Nanodielectrics for use in HVDC power systems and their structure-property relationships using Chemometric methods

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ABSTRACT

This paper deals with the development of new thermoset based nanocomposite electrical insulation materials for HVDC power transmission applications. A wide range of insulation properties were determined and some are discussed. With sufficient understanding of these properties, their trade-offs and process requirements, it is possible to obtain balanced materials for specific use in improved HVAC or HVDC components. It has been demonstrated that the application of multivariate statistical analysis (MVSA) methods can establish relationships between key properties and molecular information obtained spectroscopically. It was found that the electrical properties of a material are heavily dependent on the chemistry of the materials system and its degree of curing with particular factors responsible for the greatest improvement in electrical properties, such as electrical breakdown strength.

Keywords: Nanodielectric, FTIR, HVDC, chemometrics, surface functionalisation

1 INTRODUCTION

There is a need to develop materials with controlled electrical resistivity, reduced space charge accumulation, higher thermal conductivity, higher dielectric strength, enhanced voltage endurance and surface discharging erosion resistance to cope with DC stresses in high voltage direct current (HVDC) transmission systems in addition to supporting HVAC requirements. If the balance of properties, performance and process requirements are achieved, this may lead to HVDC insulation systems and equipment having a reduced footprint, larger power densities, and greater multi-stress resilience with longer service lifetimes.

This paper deals with the development and process scaling of new thermoset based nanocomposite electrical insulation materials for HVDC power transmission applications based on epoxide functionalized nanosilica and boron nitride based composites.

A number of hgh purity resin systems were investigated and compared to a benchmark resin used in the conventional manufacture of HV components in the power sector. Functionalized nanofillers were then added to the resin systems at filler loading levels ranging from 0.5 wt.% to 10% wt and dispersed via planetary mixing. Key candidates investigated include untreated nano boron nitride and both treated and untreated nano silica. A challenge in producing dielectric nanocomposites is the tendency of the filler material to aggregate when mixed with the matrix polymer and obtaining good interfacial bonding. To overcome these challenges surface functionalized nanosilica was also investigated. Although several were investigated key candidates for the chemical functionalization of nano particles include epoxide terminated (3-glycidyloxypropyl)trimethoxysilane and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, both of which showed superior dispersion characteristics (as shown in Figure 1) and enhanced electrical breakdown (Figure 2) and thermal properties.

Some of the results, such as increased electrical breakdown strength, reduced electrical conductivity for reactively surface functionalized nanosilica, increased thermal conductivity for nano boron nitride, and their significance in regard to the wider application of these electrical insulation materials are discussed. With sufficient understanding of these properties, their trade-offs, and process requirements it is possible to obtain balanced materials for specific use in HVAC or HVDC components.

To provide material development support and quality assurance, use was made of FTIR and NIR spectroscopy in conjunction with MVSA. This paper also demonstrates the potential of MVSA methods to determine structure-property relationships central to establishing materials design and process rules. Further, with additional factored measurements linked to specific process conditions it will be possible to expand the knowledge base to include structure-process-property relationships and use these in process optimization leading to process design rules. The potential exists to obtain quantitative metrics, but this would require more extensive work in the acquisition of full data sets regarding property measurements. The careful consideration of all property measurements is required when developing a new material for use in HV applications, be they HVDC or HVAC. With full and balanced consideration of nanofiller type, loading reactive surface treatment and the application of MVSA modelling to confirm property relationships to these controllable factors, optimized materials can be produced.

Achieving this will be of immense benefit to power equipment manufacturers and network operators that use this equipment, particularly in the context of renewable generation integration.

2 CHEMOMETRIC MODELING

Mathematically we examine the statistical variance of spectral information across a defined set of materials with known characteristics. The variance between spectra can relate to both chemical and physical changes, such as the cross-link density, degree of reaction, glass transition temperature or state of oxidation. Using this technique, a series of analytical results are generated for a set of control samples, which are then mathematically processed using well-established algorithms like principal component analysis (PCA). The purpose of the PCA algorithm is to express the variation within the dataset in the simplest terms. Calibration models such as partial least squares (PLS) and multiple linear regression (MLR) are calculated for the property values to generate a principal component regression (PCR) model. These models are then used to establish a relationships between the principal components and the chemical characteristic or physical property being measured.

