NEW DIAGNOSTIC METHOD FOR THE DETERMINATION OF TEMPERATURE AND TIME OF THERMAL AGEING IN GENERATOR STATOR INSULATION

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Abstract: Classically, the analysis of thermally aged epoxy impregnated materials with conventional techniques is particularly difficult. This paper demonstrates methods, based on wide-wavelength reflectance spectroscopy, that provide good predictions of the exposure time at a known temperature over a wide range of temperatures. Further, using a time-temperature (t – T) superposition function based on first-order kinetics it is possible to rationalize the widely different temperatures and exposure times examined in the study - this occurs from the varying sensitivity to different molecular species and degradation products over the very wide spectral range examined. These calibrations are constructed using multivariate statistical analyses of the wide–wavelength spectral behaviour. One of the outputs is a spectral fit coefficient that shows which chemical components are correlated with the cumulative ageing metric, and so gives insight into the composition under expected conditions of use. As the analysis methods can be applied *in-situ*, are non-destructive and can be applied rapidly, it is possible to spatially map the degree of thermally accumulated ageing in the insulation material.

1 INTRODUCTION

The measurement and prediction of the durability and residual lifetime of polymers and polymer composites, especially at higher service temperatures, is a major problem both in research and application. In order to characterize the durability of polymers, it is common practice to follow some important properties with time within the temperature range of interest, until a certain preselected limit is attained [1]. Although reliable data are obtained, the method is tedious and requires lots of experiments. In addition, these data are only valid for the actual temperature under consideration and cannot be transformed to other service temperatures.

If these important properties could be linked directly to molecular processes, this unsatisfactory situation could be overcome [2]. If the kinetics of thermal degradation could be obtained, the data could be transformed over the whole temperature range and the temperature-dependent service lifetime calculated from these data.

Thermal ageing of polymers results from molecular degradation as a result of overheating. At high temperatures the components of the polymer begin to separate (molecular scission) and react with one another to change the properties of the polymer and present an upper limit to the service temperature of epoxies. Unless prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation manifest in physical and optical property changes relative to the initial properties. Thermal and oxidative degradation generally involves changes to the molecular weight and chemistry of the polymer, and typical property changes include reduced ductility and embrittlement, chalking, colour changes, cracking, and a general reduction in most other desirable physical properties.

A simple way follow the degradation of a thermoset polymer network is through measurement of the glass transition temperature Tg. Since at high degrees of cure the glass temperature is primarily governed by the crosslink density, the influence of the end groups is small. In addition, the Tg is one of the most important properties of the polymer, because it usually determines the upper limit of the service temperature.

Electrical machines use a variety of insulating media in their construction. The epoxy glass mat EPGM 203 is one of a family of rigid laminates fabricated according to IEC 60893 (2004). According to the standard, the combination of epoxy resin on a glass mat substrate provides high mechanical strength at elevated temperature, and the electrical properties are stable under high humidity conditions.

We have explored the use of a hyperspectral (wide-wavelength) analyzer to provide rapid quality assessment of these materials as used in the manufacturing and operation of electrical generators.

2 METHOD

Spectroscopic data in the ultra violet (UV, less than 400 nm), visible (400 to 750 nm), near infrared (NIR, 750 to 2500 nm) and infrared (IR, greater than 2500 nm) spectral ranges contain information on the constituent chemistry of the materials. These wavelengths have different penetration depths: we estimate that in the NIR region the analysis depth can be up to 4 mm - so this sampling technique is not confined to just the surface. In addition a method based on the wavelength range from 350 to 2500 nm can be made portable and hence useful in research, production and service applications.

The thermal and oxidative degradation of epoxy resins is thought to proceed by firstly breaking, detaching, or oxidizing some of the OH, -CH2, -CH3, OC=O, and C-O-C molecular groups, and thereafter the carbonization and oxidation of aromatic rings.

The absorptions observed in the NIR region relate to overtones and combinations of molecular vibrations of specific functional groups (e.g. C-H, C=C, O-H, C=O etc.) that are present. These match precisely those moieties that are affected by the epoxy degradation. The absorptions in the UV and visible region provide additional "colour" derived from electronic transitions in the material that relate to degradation products.

