Rapid Evaluation of Electrical Insulation Materials along the Supply Chain – using Chemometric Methods

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Overview

• Rationale for Spectroscopy and Chemometrics
• What tools should we use?
• What is Chemometrics?
• Application examples?
• The benefits of using these methods along the supply chain
Rationale - Rapid Supply Chain Evaluation

• Goods inward, materials supply, component processing and condition monitoring need to be fast and robust
• Mechanical, electrical and chemical tests can be difficult, time-consuming and destructive
• Molecular spectroscopy methods can access material chemistry and structure, prime factors that influence properties and performance
• Spectroscopy methods are quick and can be remote, mobile and low-skill to answer questions like ..... What is it? Does it meet specifications? Will it do the job? In service is it fit for purpose?
What Does Molecular Spectroscopy See?

1. Chemical composition - monomers, oligomers, polymer, blends, additives, water / hydroxyl / carboxyl / carbonyl / amide content ...
2. Chemical changes - polymerisation, cross-linking, pyrolysis, kinetics, degradation, oxidation, hydrolysis and kinetics ....
3. Physical structure - crystallinity, dispersion, domain and inter-phase structure, phase separation ....

Relates to:

4. Density, molecular weight, melt flow rate, viscosity, crystallinity, network structure, ......

Which governs:

5. Physical properties, performance and ageing
Some Hand-Held/Portable Spectroscopies

**Transpec Raman**
- Raman scattering
- 175-3200 cm\(^{-1}\)
- Fundamental vibrations
- 5 cm\(^{-1}\) resolution
- Generally sharper peaks than IR for assignment

**Transpec Infrared**
- Infrared ATR, reflectance
- 400-4000 cm\(^{-1}\)
- Fundamental vibrations
- 4 cm\(^{-1}\) resolution
- Generally more sensitive than Raman

**Transpec Wide-wavelength**
- UV-Vis-NIR
- 350-2500 nm
- 3-10nm resolution
- Variety of probe options
- Colour
- Molecular overtones
**But Spectroscopy is not enough**

- Need to turn spectral data into information and actions
  - use **spectroscopy** to gather high quality data
  - use **chemometrics** to find correlations between spectral variance and properties / performance of interest
  - combine to allow multiple property measurements
- The Chemometrics “learning” process is:
  - scan “known” samples – *this is the tedious bit*
  - enter properties – *this is the chasing around bit*
  - build model – *this is the knowledge bit*
  - validate on “unknown” samples – *this is the critical bit*
  - apply – *this is the reward bit*
Chemometrics – an overview
Chemometrics – an overview

• Chemometric models are a form of multi variate statistical analysis that utilises variance in materials and their spectral data sets.

• In this work molecular spectra are used to construct property “prediction” models - built using Gnosys Transchem™ software.

• Raw data is first processed before Principal Component Analysis (PCA) and Linear Regression Analysis are carried out and validated.

• Spectral variance and PCA studies are conducted to inform regression models targeting physical properties and performance - such as filler loading level, polymer viscosity, mechanical, thermal and electrical properties, .... etc.

• Unique correlations are used for rapid identification, concentration and property measurements together with a variety of performance metrics.

• Use regression coefficient spectral dependence of property models to explore structure-property relationships
Example 1 – Epoxy Nanodielectric Insulation for HVDC switchgear applications

• Based on Bisphenol A diglycidyl ether epoxy resin with the corresponding anhydride hardener and 1-Methylidiazole catalyst (CY1300).
• untreated nanosilica (80 nm)
• variety of surface capped and functionalised nanosilicas
• reactive epoxide functionalized nanosilicas

• *Also used chemometrics to monitor large volume VPI resin vats for viscosity and reactivity and to monitor stator bar impregnation and cure condition.*
### Silica-Epoxy Nanodielectric IR Data - normalised