3 EXPERIMENTAL

Initally a number of high purity resin systems were investigated and compared to a benchmark resin, used in conventional manufacture of HV components in the power sector. Due to viscosity issues, this was later reduced to one high purity system for detailed assesment as a matrix resin. The high purity BADGE epoxy resin araldite CY1300 (Huntsman), anhydride hardener Aradur A-917 (Huntsman), and catalyst 1-methylidiazole (Sigma Aldrich) were combined in the weight ratio of 100:85:1 and subjected to high shear mixing at 4000 rpm for 20 min. The combined resin was then subjected to a low vacuum at 60^{O}C for a further 20 min to remove any gas from the sample. The resin was poured into stainless steel moulds and subjected to the following curing regime in a fan oven: isotherm at 80^{O}C for 2 h, ramp at 1^{O}C min^{-1} to 120^{O}C, isotherm at 120^{O}C for 2 h, before leaving to cool to room temperature and releasing from moulds. Before testing, all samples were subjected to postcuring at 160^{O}C under a medium vacuum for 1 h.

Functionalized nanofillers were then added to the resin system at filler loading levels ranging from 0.5% wt to 10% wt and dispersed via planetary mixing. Key candidates investigated include untreated nano boron nitride and both treated and untreated nano silica. Surface functionalisation was undertaken to aid compatibility and dispersion and influence interfacial bonding. Several epoxide terminated surface functionalization treatments were investigated. Treatment 2 (T2 Silica) and 3 (T3 Silica) showed superior dispersion characteristics (as shown in figure 1) and Treatment 1 (T1 Silica) showed enhanced electrical breakdown (figure 2) and thermal properties (table 1) [1, 2].

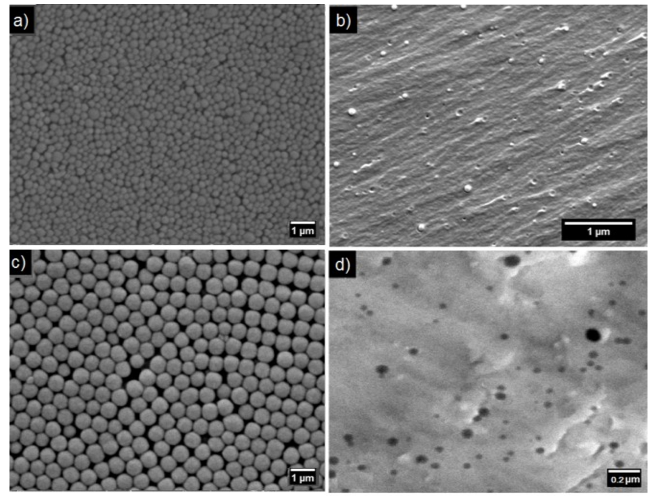

Figure 1. SEM and TEM images showing achieved dispersion of nanocomposite dielectrics in this study a) and c) show the particles prior to dispersion and images b) and d) after dispersion into the resin.

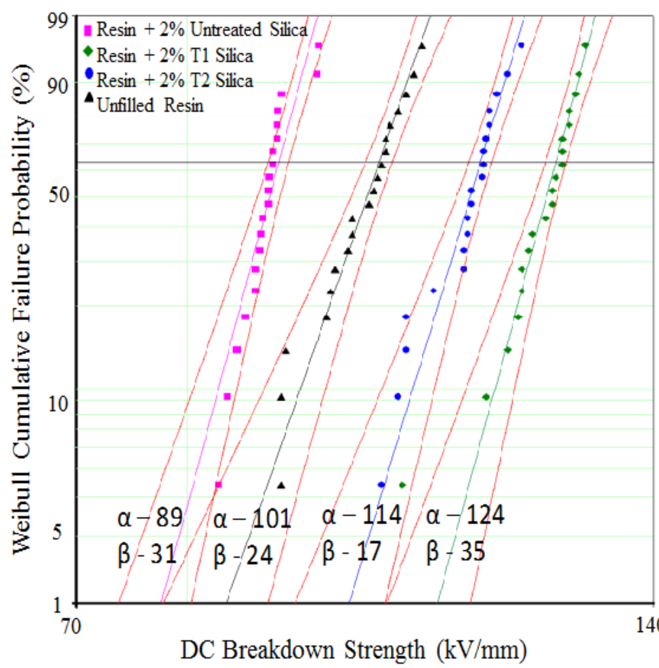

Figure 2. Weibull plot showing increased breakdown strength of the 2 wt. % composites and reference epoxy

Table 1. Summary table of Electrical breakdown and glass transition temperature values for resin containing surface treated Nano silica

Filler	Filler %	E_b (kV/mm)	T_g (°C)
Unfilled Resin		87.9	141
T1 Silica	2	124.8	132
T2 Silica	2	114.1	**128**
T3 Silica	2	114.1	143
Untreated Silica	2	89.4	143

An Agilent Cary 660 FTIR spectrometer with diamond ATR was used for infrared spectroscopic measurements between 400 and 4000 cm^{-1}. Spectral chemometric analysis on all spectral data was performed using Gnosys Transchem^{TM} software.