Conventional spectroscopic techniques as commonly applied are limited in such analyses because narrow spectral band information is normally used in isolation. Common typical analyses concentrate on identifying and assigning individual bands observed, and then to use simple methods to look at ratios of band areas, heights and widths. Multivariate spectroscopic analysis (MVSA) techniques use all the spectral information available and enable the extraction of relevant information by regression of the spectral data against the property data of interest. Examining the correlations of spectral features with various properties provides a means of assigning a chemical interpretation to these properties. If regression models for a large range of "calibration" samples can be produced, these can serve as a robust predictive model for similar samples – and provide a means of non-destructive measurement of these properties.

The validation process typically uses a subset of "test" sample data that were left out of the modelling process, and applies the model to them to estimate the property values. Providing the model is successfully validated, it can be used to predict property values for subsequent new data.

3 METHOD AND SAMPLES

The wide-wavelength TranSpec diffuse reflectance analyzer was used to examine the sample reflectance over wavelength range from 350 to 2500 nm at a resolution of 8 nm. Forty scans were co-added to improve signal-to-noise, resulting in a measurement time of 4 seconds.

A number of laboratory aged samples of EPGM 203 had been subject to thermal oxidative degradation over a range of temperatures between 100 and 200 °C, for exposure times up to 28 days. 63 spectra were captured, and some of these are shown in Figure 1.

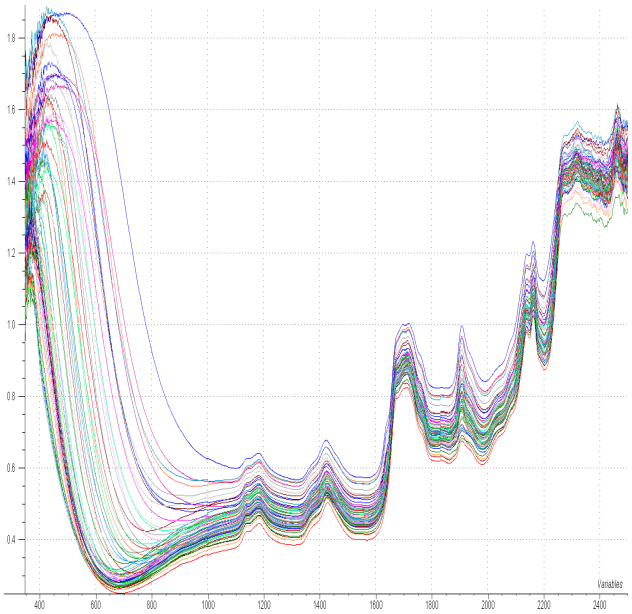


Figure 1: Spectral Data of Aged EPGM 203 following normalisation to the 1st overtone of CH stretch.

Because the data are obtained from diffuse reflectance and the depth of penetration can be colour and hence degree of degradation dependent, the spectra were normalized to the 1st CH stretch overtone band around 1700 nm.

4 RESULTS

All the observed spectral bands can be assigned to the insulation.

Table 1. Spectral Bands seen in the Sample Set.

Band / cm^{-1}	Band / nm	Component	Assignment
8749	1143	resin	C-H str 2nd overtone (CH3)
8396	1191	resin	C-H str 2nd overtone (CH3)
8258	1211	resin	C-H str 2nd overtone

			(CH2). OH combination
6105	1638	resin	=CH2 1st overtone
5970	1675	resin	Aromatic C-H stretching 1st overtone
5784	1729	resin	C-H str first overtone (CH2)
5679	1761	resin	C-H str 1st overtone (CH2)
5249	1905	resin	C=O str. 2nd overtone
5128	1950	resin	Combination O-H str. + O-H def.; C=O str. 2nd overtone
4812	2078	resin	Combination C=O str. 1st overtone +CH bend
4669	2142	resin	Aromatic combination band; Combination of C-H str. + C=C
4619	2165	resin	Aromatic combination band
4554	2196	mica	Combination of OH str. + OH def.
4448	2248	resin	Combination of OH str. + OH def.
4342	2303	resin	Combination bands of aliphatic methyl group
4255	2350	resin	Combination CH str. + =CH2 def.; C-H def. 2nd overtone

Of immediate note in Figure 1 is the strong and changing colour information at wavelengths shorter than 1100nm and the large variance in the strength of the C=O and OH bands between 1900 and 1950 nm.

