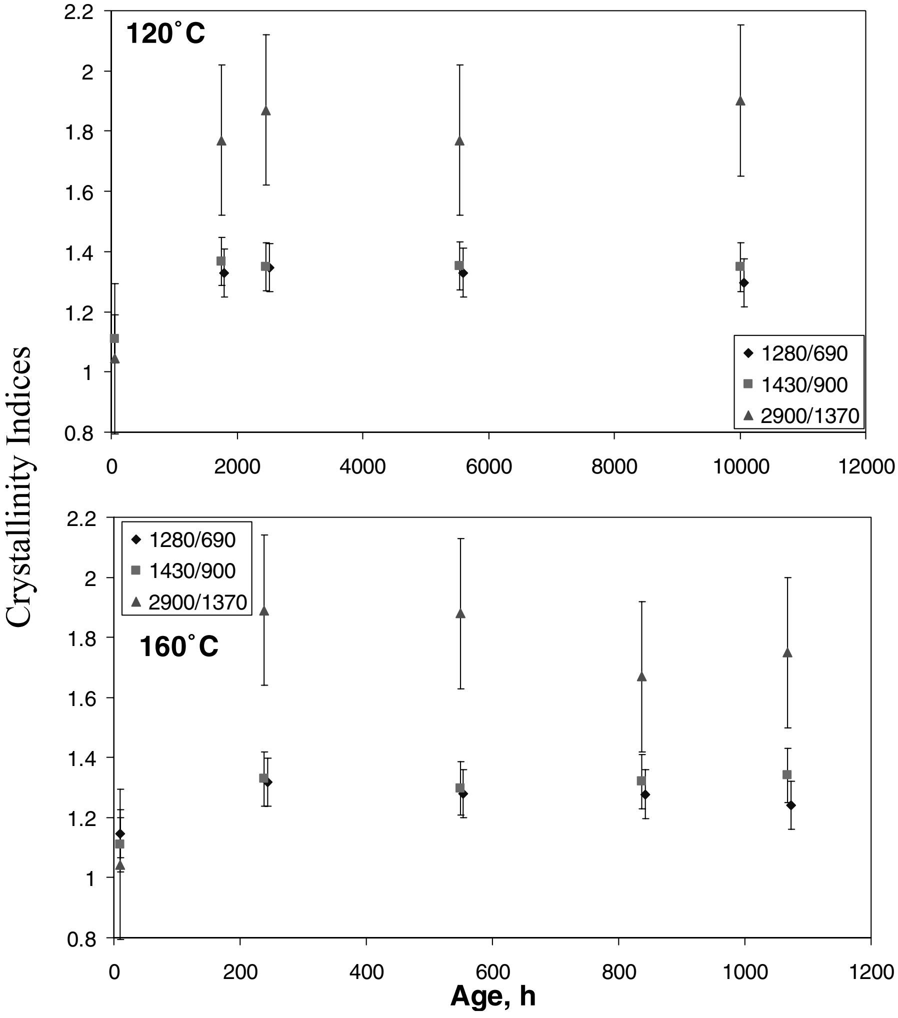

Fig. 1. Crystallinity ratios in aged paper as a function of ageing time.

