POLYMER END OF LIFE INDICATOR

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ABSTRACT

Rapid, cost-effective, non-destructive identification and diagnosis of insulation materials, equipment casings and other polymeric materials under the remit of DSOs is an increasingly important area of asset management. This is necessary to assess the reliability and potential risks presented by equipments in a particular population as well as gauging the prospective life expectancy of individual units.

Within the PAS 55 certified Risk Based Asset Management process [1], Enexis has started to test and introduce a remote sensing Raman-spectroscopy method as developed by GnoSys UK.

A portable fibre-optic spectroscopic probe system has been developed which can remotely and non-destructively identify the polymer and then provide an estimate of glass transition temperature, tan δ, and an indicator of "extent of damage". The system uses a hand-held optical probe that gathers spectral information which is analysed using dedicated multivariate analysis software. Following calibration and measurement trials in the laboratory, the instrument has been used in the field, to provide quality values based on in-situ measurements of buried components of switchgear.

INTRODUCTION

The non-destructive identification of polymers, insulators and composite materials is a challenge for maintenance of components in the electrical industry. Extending this to provide a measure of quality – degradation, mechanical strength or remaining life – can be harder.

In a first field trial Enexis and GnoSys were able to use known laboratory and field-aged samples to build a model for classifying samples as "good", "average" or "bad".

This model was originally based on five independent MV switchgear equipments that was then validated by six "unknown" equipments. Property and quality data were obtained by a destructive dynamic mechanical analysis to provide loss and storage moduli in addition to an inspection of the number of visible cracks in the polycarbonate parts.

REMOTE NON-DESTRUCTIVE METHODS

Remote analysis that can access molecular information is primarily through vibrational spectroscopy, which includes infrared (IR) and Raman methods, which are particularly suited to identifying and quantifying molecular structures rapidly and non-destructively. The spectroscopic data can also provide information on the local environment seen by particular molecular bonds and these give access to sample crystallinity and polymer chain interactions. However, both methods have some limitations when investigating polymers: IR has limited depth of penetration, and can be strongly skewed by non-representative surfaces, whilst Raman can be confounded by fluorescence. Despite this, the Raman methodology is favoured for several reasons:

1. As most of the spectral information comes from a focused spot, this can access buried parts that are up to 10 mm from an accessible surface.

2. The visible laser spot provides its own indicator so small areas (~0.2 mm) can readily be targeted and examined. With a laser power of 300 mW, good quality spectral can be obtained within 40 seconds.

3. The entire process is completely non-destructive.

The portable instrument, TRANSPEC™, consists of integrated laser and miniature spectrometer coupled to a hand-held fibre-optic probe, shown in Figure 1.

Figure 1: Raman probe with hand-held fiber-optic probe.

Instead of the conventional spectroscopic method of a band-by-band analysis, a method for multivariate statistical analysis (MVSA) is applied to use the complete spectral data set and classify the samples as being similar or dissimilar through tools such as the Mahanalobis distance [2]. This can then be used in both qualitative and quantitative methods to discover the relationship between very rapid and convenient spectroscopic methods and properties such as glass transition temperature (T_g), yield tensile strength and even qualitative "good" and "bad" descriptors. Calibration data is provided using "conventional" destructive dynamic mechanical analysis (DMA) methods and then correlated to the spectral information obtained from well-characterised samples. This is unlike the traditional spectroscopic approach of band assignation. MVSA utilises all the spectral data and looks for the most parsimonious approach to correlating spectral, chemical and mechanical information. A schematic of the method is shown in Figure 2.

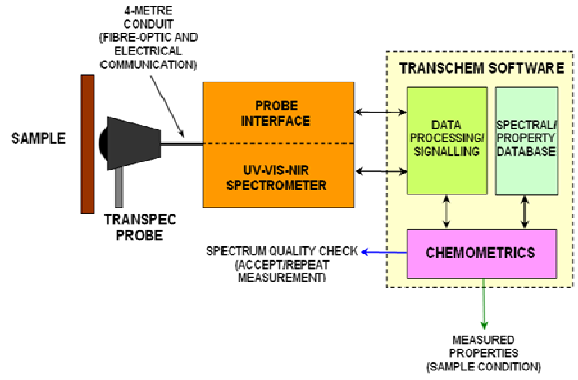

Figure 2: Non-destructive spectroscopic analysis method

The MVSA methods used in this analysis are principal component analysis (PCA), for looking at sample-related spectral variation, and principal component regression (PCR), for constructing spectroscopic prediction models using samples with known properties as calibration. The quality of the correlation between spectroscopy and DMA depends on a number of factors, the most important being the quality of spectra and calibration data. Examples of raw spectral data obtained from various polycarbonate samples are shown in the plot in Figure 3.

