Monitoring Cure in High Performance Composites

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Thermosetting resins and their composites

- The **curing reaction** of the resin is a critical process in composites manufacturing.

- Physico-chemical effects can be followed by process monitoring techniques, such as **dielectric sensing**.
Thermosetting resins and cure reaction

Resin chemistry complex and usually unknown

Monitoring achieved through following changes in mobility of the growing macromolecular networks

+ heat

Unreacted resin
Liquid

Curing reaction
Liquid

Gelation
Rubber

Vitrification
Glass
Thermosetting resins and cure reaction

TTT diagram of resin system
Cure process – critical phenomena/process milestones

- **Point of maximum flow**
  Viscosity of the resin is minimum → minimum flow resistance.

  *Manufacturing:* Onset of reaction, practical end of mould filling in Liquid Composite Moulding, onset of pressure application in autoclave

- **Gelation**
  Transition from the liquid state → rubber state

  **Matrix does not flow after gelation, no-return point in cure!**

  *Manufacturing:* Fibre wetting, phase separation processes stopped by gelation

- **Vitrification**
  Transition from the rubber state → glass state - Polymerisation reaction essentially stops.

  *Manufacturing:* Final glass transition temperature reached - defines upper temperature limit for material usage
Dielectric measurements

Charged species contributing to signal

The charged species respond differently at various frequencies in the spectrum.

Main contributions in resin systems:
- from ions and interfaces
- Applied field, $E > 0$
- No field, $E = 0$
Dielectric measurements

Signal analysis and property derivations

Moving from circuit properties to material properties

\[ v(t) = V_m \sin(\omega t) \]

\[ i(t) = I_m \sin(\omega t + \theta) \]

\[ \frac{v(t)}{i(t)} = |Z|, \theta \]

\((Z, \theta) \rightarrow Z', Z''\)

\((Z, \theta) \rightarrow C_p, R_p\)

Circuit analysis

C-R parallel circuit analysis

\[ R_p, f, \text{geometry} \rightarrow \varepsilon'' \]

Interdigital sensor calibration

\[ C_p, \varepsilon'', f, \text{geometry} \rightarrow \varepsilon' \]

\[ C_p, R_p \rightarrow \varepsilon', \varepsilon'' \rightarrow \varepsilon', \sigma \]

Derivation of conductivity
Dielectric cure monitoring

Impedance representation

- Electrode polarisation
- Charge migration
- Dipolar relaxation

**logf**

- Minimum, maximum and shoulder in the imaginary impedance spectrum
- Two plateaus in the real impedance spectrum
Dielectric cure monitoring

Degree of cure estimation under dynamic conditions

Commercial epoxy
**Sensor development**

**Dielectric sensor**: flat interdigital layout of capacitor, creating fringing (curved) electric field as the terminals are subjected to alternating voltage

**Thin polymer film substrate** – suitable for embedded sensors

Always require protection against shorting out on conductive fibres

Ceramic substrate–suitable for tool mounted, reusable sensors (photo courtesy of INASCO)
Application to composites processing

Installation of monitoring system in composite processing tools

RTM moulds
(IAI, Israel)

underside of mould

autoclave (Bombardier UK)

inside mould

cure monitoring system

outside autoclave

pultrusion
(Excel, UK)

Sensor at die exit

Underside of tool

Inside autoclave

(Images supplied by INASCO)
Resin flow monitoring in Resin transfer moulding

Dielectric lineal sensor in non conductive reinforcement
Modelling and monitoring

Flow Model

Heat Transfer Model

Cure Kinetics Model

Strain Development Model

Chemorheology and Structure Models

Degree of cure

Gelation Vitrification

Cure Monitoring

Flow Monitoring

Filling progress

Strain Monitoring

Strain
Towards feedback loop control

Cure monitoring system also controls the oven heating/cooling.

Material properties in current database:
• Degree of cure
• Viscosity advancement
• Tg advancement

User defined cure cycle
Material property evolution in real time.

INASCO dielectric cure monitoring equipment and controlled oven, Airbus UK/National Composites Centre
Matrices for high performance composites

Thermoplastic particles occluded within epoxy matrix (low concentration of thermoplastic)

Or ‘phase inverted’ structure such as in TGDDM epoxy/ PEI thermoplastic

Initial work at Cranfield prompted by interest in phase separation. Using laboratory equipment, a well pre-characterised epoxy-rubber blend and Dek-Dyne sensors ($50 a piece, non-reusable !!)
Phase separation in thermoset - thermoplastic resin blend

Liquid epoxy & hardener and Dissolved thermoplastic

Solid toughened epoxy

Heat and time
Dielectric monitoring of phase separation during cure of blends of epoxy resin with carboxyl-terminated poly(butadiene-co-acrylonitrile)

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Figure 1 Variation in temperature $T$ of the dielectric sample cell during cure of the neat resin at an oven temperature of 80°C, compared with conversion $\alpha$, gel fraction and viscosity $\eta$ for the same system, also at a nominal cure temperature of 80°C. The cure time, $t_{\text{cure}}$, to reach $T_{\text{c}}$ was obtained from a d.s.c. curve.

Figure 4 Dielectric data on the blend of epoxy resin and hardener with 15 wt% CTBN rubber, cured at 80°C. Plots of: (a) relative permittivity $\varepsilon'$, and (b) dielectric loss $\varepsilon''$, against frequency and cure time. Sample contains highest concentration of adventitious mobile ions (see Figure 3). Note that scales for $\varepsilon'$ and $\varepsilon''$ are different from Figure 3.

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Dispersion monitoring in epoxy/CNT

- Additional polarisation due to interfaces created by ultrasonication

- New interface results in an additional relaxation mechanism
- Strength of relaxation can provide a metric of dispersion
- Response controlled by the shape factor of dispersed phase and volume fractions
- Details see Dr A Skordos at Cranfield
Dielectric cure monitoring usable to reduce cure cycles and provide certification on-line; possibility of feedback-loop process control, management of residual stresses

Next generation aircraft – composite structure performance really critical?? If so............may come back to **phase separation** monitoring in aerospace grade resin blends........

Driving dispersion quality in future commercial nanocomposites......