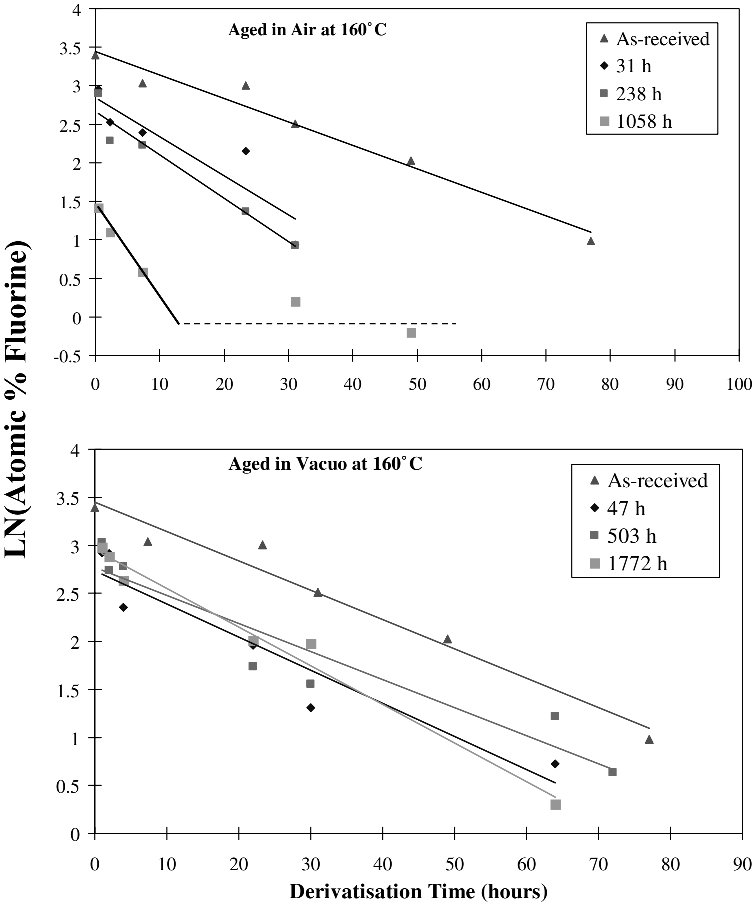

Fig. 2. First-order rates of derivatisation of aged papers from XPS measurements of surface fluorine concentration.

Verlhac et al. [13] and Tasker et al [12] used this technique to show that the ease with which a hydroxyl centre can be derivatised in a cellulosic material is directly dependent upon its crystallinity.

3. Results and discussion

Measurement on papers from the transformer removed from service proved difficult to interpret. The crystallinity appeared to go through a minimum as the degree of polymerisation (DP) decreased, but the errors in the measurement were too large to allow a quantitative interpretation. The appearance of the carbonyl stretching band was, however, clear in the spectra and increased with age. Some variations in absorbance with DP were also found in the near infrared in the region of 1300–2500 nm, which could be interpreted as due to ageing or may be attributed to differences in the base material. The rest of this paper will concentrate on a detailed study of these effects in well-characterised samples aged under controlled laboratory conditions in air and under a mineral insulating oil, starting with characterisation of papers from different sources.

3.1. Characterisation of materials type in the NIR

A variety of cellulose-based materials are available for insulating transformers, ranging from purely cotton based, to purely wood based, to a mixture of the two. In addition, different manufacturers will use different sources of raw material, which means that the precise chemical composition of the insulation can vary widely. A systematic study of a series of Kraft papers was therefore undertaken to establish a method to discriminate between samples from different sources, in order that spectral features due to materials differences can be separated from effects due to ageing. The NIR was chosen as the preferred technique, and standard discrimination techniques were applied [14]. Second derivative spectra were used to remove baseline variations, due to differences in reflectivity, packing and orientation. The spectra were analysed by principal components analysis (PCA), which is a powerful multivariate analysis method which aims to express the variation in the spectral data in as few terms (principal components — PCs) as possible. In this sense it is a maximal data compression scheme. These PCs can then be regressed against the property values, in this case the accelerated age of the sample, to create a predictive model.