All FTIR spectral data was subjected to a Savitsky-Golay smoothing algorithm with a polynomial order of 3, and were normalised such that the peak area of the C-H stretch peaks between 2800 and 3000 cm^{-1} were equal. The spectral regions between 600 and 700, 2000 and 2600, 3800 and 4000 cm^{-1} were excluded from any models built, due to spectral peaks not relating to the sample, increased noise and a decrease in the accuracy of the spectrometer in these regions. It is important to ensure that the data contributing to these models are carefully selected such that the models produced are simple and effective. If more than one of the controllable properties (such as resin type, nanofiller type, nanofiller loading, and surface treatment) is varied in each model, then the resulting predictions and PCA analysis will be overly complicated and clarity will be difficult to obtain. So the preferred approach is to vary only one variable at a time in model building.

4 RESULTS

In order to understand fully the relationships between different physical properties and achieve the neccesary improvement and balance in physical properties, the underlying molecular structure of the material must be understood. By understanding the contributions of molecular contributions to the properties in question, the mateial can be taylored to gain the desired properties. In the case of HVDC systems and the resins investigated here an improvement in electrical and thermal properties are required without a detriment to the mechanical properties. These molecular indications can be modelled using chemometrics.

If chemometric modelling methods are applied to reactive surface treatments of nanosilica at a 2% filler loading level in the CY1300 resin, the plots in Figure 3 are obtained. In Figure 3a) it can be seen that, in this case, PC1 and PC9 yield the best separation of the clustering in PC space, with untreated silica, T4and T5 treated silica samples containing high levels of PC1 whilst the T1, T2 and T3 treated silicas treatments have negative amounts of PC1. This indicates (as in previous sections) that the 2% silica with T1,T2 and T3 functionalisation treatments yield a higher level of crosslinking than the other surface treatments. The T4 and T5 Silica surface treatments contain higher levels of C-O ester formation. A regression analysis against surface treatment was then perfomed on this PC cluster plot. A plot of the resulting regression coefficients against wavennumber can be seen in Figure 3b). This regression plot can then be used to predict the probability of a spectra yielding the values seen in the cluster plot. In this case, as seen in Figure 3c), the predictive plot yields a slope of 0.858, and a correlation of 0.926.. This indicates that, for

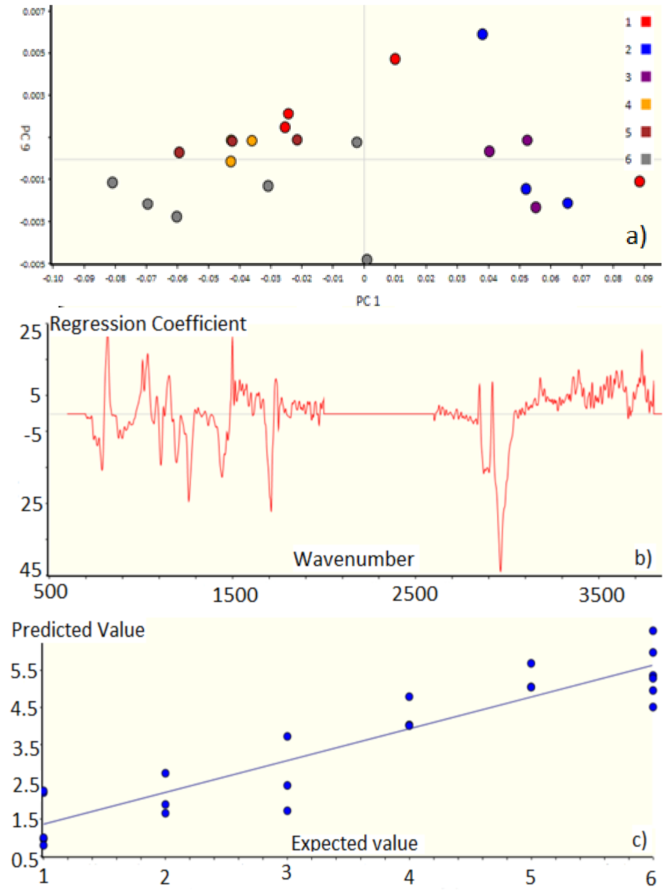

Figure 3: a)spectral variance contributions of PC1 and PC9; b) average regression coefficient contributions; c) predicted value of regression coefficient against filler loading level from FTIR data related to surface treatment.

some individual specimens, there is a greater variability in the spectra obtained from that sample and hence has a reduced homogeneity possibly related to poor dispersion.

If the model for surface treatment is compared and regressed against the measured values for breakdown strength for these samples, the regression coefficient seen in figure 4 is obtained. With the exception of the T6 silica samples, which have a low breakdown strength and high levels of PC2, breakdown strength appear to be dependent on the degree of crosslinking and C-O formation. It is possible to control these bonds with the addition of surface treated nanofillers and 2% nanosilica treated with T1 silica or the T2 and T3 silica treatments generate an improvement in these properties in comparison to the unfilled and untreated systems.