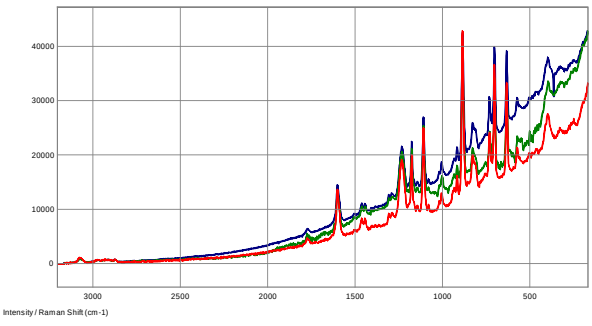

Figure 3: Spectra of transformer coils

POLYCARBONATE ANALYSIS

The structures under investigation were manufactured from polycarbonate. This has a very distinctive spectroscopic signature as seen in Figure 3. All these bands can be assigned [3].

Bisphenol-A–polycarbonate (BPAPC) is known for its unusual ability to withstand a sudden impact of energy. For weaker polymers impact is often sufficient to break chemical bonds leading to macroscopic failure.

In the polycarbonate system, however, the energy is dissipated through the movement or reorientation of molecular segments leaving the chemical bonds intact. Forming processes, such as injection moulding which employs extreme conditions (high temperature and pressure), are routinely used when making components out of BPAPC. These extreme conditions force the polymer chains to reside in high energy, high volume conformations (q.v. Figure 4). Once moulded, the component is usually quenched to below its glass transition temperature (Tg). This sudden removal of heat energy locks in the high-energy conformations, even at ambient conditions. It is in this state that the polymer is at its toughest, with sufficient residual volume for the molecular segments to rotate and dissipate energy as needed.

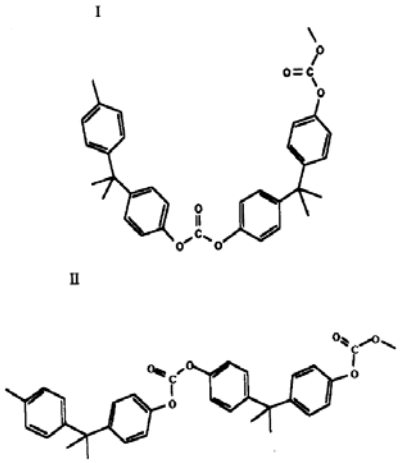

Figure 4: The Structural Conformation of BPAPC: cis-cis (I) and cis-trans (II) around the carbonyl group

Over time, however, thermodynamics pushes the chains to reach a lower energy equilibrium state. Through this process, a densification of the material is observed indicating that the packing efficiency of the polymer chains has increased. This packing does not lead to crystallization, making this behaviour unique. It is believed that the increased steric repulsions between the chains prohibit rotations of molecular segments. Thus, should an external force be applied to the polymer in this condition, the added energy cannot be dissipated and the material becomes brittle and suffers macroscopic failure. This phenomenon is referred to as "physical aging".

Thus, it is the chemical structure of BPAPC that contributes not only to the observed toughness of this polymer, but also to the physical aging process.

The manifestation of failure in these materials is brittle fracture. This is measured by "impact resistance" - for example, the ASTM Drop Weight Impact (DWI) method D-3029 requires an impact measurement on as many as 30 samples to obtain good statistical results. In addition, each sample must be prepared by high quality injection moulding, followed by temperature conditioning at -29°C for 24 hours before testing. Other mechanical tests can reduce the burden, but cannot access buried sub-surface materials or those in service.

MECHANICAL ANALYSIS

Calibration samples were extracted from field-aged samples. They were initially visually inspected and sorted into three qualitative categories of "good", "bad" and "intermediate" by the number of cracks visible under a 10x magnifier around the stress point. Such an inspection can not be performed in the field. The discussed system however can take samples without taking out these parts.