<table>
<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shoulder at 806</td>
<td>Si-O-Si stretch</td>
</tr>
<tr>
<td>829</td>
<td>C-O-C stretch</td>
</tr>
<tr>
<td>1011</td>
<td>aromatic ring stretch</td>
</tr>
<tr>
<td>1043</td>
<td>C-O-C ether stretch</td>
</tr>
<tr>
<td>1099 double band</td>
<td>Si-O-Si stretch</td>
</tr>
<tr>
<td>1117</td>
<td>Epoxy ring deformation</td>
</tr>
<tr>
<td>1180</td>
<td>C-O ester stretch / C-H wag</td>
</tr>
<tr>
<td>1230</td>
<td>C-O ester stretch</td>
</tr>
<tr>
<td>1364</td>
<td>Deformation of CH$_3$ of C-(CH$_3$)$_2$</td>
</tr>
<tr>
<td>1384</td>
<td>Deformation of CH$_3$ of C-(CH$_3$)$_2$</td>
</tr>
<tr>
<td>1458</td>
<td>Deformation C-H of CH$_3$ and CH$_4$</td>
</tr>
<tr>
<td>1509</td>
<td>C=C aromatic stretch</td>
</tr>
<tr>
<td>1583</td>
<td>aromatic ring stretch</td>
</tr>
<tr>
<td>1607</td>
<td>C=C aromatic ring stretch</td>
</tr>
<tr>
<td>1732</td>
<td>C=O non conjugate ester stretch</td>
</tr>
<tr>
<td>2338</td>
<td>C=O stretch from CO2</td>
</tr>
<tr>
<td>2359</td>
<td>C=O stretch from CO2</td>
</tr>
<tr>
<td>2875</td>
<td>CH$_3$ symmetric stretch and CH stretch</td>
</tr>
<tr>
<td>2925</td>
<td>CH$_3$ asymmetric stretch</td>
</tr>
<tr>
<td>2963</td>
<td>CH$_4$ asymmetric stretch</td>
</tr>
<tr>
<td>3034</td>
<td>CH Phenyl stretch</td>
</tr>
<tr>
<td>Wide band between 3300 and 3600</td>
<td>O-H stretch</td>
</tr>
</tbody>
</table>
Glass transition temperature

• 2% nanosilica loading level
• Surface functionalisations
• Measurements using TA Q2000 DSC
• PC scatter plot of PC1 verses PC2 yields clustering despite the small sample set.
• Obtain a good predicted value against expected value.
• Some sample separation possible
• Slope = 0.905, correlation coefficient = 0.951
• Good model despite its complexity
• Becomes possible to generate design rules and tailor the surface treatment of nanofiller in order to improve thermal properties.
Glass transition temperature

Regression plot can be used to determine the probability of a spectrum yielding the values seen in the cluster plot.

- Positive peaks in the regression coefficient yield high Tg, negative yields a low Tg.
- High Tg related to presence of, crosslinking and ester formation - nanofiller and epoxide ring negatively correlated.
DC conductivity

- Untreated nanosilica at filler loading ranging from 0.5 to 10% wt
- Measure conductivity on 150 µm film at 100V and 30 °C
- Other temperatures and voltages modelled
- These results can be informed by molecular dynamics calculations
DC conductivity

- Positive contributions associated with ether C-O-C, CH₃, CH₂ and -OH groups
- Positive contributions from lower trap depth groups.
- Negative correlations with ester and related CH₂/CH₃ groups
- Negative contributions from higher trap depth groups.
- Factors that promote charge carriers or are shallow trapping facilitate DC conductivity.
- The predictive model has a slope of 0.963, and a correlation coefficient of 0.981
Electrical Breakdown Strength

Experimental data

Regression model
Example 2 – Thermal ageing and condition assessment of rigid EPGM laminate

• Thermal endurance by IEC 60216
• Usually valid for times and temperatures actually measured (in the laboratory) – cannot be used for other ageing temperatures and times
• Can the key properties (and ageing kinetics) be linked to molecular characteristics, enabling transformation to other temperature and time domains?
• **Can we differentiate high-T short time ageing from low-T long time ageing for unknown ageing conditions?**
Molecular consequences of thermal degradation

• **Side group elimination**
  1. Loss of side groups attached to polymer backbone
  2. The resulting unstable polyene reacts further, forming aromatic molecules, scission or carbon ring based chars

• **Random scission and oxidation**
  1. Formation of a free radical, giving series of oligomers
  2. Possible oxidative and hydrolytic degradation
  3. Breaking of backbone / C-C bonds / 1,3 H shifts

• **Depolymerisation**

_All potentially visible to molecular / electronic spectroscopy_
EPGM Degradation - Materials and Methods

**EPGM 203**

- Epoxy glass mat (IEC 60893 – 2004)
- Reference - Isothermal laboratory ageing between 100 and 200 C, and from 0 to 28 days

**Wide wavelength reflectance spectroscopy**

- 350 to 2500 nm (wide-wavelength)
- 8 nm resolution
- 4 seconds analysis time
Non-destructive wide-wavelength reflectivity