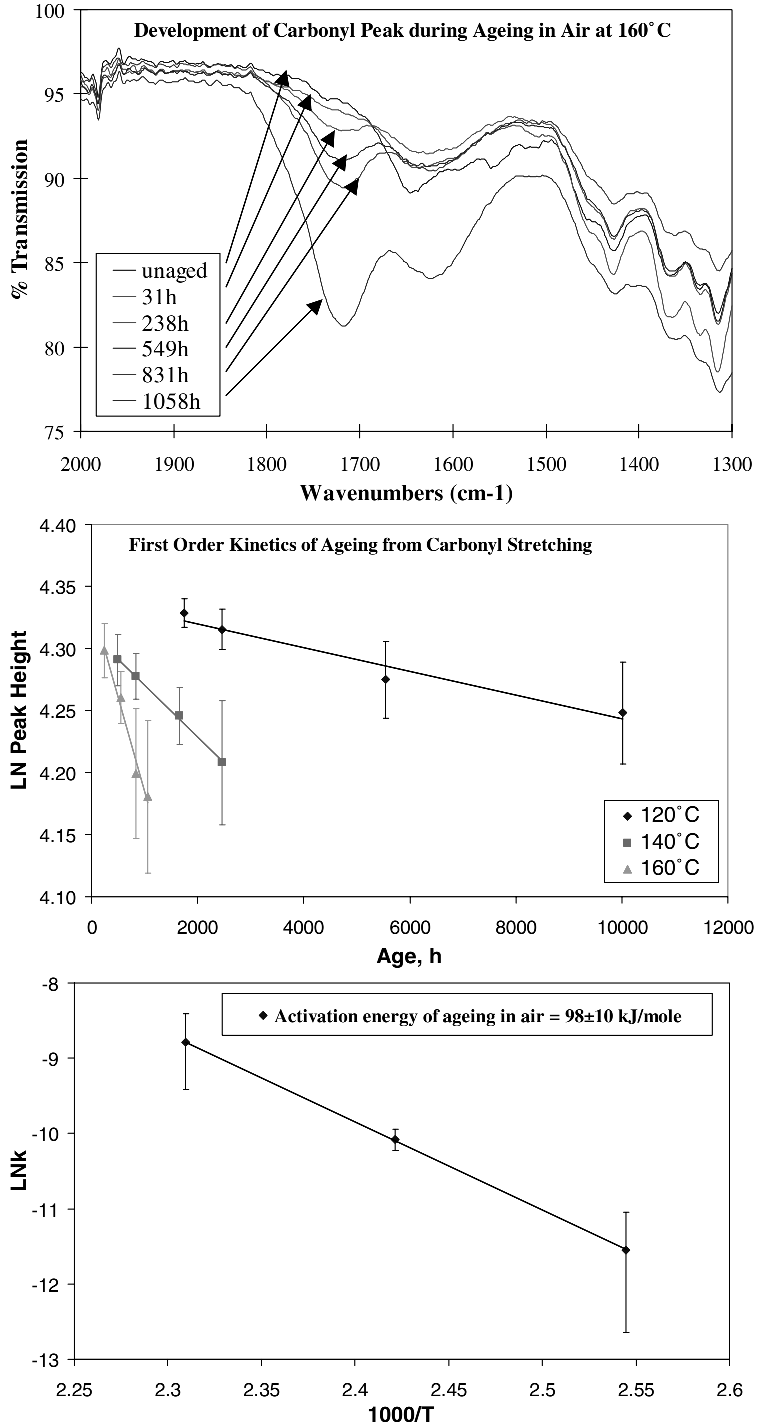

Fig. 3. Development of a carbonyl peak during ageing of paper in air.

The NIR spectra of three repeat samples of nine different papers, supplied by Whiteleys and Tullis Russell Ltd, and containing different levels of wood, cotton and lignin, were used to create a library of standards. Each sample was then tested against the library and the correlation against the standards noted and a perfect correlation was obtained in most cases, which promises the possibility that NIR can distinguish papers from different sources, at least in their as-received state. Samples coloured by blue dye were omitted, because the dye makes the correlation less meaningful. When we compared samples removed from transformers with the library, we identified three samples from one transformer as probably Tullis Russell all-wood paper and another sample from a different transformer as probably Tullis Russell 60% wood/40% manilla. Both assignments are very possible, considering the age of the transformers.