Representative samples were cut, prepared and then subject to DMA which provided loss modulus (Figure 5) and storage modulus as a function of temperature between 20 and 180 °C. This enabled the calculation of the ratio between the two moduli, tan δ, and hence the measurement of T_g as seen in Figure 6. The peaks correspond to T_g.

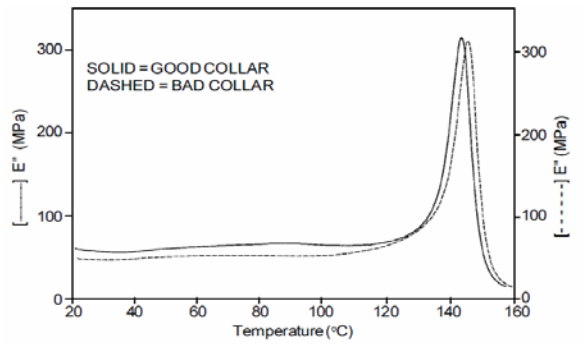

Figure 5: Loss Modulus Comparison for Polycarbonate

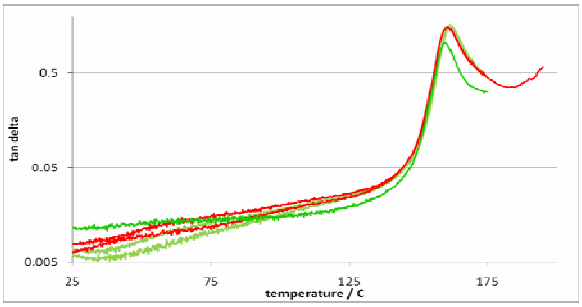

Figure 6: Tan delta comparison for Polycarbonate calibration samples

FIELD ANALYSIS

About twenty pieces of switchgear were examined live in the field. An example is shown in Figure 6 with an arrow indicating the required measurement spot on the pivot of the lever arm, which is about 10 mm below the surface of the outer housing.

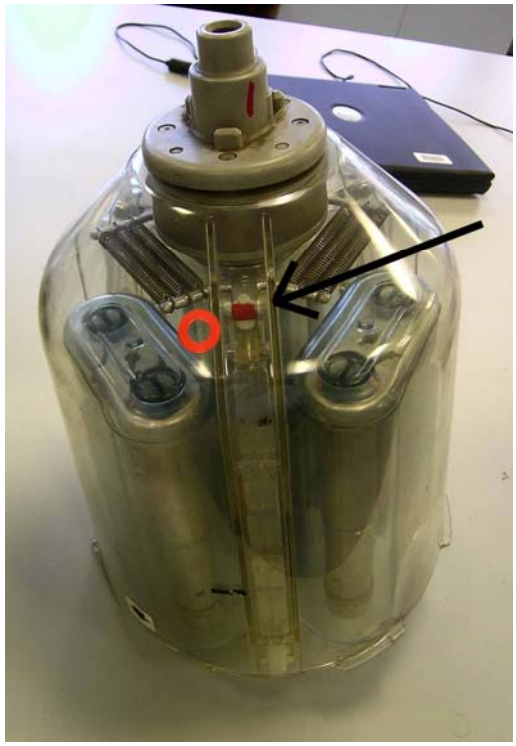

Figure 6: Example of Switchgear Examined

The TranSpec probe was placed on the outer housing, and the focused spot adjusted to illuminate the pivot point. Four scans, each of 20 s duration, were co-added and averaged to provide spectral quality similar to that observed in the laboratory (Figure 3). The MVSA predictor then provided a quality indicator instantaneously, and this was used to extract four pieces for validation.

SPECTRAL ANALYSIS

MVSA was used to look for correlations between the spectral data, the mechanical data and the quality metric for the calibration samples. To determine if there was any utility in this approach, the analysis looked for "clusters" of similar samples, and if these were well separated. The cluster plot showing the spread of tan δ, indicating the three qualitative categories, is shown in Figure 7.

