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Multivariate analysis of spectra of cyanate ester/bismaleimide blends and correlations with properties

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Abstract

A multivariate approach to the analysis of cured resin blends comprising cyanate ester and bismaleimides is reported. An analysis of samples subjected to accelerated ageing tests by immersion in water at temperatures up to 70 °C shows that simple near infrared spectroscopic measurements on *virgin* materials can predict dynamic mechanical thermal analysis results, and provide correlations with thermogravimetric analysis. This suggests a rapid screening method for a range of materials, perhaps in conjunction with a combinatorial approach to advanced composites manufacture. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Bismaleimides (BMIs) are probably the most important class of thermosetting, addition polyimides currently in use for advanced material applications due to their high performance-to-cost ratio. It is well documented that BMI homopolymers may suffer from brittleness due to the high crosslink density generated during cure, and several approaches have been developed to increase the impact resistance, fatigue resistance and fracture toughness of the cured BMI resins [1].

One such has been the formation of thermoset–thermoset blends when BMIs have been blended with cyanate ester (CE) resins, a more recent arrival to the field of high performance polymers [2], to form bismaleimide-triazine ‘BT’ resin systems [3]. Some work has been carried out to study the thermo-mechanical properties of these resin systems, but to date little published work exists concerning their long-term hydrothermal stability.

The presence of absorbed water can have a devastating effect on the thermo-mechanical properties of some thermoset resins. Consequently, water uptake characteristics (and T_g values) are of great interest for high performance applications such as aircraft primary structures. In a previous paper [4], various spectroscopies (infrared, Raman and near infrared (NIR)) together with thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA) were carried out on a range of virgin CE/BMI blends and ‘aged’ blends (having undergone immersion in water at several different temperatures). Although qualitative arguments were used in the analysis, quantitative links between spectra and properties were not discussed. This short paper aims to show how the application of statistical methods, known collectively as chemometrics, can extract data from large data sets, and provide predictive models for material quality assurance and control.

Principal components analysis (PCA) is used to reduce the rather complex data set to a small number of principal components (PCs) that span the entire variance of the data set. This technique uses the complete data set, and makes no prior assumptions about the importance of the various features. These are then regressed against the measured properties, such as thermo-mechanical and compositional, and the regression coefficients show which NIR bands, and hence molecular moieties, contribute to these properties. This approach is also very robust to errors in the measurement of the properties.

2. Experimental

The resin blends comprised two commercially available materials: one, a low molecular weight (30% reacted) prepolymer of bisphenol A dicyanate, DCBA; the other, a

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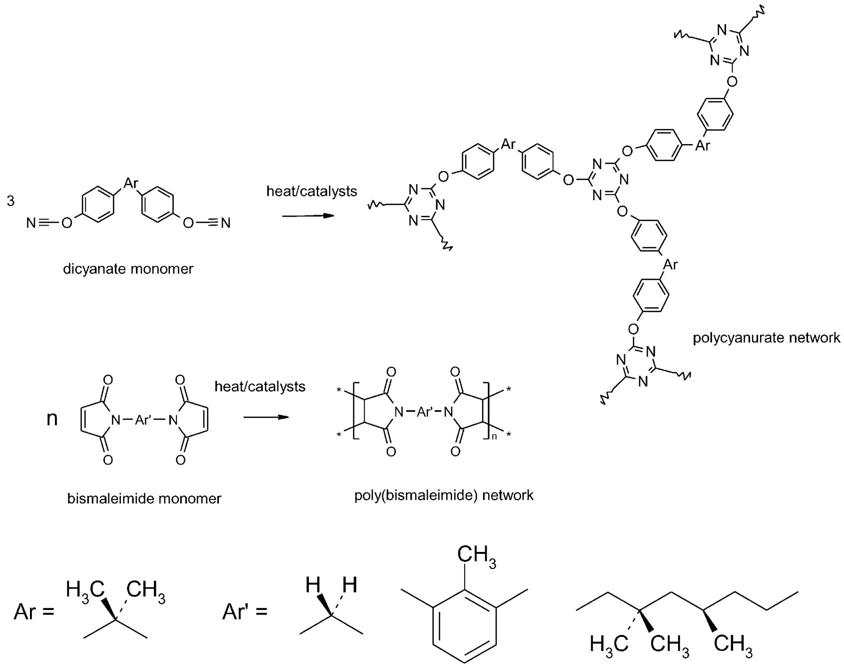

Fig. 1. Simplified reaction schemes for the independent polymerisation of dicyanate and bismaleimide monomers.

low melting point blend of three BMI components. The latter comprised bis(4-maleimidophenyl)methane, 2,4-bismaleimidotoluene and 1,6′-bismaleimido-2,2,4-trimethyl hexane blended in an approximate ratio of 55:30:15 and is designated 'BMI' in the rest of this work. All sample blends were catalysed with copper(II) naphthenate (300 ppm Cu^{2+} by weight) and 4 parts per hundred parts resin (phr) nonylphenol (Fig. 1) [4].