The resulting predictive model has a slope of 0.702, and a correlation of 0.838, indicating that although a predictive model can be built using this data there is a large amount of variability between samples.

If the spectral contributions are regressed against measured values for the glass transition temperature, the regression coefficient plot in figure 5 is obtained. This suggests

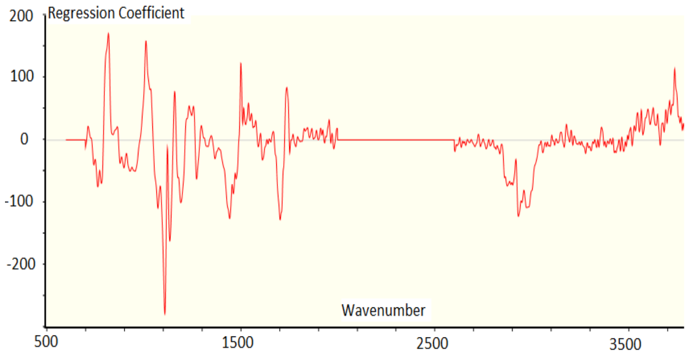

Figure 4: Regression coefficient contributions spectrally from FTIR data related to surface treatment and breakdown strength.

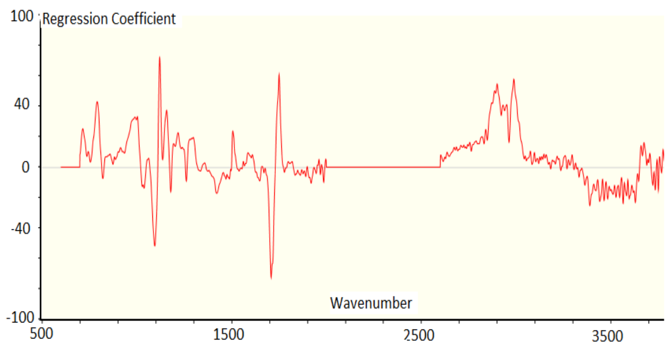

Figure 5: Regression coefficient contributions spectrally from FTIR data related to surface treatment and glass transition temperature.

that the chemistry related to T_g is highly complex. Samples with a high T_g show spectra where the CH_2 and CH_3 bond formation seen in the 2800 to 3050 cm^{-1} region are highly contributing as are the spectral peaks seen at 795, 1010, 1117, 1180 and 1732 cm^{-1} to name a few which are related to the presence of epoxy rings and ester formation. Strongly negative contributions to the coefficient, and therefore not related to increased values of T_g, can be seen at 1099 and 1700 cm^{-1} and which are related to the silica nanofiller itself. This indicates that samples with fewer crosslinks and a higher ester content are characterised by a higher value of glass transition temperature but, due to the complexity of the spectral contributions, many other factors are also involved.

The predictive plot obtained from the regression analysishas a slope of 0.905 and a correlation of 0.951 indicateing that, although the model is complicated, it is reletively accurate and could form the basis of tailoring the surface treatment of the nanofiller in order to improve the thermal properties of the insulating material.

5 DISCUSSION AND CONCLUSIONS

High purity nanofilled thermoset resin materials with increased electrical breakdown strength and glass transition temperature have been developed. These have been used to produce insulator components successfully using conventional industrial manufacturing processes suitable for HVDC and HVAC transmission component production.

This paper demonstrates the potential of MVSA and chemometric methods to determine structure-property relationships central to establishing materials design rules in HVDC and HVAC insulation materials. Further, with additional factored measurements linked to specific process conditions it will be possible to expand the knowledge base to include structure-process-property relationships and use these in process optimisation, leading to process design rules.

The careful consideration of all property measurements is required when developing a new material for use in HV applications be they HVDC or HVAC. With full and balanced consideration of nanofiller type, loading, reactive surface treatment, and the application of MVSA modelling to confirm property relationships wioth the identification of control factors, an optimised material can be produced. Careful consideration must also be given to process design rules such that the production methods of new nanofilled thermoset resins for use in HV components is also optimised, where traditionally this optimisation identified best conditions determined using rules of thumb and best practice methods.

This work has also demonstrated the usefulness of FTIR spectroscopy when used in conjunction with multivariate statistical analysis. This can provide rapid assessment of various property metrics such as breakdown strength and space charge accumulation with the potential to support materials selection and formulation and to act as a quality control tool. In combination with the understanding of the structure-process-property relationships this will produce a paradigm shift in the way nanocomposite insulation systems are developed.

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