Although this sample set has not yet had the Tg measured, a MVSA calibration for samples aged at one temperature shows a particularly simple relationship.

Figure 2 shows the relationship between length of exposure to 160 C, and the time predicted from the calibration.

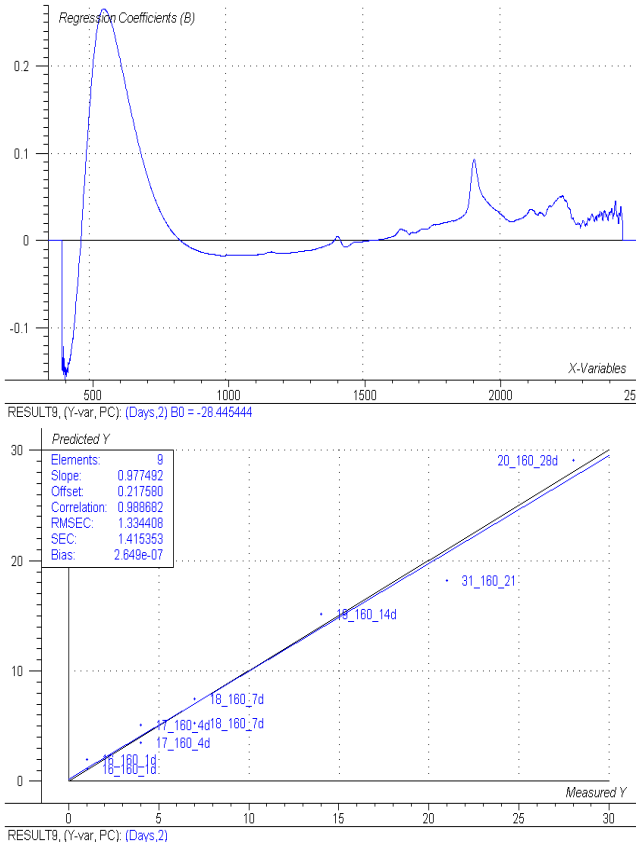


Figure 2: MVSA Calibration for Ageing at a Single Temperature – 160 °C.

The regression coefficient in Figure 2 describes the correlated molecular changes going on in this system. There is a loss of UV-absorbing molecules, seen in the negative "band below 500 nm, and a corresponding increase in the longer wavelength band around 570 nm. This corresponds to the well-known darkening of the epoxy as it darkens, but this method provides a quantitative measure of that, as well as providing an estimate of the aromatization and increasing oxidation of the samples. This is reinforced by the pronounced C=O structure around 1900nm. Thus this demonstrates that if the temperature is known, an exposure time can readily be predicted from the spectral data. The spectral data is simply multiplied point-by-point by the regression coefficient and the results summed to directly predict the exposure time.

The calibration at 100 °C is equally informative, as seen in Figure 3.