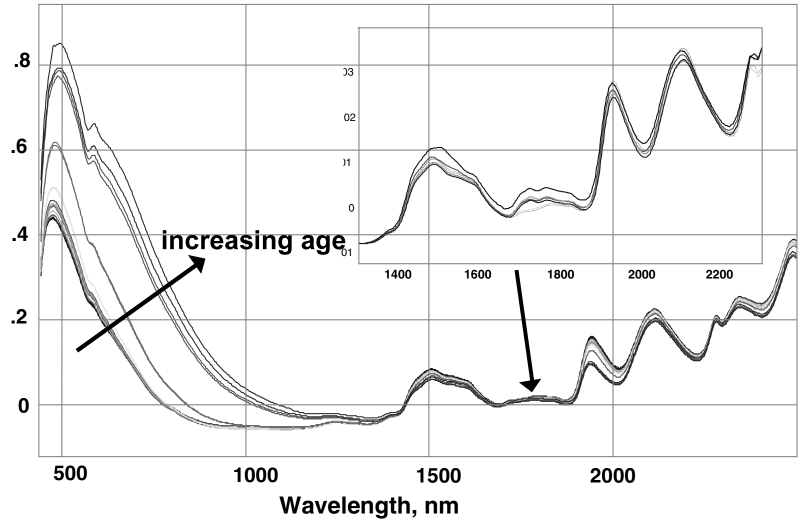

Fig. 4. Development of IR overtones in the NIR.

3.2. Crystallinity changes during ageing

Fig. 1 shows the variation of three of the commonly used crystallinity indices with ageing time at 120 and 160°C. It is clear that the crystallinity of aged paper is higher than that of the as-received material, but the scatter in the data is such that it is not possible to identify any clear trends during extended ageing. However, Fig. 2 clearly shows that the rate of derivatisation of cellulose with TFAA decreases with increasing ageing time, which indicates a steady decline in the concentration of accessible –OH in the paper. It is tempting to interpret this as decreasing crystallinity [2], but a more likely explanation (in view of Fig. 1) is progressive de-hydroxylation as a result of the ageing process.

3.3. Carbonyl/carboxyl peak formation during ageing

Preliminary ageing studies of papers in the laboratory, in air and under transformer oil, showed an increase in absorbance in the FTIR spectrum in the region of 1600–1700 cm^{-1}. However, the changes were masked by sample to sample variation, due to the presence of an O–H stretch from free water in the paper near 1700 cm^{-1}. This peak can be shifted to lower wavelength if the water is replaced by D_2O and the development of the ageing peak at about 1710 cm^{-1} is then be clearly seen, as shown in Fig. 3, for paper aged in air. The intensity of the carboxylic peak near 1600 cm^{-1} also increases with ageing. The actual peak heights vary slightly with position on the surface of the sample, due to local inhomogeneity of the surface of the paper. Fig. 3 also shows the logarithm of the peak heights, averaged over 10 different positions on the surface, as a function of time and temperature of ageing and the Arrhenius relationship of the slopes to reciprocal temperature, from which an apparent activation energy of 98 kJ/mol can be calculated. This is lower than the average value of

Table 1
Assignment of the NIR bands from aged papers (asym., asymmetric; sym., symmetric; str., stretching; def., deformation)

Wavelength (nm)	Assignment
890	C–H stretch third overtone
1220	C–H stretch second overtone, cellulose
1366	2 × C–H str. + C–H deformation, cellulose
1387	Isolated O–H str. first overtone
1440	O–H str. first overtone, cellulose
1489	O–H str. first overtone (intramolecular H-bond), cellulose
1545	O–H str. first overtone (intramolecular H-bond), cellulose
1583	O–H str. first overtone (intramolecular H-bond), cellulose
1703	C–H str. first overtone, cellulose
1793	C–H str. first overtone, cellulose
1811	O–H str. + 2 × C–O str., cellulose
1933	O–H str. + O–H def.
1967	N–H asym. str. + amide II C=O str. second overtone
2000	2 × O–H def. + C–O def. N–H sym. str. + amide II
2057	N–H sym. str. + amide II N–H asym. str. + amide III isolated O–H str. + O–H def.
2108	O–H str. + O–H def. 2 × O–H def. + 2 × C–O str.
2215	Isolated O–H str. + O–H def.
2277	O–H str. + C–C str. C–H str. + C–H def.
2343	C–H str. + C–H def.; C–H def. second overtone, cellulose