- Increasing absorbance
- Increasing discoloration
- Increasing molecular degradation
<table>
<thead>
<tr>
<th>Band / cm(^{-1})</th>
<th>Band /nm</th>
<th>Component</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>8749</td>
<td>1143</td>
<td>resin</td>
<td>C-H str 2nd overtone (CH(_3))</td>
</tr>
<tr>
<td>8396</td>
<td>1191</td>
<td>resin</td>
<td>C-H str 2(^{nd}) overtone (CH(_3))</td>
</tr>
<tr>
<td>8258</td>
<td>1211</td>
<td>resin</td>
<td>C-H str 2(^{nd}) overtone (CH(_2)). OH combination</td>
</tr>
<tr>
<td>6105</td>
<td>1638</td>
<td>resin</td>
<td>=CH(_2) 1(^{st}) overtone</td>
</tr>
<tr>
<td>5970</td>
<td>1675</td>
<td>resin</td>
<td>Aromatic C-H stretching 1(^{st}) overtone</td>
</tr>
<tr>
<td>5784</td>
<td>1729</td>
<td>resin</td>
<td>C-H str first overtone (CH(_2))</td>
</tr>
<tr>
<td>5679</td>
<td>1761</td>
<td>resin</td>
<td>C-H str 1(^{st}) overtone (CH(_2))</td>
</tr>
<tr>
<td>5249</td>
<td>1905</td>
<td>resin</td>
<td>C=O str. 2(^{nd}) overtone</td>
</tr>
<tr>
<td>5128</td>
<td>1950</td>
<td>resin</td>
<td>Combination O-H str. + O-H def.; C=O str. 2(^{nd}) overtone</td>
</tr>
<tr>
<td>4812</td>
<td>2078</td>
<td>resin</td>
<td>Combination C=O str. 1(^{st}) overtone +CH bend</td>
</tr>
<tr>
<td>4669</td>
<td>2142</td>
<td>resin</td>
<td>Aromatic combination band; Combination of C-H str. + C=C</td>
</tr>
<tr>
<td>4619</td>
<td>2165</td>
<td>resin</td>
<td>Aromatic combination band</td>
</tr>
<tr>
<td>4554</td>
<td>2196</td>
<td>mica</td>
<td>Combination of OH st. + OH def.</td>
</tr>
<tr>
<td>4448</td>
<td>2248</td>
<td>resin</td>
<td>Combination of OH st. + OH def.</td>
</tr>
<tr>
<td>4342</td>
<td>2303</td>
<td>resin</td>
<td>Combination bands of aliphatic methyl group</td>
</tr>
<tr>
<td>4255</td>
<td>2350</td>
<td>resin</td>
<td>Combination CH str. + =CH(_2) def.; C-H def. 2(^{nd}) overtone</td>
</tr>
</tbody>
</table>
Regression Coefficient for Ageing of EPGM 203 at 160°C and resulting ageing time prediction.
Regression Coefficient for Ageing of EPGM 203 at 100°C and resulting prediction

Colour change

Resin chemical change

Laboratory aged / days

Predicted age/ days

Regression Coefficients (E)

RESULT 10: (Y-var. PC) (Days, 4) 50 = -268.514191

Predicted Y

Elements: E
Slope: 0.879309
Offset: 0.140727
Correlation: 0.999600
RMSE: 2.16e-07
SEC: 1.266174
Bias: 9.213e-06
General Ageing of EPGM 203 and resulting prediction

- Colour change
- Resin chemical change

**Laboratory aged metric**

**Predicted aged metric**

Regression Coefficients (B)

<table>
<thead>
<tr>
<th>Predicted Y</th>
<th>Elements: 56</th>
<th>Slope: 0.000938</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Correlation: 0.997926</td>
<td>Error: 0.00000</td>
</tr>
<tr>
<td></td>
<td>SEC: 103.9952</td>
<td>Bias: 44.4522</td>
</tr>
</tbody>
</table>

RESULT19, (Y-var, PC): ((temp+200) * (10*log(days)))

$E_0 = 1379.793467$
Example 3: Application to Generators
Application to Generators ground wall insulation:

NIR – UV/VIS data

Structure of muscovite viewed approximately perpendicular to c

Properties (Voltage Endurance, Resistance ...
Quality Factors in Stator Bar Insulation:

- Quality of VPI resins
- Degree of impregnation
- Degree of curing ($T_g$)
- Mica / resin ratio
- Voids / delamination

H2O Sensitivity $\sim 0.05$ wt%
Application to Generators
“In-field” Data compared to Mica tape

Insulation measured by depth profiling sampling distance 0-4mm
Application to Generators - Mica condition

- OH band changes position
- Related to Fe-Mg substitution in octahedral Al sites
- Related to Na:K ratio
Generator Ground Wall Insulation Megger test