By way of example, NIR diffuse reflectance spectra were run on powdered virgin samples using a diffuse reflectance accessory in the sample chamber of a PE System 2000 FT-NIR spectrometer. Spectra were run between 2700 and 10 000 cm^{-1}, with 4 cm^{-1} resolution, and 32 scans were co-added to improve the signal-to-noise ratio. This region was chosen as it is amenable to remote analysis using long fibre optic probes. The materials' spectra were trimmed to

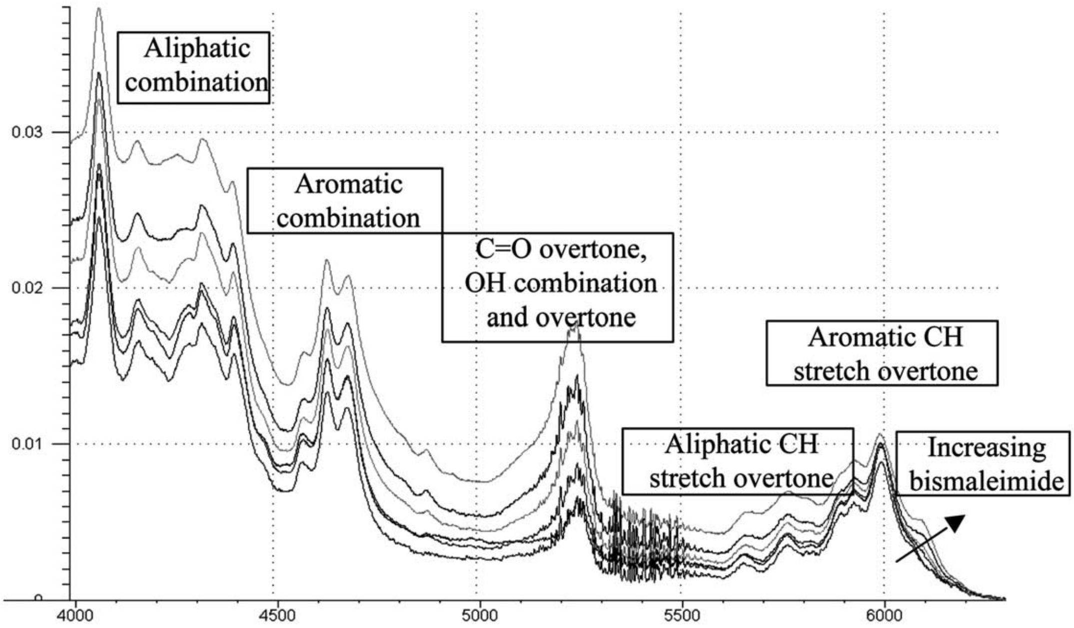

Fig. 2. NIR spectra of virgin samples showing the combination and overtone region between 4000 and 6300 cm^{-1}. Spectra were 'normalised' to the integrated aromatic C–H overtone-stretching peaks between 5820 and 6215 cm^{-1}.