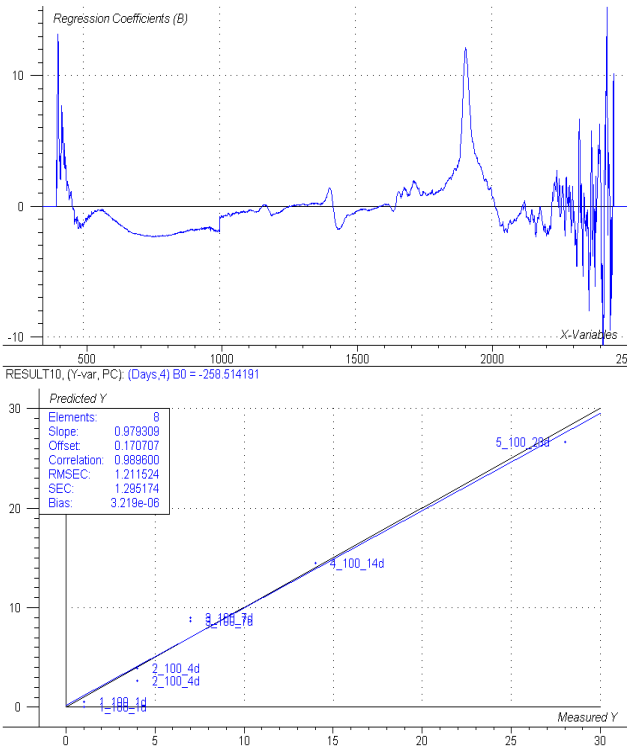


Figure 3: MVSA Calibration for Ageing at a Single Temperature – 100 °C.

Here there is little colour change but a significant increase in the C=O concentration.

A simple Principal Component Analysis (PCA) of all the time-temperature data shows a clear clustering at each ageing temperature – Figure 4.

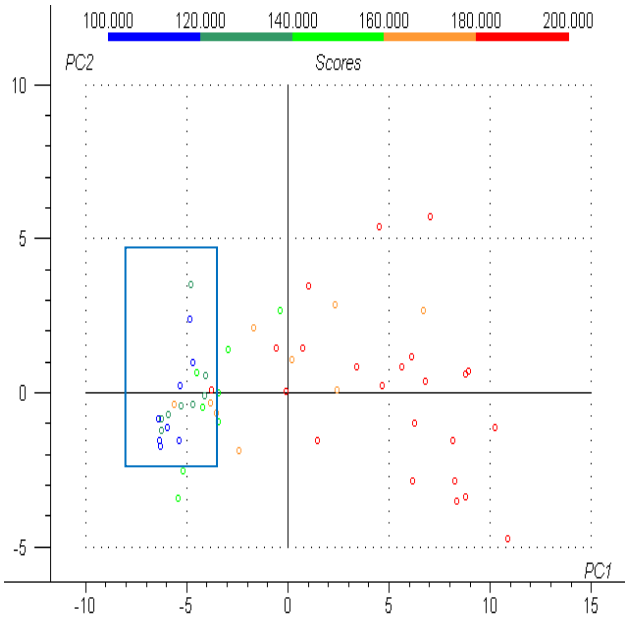


Figure 4: MVSA calibration for Time-Temperature Superposition Prediction showing the regression coefficient and the prediction of the ageing.

This figure shows the reduction of each spectrum to a point in Principal Component space, with its position determined solely by how different that spectrum is from the mean. Thus all the spectra accumulated between 100 and 120 °C as shown in the rectangle, cluster at the left of the Figure, irrespective of the length of exposure, whilst samples at higher temperatures are found to the right.

Examination of the literature on thermal degradation suggests that time-temperature "master" curves for first order reactions can be generated [3]. The following relationship is a useful starting point:

(a+temperature/K)*(b+log(time/days)) (1)

where a and b are constants.

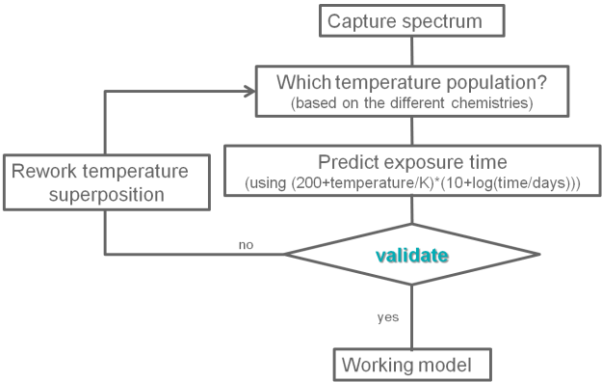
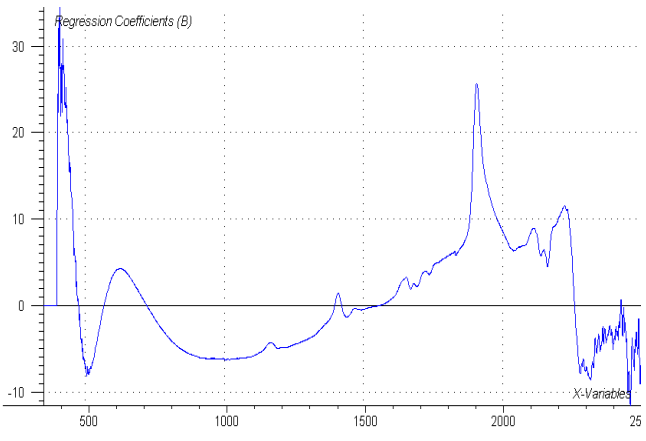


Figure 5: MVSA calibration for Time-Temperature Superposition Prediction showing the regression coefficient and the prediction of the ageing metric.