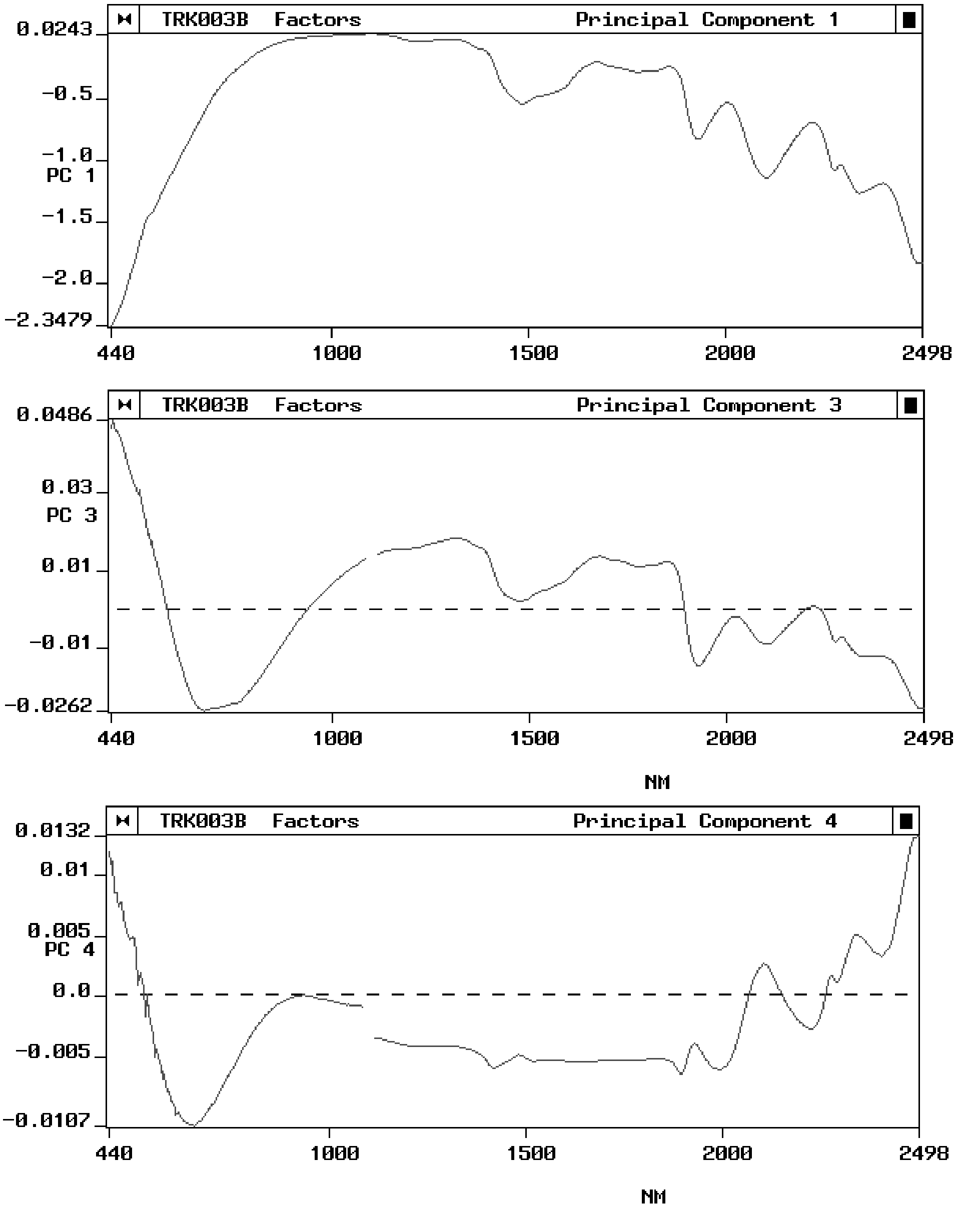

Fig. 5. Three of the principle components of the NIR spectrum of paper.

112 kJ/mol previously reported for the low temperature degradation of cellulose by Emsley and Stevens [1], but other workers have also reported lower values for the oxidation of cellulose in air or oxygen [15,16].