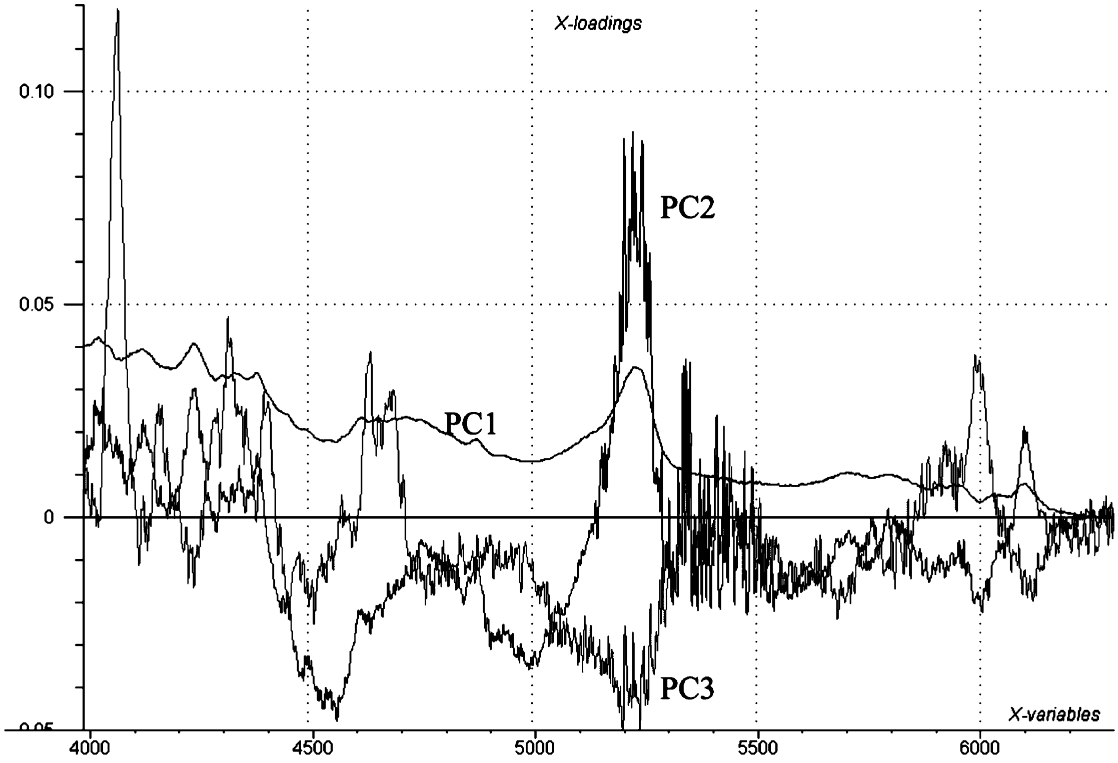

Fig. 3. Plot of PC1 to 3, which describe 99.97% of the variance in the spectral data.

only include the first combination and overtone regions, between 4000 and 6300 cm^{-1}, baselined at 6300 cm^{-1} and then normalised to the integrated aromatic C–H stretching band overtone between 5820 and 6215 cm^{-1}, on the assumption that the overall aromatic concentration remained unchanged. These are shown superimposed in Fig. 2, and initially appear quite similar, apart from the overlapped C=O overtone, OH combination and overtone bands near 5220 cm^{-1} [5].

Both virgin and fully aged samples were analysed in duplicates, providing 24 spectra. The mean-centred data were then subjected to principal components' regression (PCR—Camo, Unscambler v7.5) [6]. PCR is particularly robust with respect to errors in the target variable or property data.

Using cross-validation, the model requires just three PCs to describe 99.97% of the variance in the spectral data, and these are shown in Fig. 3. An examination of Fig. 3 shows PC2 is dominated by the carbonyl moiety, the band near 5230 cm^{-1} being attributed to the overtone of C=O, and to a combination of C–O and O–H stretching vibrations, while PC3 has strong bonded and isolated hydroxyl features.

Table 1
Weight gain data for aged samples. 'Outer' and 'inner' refer to the significantly different surfaces in 50DCBA–50BMI on ageing [4]

Sample	4.9×10^5 s$^{1/2}$ m^{-1} at 50 °C		1.5×10^6 s$^{1/2}$ m^{-1} at 50 °C		2.5×10^6 s$^{1/2}$ m^{-1} at 50 °C	
	Measured	Predicted	Measured	Predicted	Measured	Predicted
100DCBA	1.80	1.82	2.10	2.13	2.30	2.48
100DCBA	1.80	1.79	2.10	2.09	2.30	2.41
90DCBA–10BMI	1.92	1.92	2.20	2.22	2.73	2.64
90DCBA–10BMI	1.92	1.85	2.20	2.16	2.73	2.55
80DCBA–20BMI	2.05	2.14	2.40	2.43	2.97	2.94
80DCBA–20BMI	2.05	2.25	2.40	2.54	2.97	3.12
65DCBA–35BMI	2.34	2.43	2.65	2.71	3.28	3.35
65DCBA–35BMI	2.34	2.41	2.65	2.70	3.28	3.43
50DCBA–50BMI (outer)	2.55	2.48	2.80	2.76	3.48	3.42
50DCBA–50BMI (inner)	2.55	2.46	2.80	2.73	3.48	3.37
50DCBA–50BMI (inner)	2.55	2.58	2.80	2.85	3.48	3.58
50DCBA–50BMI (outer)	2.55	2.29	2.80	2.59	3.48	3.21
Error (2σ)		0.24		0.18		0.30