Using a semi-empirical approach, as outlined in Figure 5, we determined that the cumulative ageing metric represented by the function

(200+temperature/K)*(10+log(time/days)) (2)

generally fulfils this requirement for the EPGM 203 data set as demonstrated by the prediction of the ageing metric seen in Figure 6.



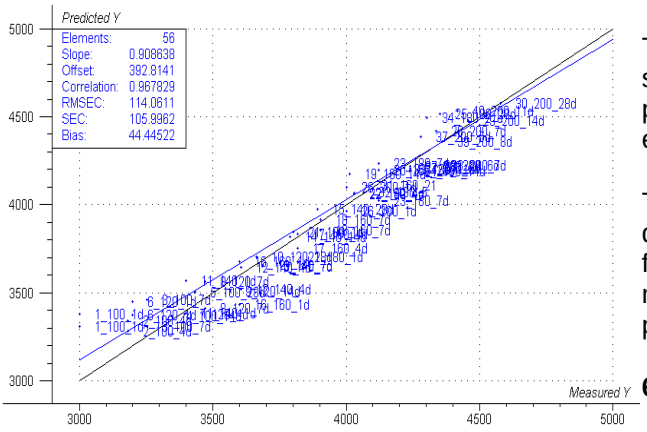


Figure 6: MVSA calibration for Time-Temperature Superposition Prediction showing the regression coefficient (above) and the prediction of the ageing metric.

As previously discussed, the dominant factor in the regression coefficient is the intensity of the C=O feature, modulated by changes in the sample colour.

5 CONCLUSION

We have shown that with some minimal material preparation, a wide-wavelength spectroscopic diffuse reflectance probe method appears to be capable of making a very useful contribution to the understanding and quality assessment of the electrical insulation materials used in electrical machines. Using multivariate statistical analysis of the acquired spectral data to identify relationships within the samples allows for predictions that relate simple spectral measurements to insulation properties. This can be done in the factory as well as in the laboratory and the rapid nature of the measurements (typically less than 5 to 10 seconds) provides an efficient method of local measurement including spatial mapping.

We have demonstrated that this method is capable of a rapid and simple analysis of EPGM 203 epoxy filled insulation, and, by extension, we anticipate its application to other similar materials.

Predictive models constructed from the spectral data provide excellent independent predictions of exposure temperature and time, and the regression coefficients associated with these models provide strong pointers to the chemical changes related to ageing.

Modelling thermal degradation at a single temperature was successful. This indicates that if the temperature is known, the prediction of exposure time should be reasonably precise.

The more general use of a time-temperature superposition model has also been successful, in particular for higher values of thermal stress and exposure time.

This approach suggests that using hyper-spectral data for predicting temperature and exposure time for epoxy filled insulation system is possible and it may be possible to extend this approach to other polymer and composite materials.

6 REFERENCES

[1] E. S. W. Kong, S. M. Lee, H. G. Nelson, Polym Comp 1982, 3, 29.

[2] H. Stultz, “Lifetime Assessment of Epoxies by the Kinetics of Thermal Degradation”, J. Appl. Polymer Sci., 9, 1881-1886 (2004)

[3] M. Ekelund, H. Edin, U.W. Gedde, Polymer Degradation and Stability 92 (2007) 617-629M. Hinow, W. Hauschild, E.Gockenbach: “Lightning Impulse Voltage and Overshoot Evaluation Proposed in Drafts of IEC 60060-1 and Future UHV Testing”, IEEE TDEI, Vol. 17, No. 5, pp. 1628- 1634, 2010