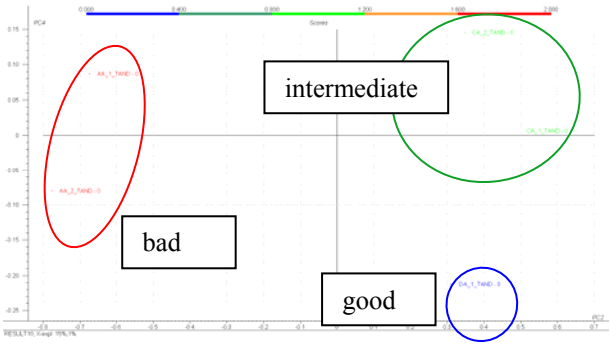

Figure 7: Cluster plot for Polycarbonate calibration samples indicated by quality metric

For the two axes indicated in Figure 7, there is good separation between the qualitative categories. These were then used to provide a prediction of unknown laboratory samples as well as the field samples for the "number of cracks" or "extent of damage" and results are shown in Figure 8 where the prediction is plotted against the quality metric. One sample is anomalous – otherwise there is good categorization.

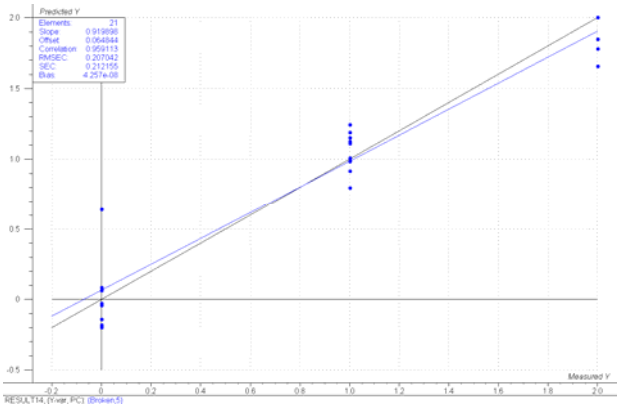

Figure 8: Predicted against observed "Extent of Damage" of Lever Samples

The model works by doing a point-by-point multiplication of the regression coefficient by the incoming spectra and summing the product to provide the quality number. This regression coefficient is shown in Figure 9 where it is compared against a raw spectrum.

It is clear that the MVSA extracts much more information from the spectrum in comparison to a visual inspection. All of the bands shown in the regression that correspond to positive-(upward going) and anti-correlated (downward going) features can be assigned to molecular structures related to density, entanglement and cross-linking.

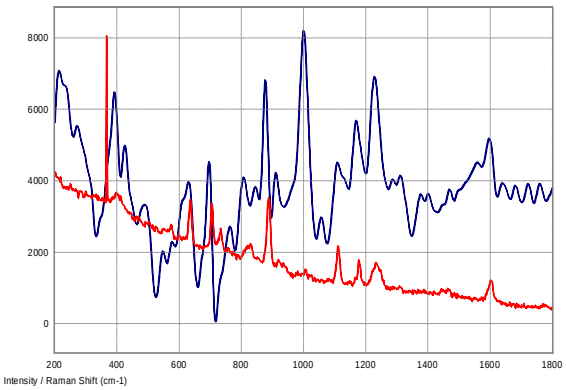

Figure 9: Comparison of DMA Tg model Regression Coefficient and the Raman spectrum (red) for Sample 1

CONCLUSION

The utility of vibrational spectroscopy, as exemplified by the Raman method, has been demonstrated to provide remote and rapid measurement of the quality of a buried interface. Although not demonstrated in this paper, the uniqueness of the polycarbonate spectra enables clean separation from other polymeric materials. Once the polymer has been identified, the use of MVSA provides an estimate of glass transition temperature, tan δ, and an indicator of "extent of damage".

The Raman-spectroscopy method enables Enexis to quantitatively identify polycarbonate parts in a non-destructive way. In 2011 additional field trials will be performed to index additional types of polymer and types of MV-switchgear. This in order to implement to Raman method and Transpec system into it's asset management approaches. This system will enable Enexis to replace MV switchgear closer to its actual individual end-of-lifetime, therefore investments in maintenance or replacement will be optimized.

REFERENCES

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[3] Lee, S.-N, Stolarski, V, Litton, A., Laane, J., "Studies of bisphenol-A–polycarbonate aging by Raman difference spectroscopy" J. Mol. Struct. 521 (2000), 19-23