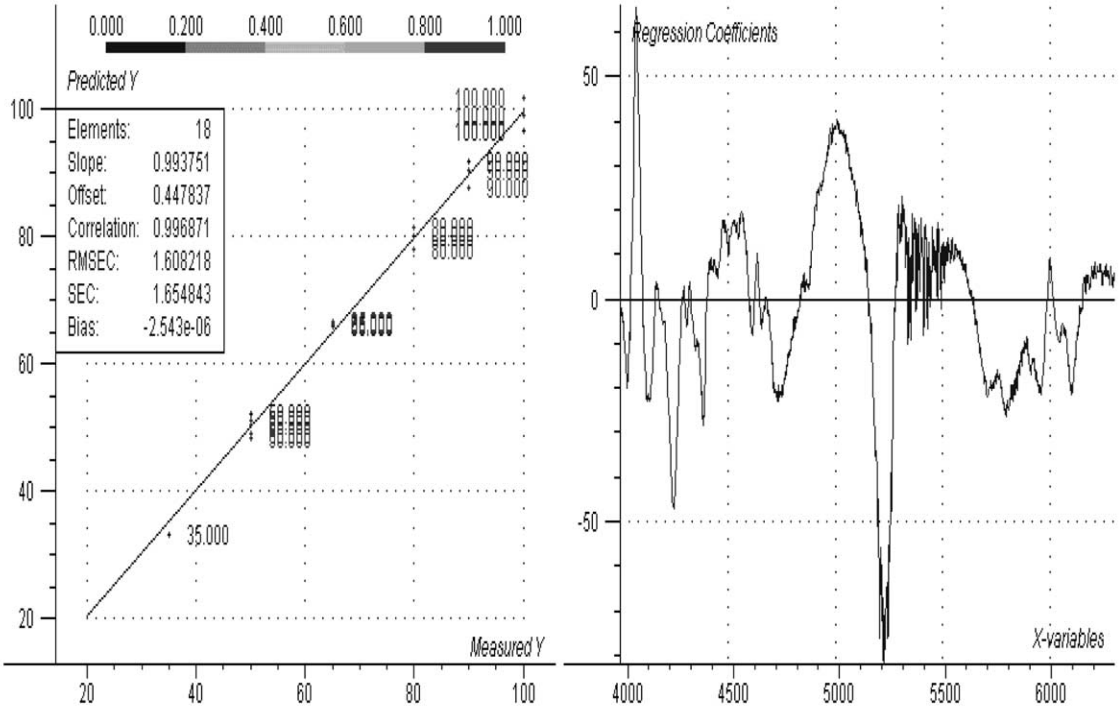

Fig. 4. Prediction of sample cyanate concentration, and the corresponding regression coefficient (a linear combination of the three PCs shown in Fig. 3).

The later components also show discrimination between various forms of aromatic substitution, as seen in the complex of bands between 4500 and 4800 cm^{-1}, and around 6000 cm^{-1}, which correspond to combination and overtone bands of the aromatic C–H stretch, respectively. What really matters is that the PCs show that some bands are in anti-phase to others. This can allow for the direct correlation of physical properties and degradation pathways with molecular functionalities.

To verify the normalisation routine, these PCs were regressed against the composition data, and resulted in the prediction shown in Fig. 4, giving an error of prediction for cyanate concentration less than 1.6%. The regression coefficient shows bands that decrease with increasing cyanate concentration as negative, and all these can be attributed to BMI. This suggests that the normalisation and baselining assumptions are not introducing errors. These same PCs are then used for further regressions against other properties of the samples.

2.1. Regression of NIR spectra against moisture absorption of the resin blends

The water absorption data of Ref. [4] were used. Three points on each curve, at 490 000, 1 470 000 and 2 450 000 $\mathrm{s}^{1/2}\,\mathrm{m}^{-1}$, normalised to thickness, were chosen to describe the data for the individual samples. Fickean type behaviour shows as a straight line with these units.