3.4. Correlations with age in the NIR

Fig. 4 shows the NIR and visible spectra of a set of paper samples aged in the laboratory in oil at 140°C, where systematic trends could be observed across the entire range of wavelengths. Water/OH features dominate the NIR spectra, but development of carbonyl/carboxyl overtones can also be seen in the region of 1700–1900 nm. The complex bands around 1500 nm shows water/OH in a variety of chemical environments. The weak band around 1389 nm is attributable to hindered OH species in the cellulose and lignin, whilst the stronger band shows an admixture of bridging OH and free water. Other bands show aromatic C–H and carbonyl functions and possible assignments are given in Table 1. The spectra in the visible range are characteristic of increasing conjugation and unsaturation, associated with loss of water and formation of degradation products.

PCA was carried out on the spectral data with minimal pre-treatment. The low signal-to-noise region between 400 and 440 nm and the detector transition around 1100 nm were removed from the analysis, and all the spectra were treated by an algorithm that corrects for multiple scattering, which was expected from these samples. The analysis,

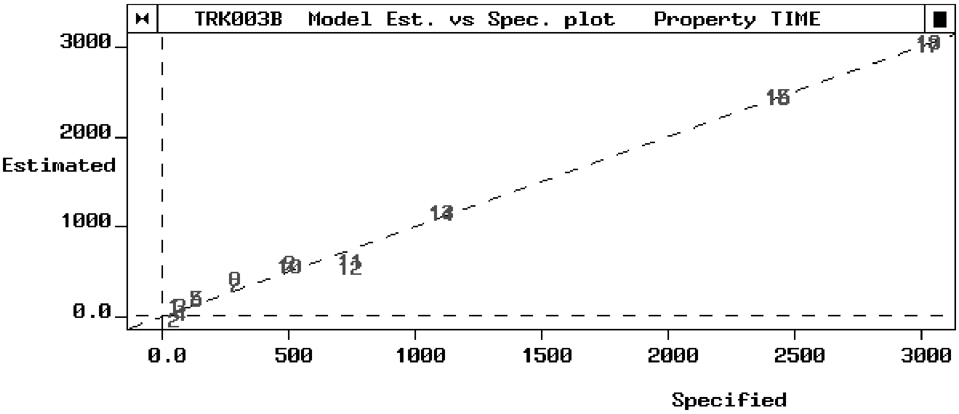

Fig. 6. Estimated versus actual ageing times from chemometric model.

using Perkin–Elmer's Quant + package, extracted three PCs, which modelled 99.4% of the variance, producing a standard error of prediction (SEP) of 95 h (2σ). These components are shown in Fig. 5a–c.

All components have spectra-like characteristics. For instance PC3 (Fig. 5c) shows that a particular part of the broad water band near 1500 nm behaves in a different manner to the rest of the band. This component also shows a distinct C=O band around 1900 nm.

These three components were then regressed against ageing time and the resulting correlation, including some duplicate samples, is shown in Fig. 6, and results in a standard error of validation of 95 h.

4. Conclusions

Vibrational spectroscopy has potential application in the study of cellulosic materials, such as those used as electrical insulation in transformers, in both the near- and mid-infrared regions. Different sources of material can be discriminated, in their as-received state, in the NIR and a carbonyl/carboxyl peak develops in the mid-infrared at ~1710 cm^{-1}, which is characteristic of ageing. Experiments have shown that the application of chemometric models to the NIR spectra can provide a good correlation with age, which could be used to estimate the age of paper in service.

Kinetic measurements from the 1710 cm^{-1} line give an activation energy for ageing in air of 98 kJ/mol, in good agreement with literature values. The use of D_2O to replace absorbed H_2O makes this line more easily visible and increases the accuracy with which it can be measured. Crystallinity indices show an initial increase in crystallinity in the early stages of ageing, but do not change significantly with further ageing. The concentration of accessible –OHs, as indicated by rate of derivatisation by TFAA does however decrease continuously throughout ageing, but it is more likely that the effect is due to de-hydroxylation during ageing than changes in crystallinity.

Acknowledgements

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