- Predicted Y
  - Elements: 20
  - Slope: 0.959499
  - Offset: 2.324110
  - Correlation: 0.979540
  - RMSE: 8.225965
  - SEC: 8.439663
  - Bias: 7.629e-07

- Measured Y

- Regression Coefficients (B)

- X-Variables
  - Megger test
  - mica
  - Resin / mica
Power Factor Test – Capacitance at 22 kV
Application to Generator Stators

• Important metrics
  – Ratio of resin to mica
  – Quality of mica
  – Degradation of resin
  – voids

• uv-vis-nir data correlate with several property parameters, including:
  – Megger readings
  – 22kV ac proof test
  – Power factor capacitance
  – Power factor tan delta
  – Short term breakdown voltage
Example 4 - HVAC Cable Insulation Ageing

Examine XLPE cable manufacturing process and changes in use:
  • Crosslinking by-products distribution
  • Acrylate diffusion from semicon versus other oxygenated species
  • Intrinsic and generated additives / impurities / degradation products

Effect on properties
  • Prediction of properties
What Happens to the Di-Cumyl Peroxide (in x-LDPE)...

These species can migrate
Infrared Analysis - Base Polymer and Reference Cable Material

Transmission / Wavenumber (cm⁻¹)

- Acetophenone
- Cumyl alcohol

Reference - middle of cable
Reference - near inner screen
Reference - thermally conditioned
Base polymer
FTIR (7630 hrs, 90C, 225 kV) at radial distances of 0.0, 0.45 and 6.0 mm, together with acetophenone and cumyl alcohol (dashed)
Changes on Ageing: Acetophenone Concentration

- Standard
  - 5600 hrs, 20C, 225 kV
  - 7630 hrs, 90C, 225 kV

And after thermal treatment

Concentration – g cm\(^{-3}\)

Radial distance from inner semicon - mm
Changes on Ageing: Cumyl Alcohol Concentrations

Standard
5600 hrs, 20°C, 225 kV
7630 hrs, 90°C, 225 kV

And after thermal treatment
Changes on Ageing: Acrylate Concentrations

Standard
5600 hrs, 20C, 225 kV
7630 hrs, 90C, 225 kV
Spatial Mapping: Interpretation of Differences

Positive differences between standard cable and base polymer
- breakdown products of DCP
- Santonox anti-oxidant
- Santanox breakdown products
- increase in \textit{trans} functionality

A small fraction of the normally volatile acetophenone and cumyl alcohol products appear bound within the system.

Negative differences
- loss of vinyl and vinylidene groups
- mixed differences in the carbonyl region indicate a reduction in the ketone linker present in the base polymer, but also some increasing oxidation
All Samples: E-Stress, AC-breakdown strength

**E-Stress**
- Dominated by: 3611, 3500 antioxidant
- Dominated by: 3035 aromatic
- Dominated by: 1737, 1714 carbonyl
- Dominated by: 1177 C-O
- Dominated by: 770 (ethyl branches)

**AC-breakdown strength**
- Dominated by: 1079 cumyl alcohol-like
- Dominated by: 891 vinylidene
- Dominated by: 814 1,3-di-aromatic
- Dominated by: 704 cumyl alcohol-like
All Samples: Space charge @ 15kV/mm and mobility @ 60kV/mm

\[ + 3092 \text{ vinyl} \]
\[ - 1740 \text{ carbonyl} \]
\[ 1694, 1265 \text{ aromatic carbonyl} \]
\[ + 1377 \delta \text{ CH}_3 \]
\[ - 890 \text{ vinylidene} \]

\[ - 3092 \text{ vinyl} \]
\[ + 1735 \text{ carbonyl} \]
\[ 1387, 1386 \text{ aromatic carbonyl} \]
\[ - 1377 \delta \text{ CH}_3 \]
\[ - 890 \text{ vinylidene} \]
Conclusions

1. Chemometrics based spectroscopy is a powerful method to understand and quality assure electrical insulation materials along the supply chain.

2. From materials identification, formulation and process monitoring to validated property and performance measurements the methods provide development support and rapid/portable quality assurance tools.

3. The approach can address liquid, solid and composite systems reliably and can monitor reacting systems e.g. thermosets, VPI resins, insulating oils, grafting, surface treatment, coatings, DCP and silane XLPE, …..

4. Insulation thermal and multi-factor ageing, nuclear radiation ageing with determination of degradation kinetics, dose and dose rate effects, gas production rates, ….

5. Application to volume and surface measurements at various length scales from 2 µm to metre dimensions with spatial mapping in all power equipment.