A simple inspection of the spectra, Fig. 2, shows that the

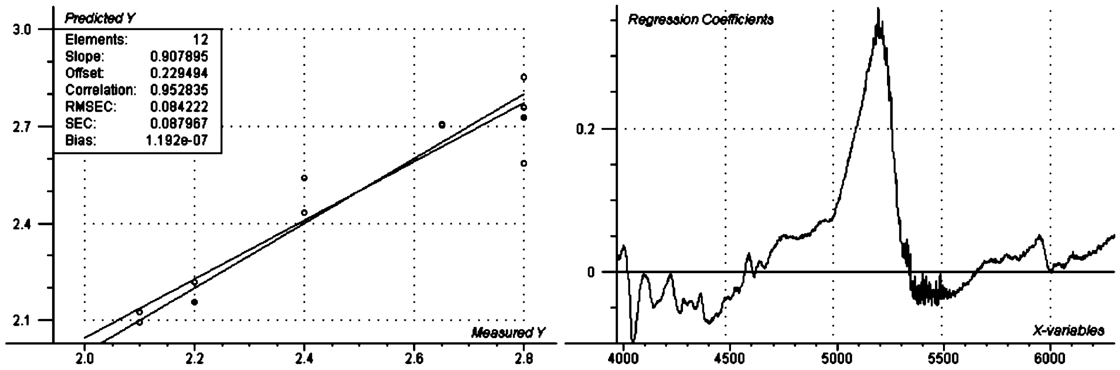

Fig. 5. Predicted water uptake (wt%) for samples at the reduced time of $1.47 \times 10^{6}\ \mathrm{s}^{1/2}\,\mathrm{m}^{-1}$ at 50 °C, and the corresponding regression coefficient.

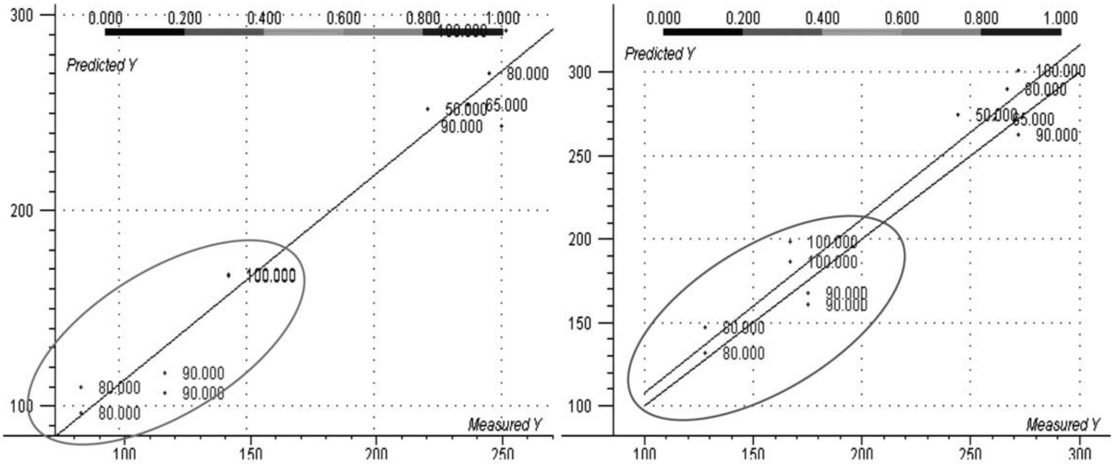

Fig. 6. Predicted versus actual log $E''_{\max}$ (left), and tan δ (right), with samples labelled by cyanate concentration.

overlapped C=O overtone, OH combination and overtone band would appear to be a good measure of the water content. Using the PCs obtained from the virgin and fully aged samples only, the water uptake at various intermediate points can be predicted. The results for samples aged at 50 °C are seen in Table 1. Fig. 5 shows the graphical results at a reduced time of $1.47 \times 10^6\ \mathrm{s}^{1/2}\ \mathrm{m}^{-1}$, together with the regression coefficient, which is dominated by the C=O and OH contribution—the correlation coefficient of better than 0.95 is quite acceptable for such a simple model.

Interestingly, by making a model using only the virgin samples, predictions of water uptake with a similar precision are possible. This will be the subject of a fuller treatment. Again, the regression coefficient is dominated by the C=O and OH contribution. This makes clear that increased water uptake correlates with increasing maleimide content.

2.2. Regression of NIR spectra against DMTA results

The same PCs shown in Fig. 3 were regressed against the

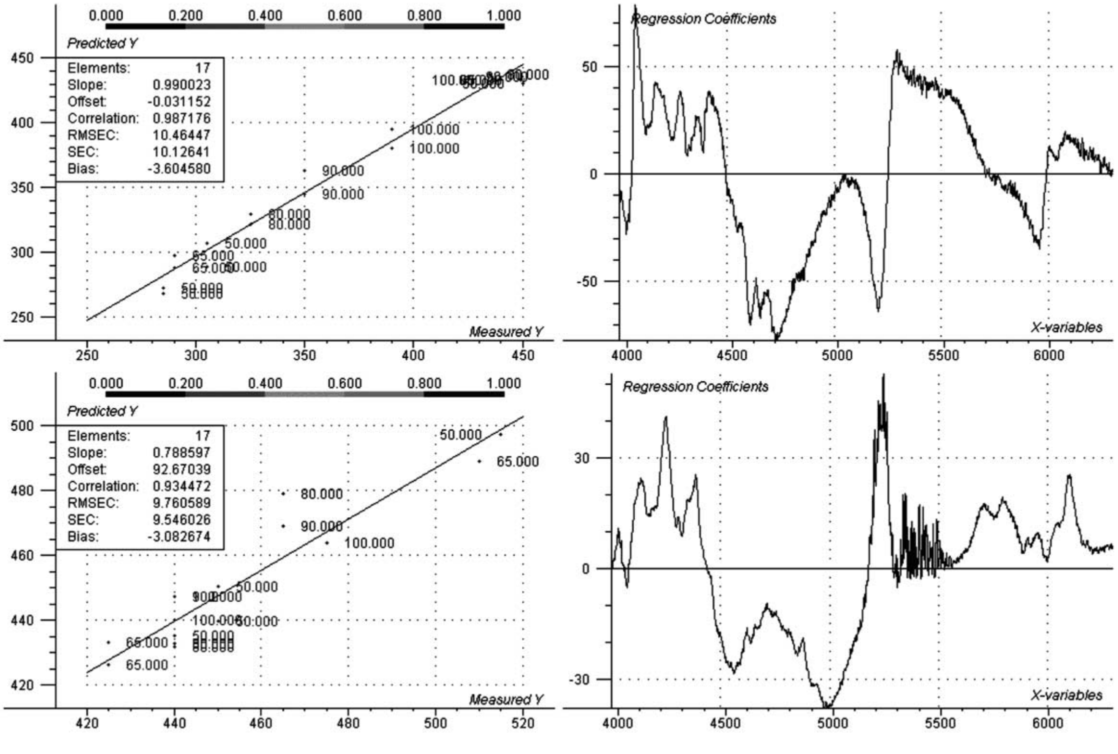

Fig. 7. Predicted versus measured for 20 and 40% weight loss, labelled by cyanate concentration, and their corresponding regression coefficients.

log $E''_{\max}$ and tan $\delta_{\max}$ values [4, Table 5], and the results are shown in Fig. 6. The regression coefficients are very similar for these two properties, with just a few minor differences near 4420 and 4790 cm^{-1}, which are tentatively attributed to the combinations O–H stretch + O–H deformation.

2.3. Regression of NIR spectra against TGA results

The model is good at predicting low weight loss in the materials, and the fit with 20% data [4, Table 4] is shown in Fig. 7. All these share a similar regression function, heavily dominated by the BMI spectrum. For the 40% and greater data, the regression function is very different, and the correlation coefficient for both the 60 and 80% is poor.

Since the model increasingly fails at these higher weight losses, this strongly suggests that the mechanism of water loss changes around the temperature required for 40% weight loss, and the changes above this temperature are less dependent on the initial composition.

3. Conclusions

The combination of a spectroscopic approach with statistical analysis provides a spectral model, which has been used to investigate correlations with material properties. To prove the pre-processing algorithms, the model was tested on virgin and aged sample composition. Hydroxyl and carbonyl features heavily dominate the regression factor, though aromatic and aliphatic combination bands also contributed strongly.

This approach was then successful at providing correlations with water uptake at two different temperatures, using either fully aged or virgin materials as the basis of the model. This suggests that a simple spectroscopic analysis may provide predictive information on material behaviour in these conditions.

The same model was used to show that interpretable correlations for results from DMTA and TGA were possible, and that it should be possible to interpret these results in terms of particular molecular groupings. This suggests a rapid screening method for a range of materials, perhaps in conjunction with a combinatorial approach to advanced composites manufacture.

Work continues in the form of a long-term ageing study of similar, and modified, CE/BMI blends in order to elucidate the nature of the degradation process.

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