University of BRISTOL

Monitoring Cure in High Performance Composites

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www.bris.ac.uk/composites

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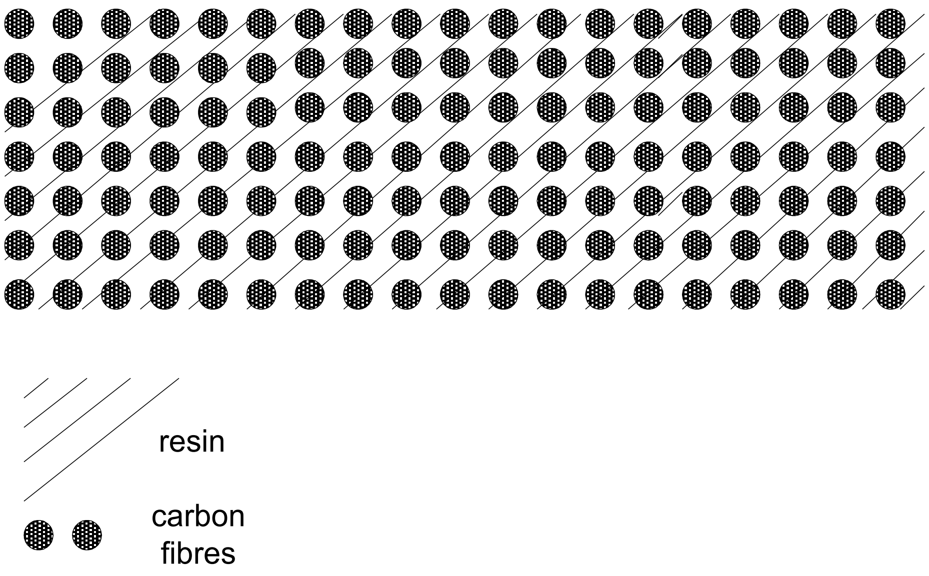
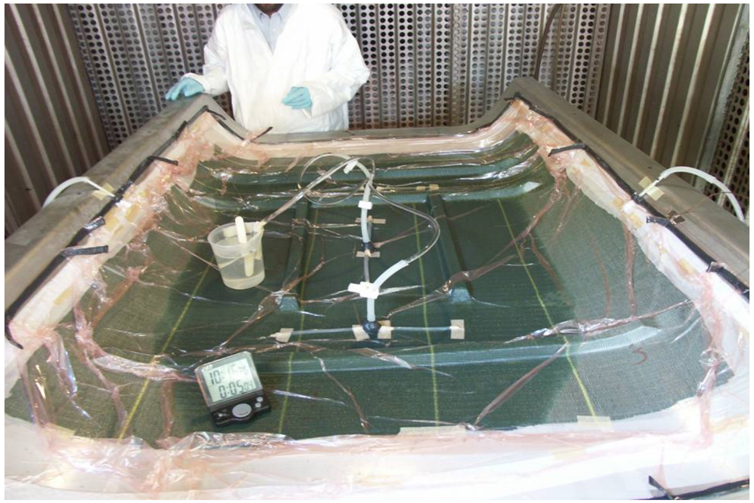
ADVANCED COMPOSITES CENTRE FOR INNOVATION & SCIENCE

Thermosetting resins and their composites



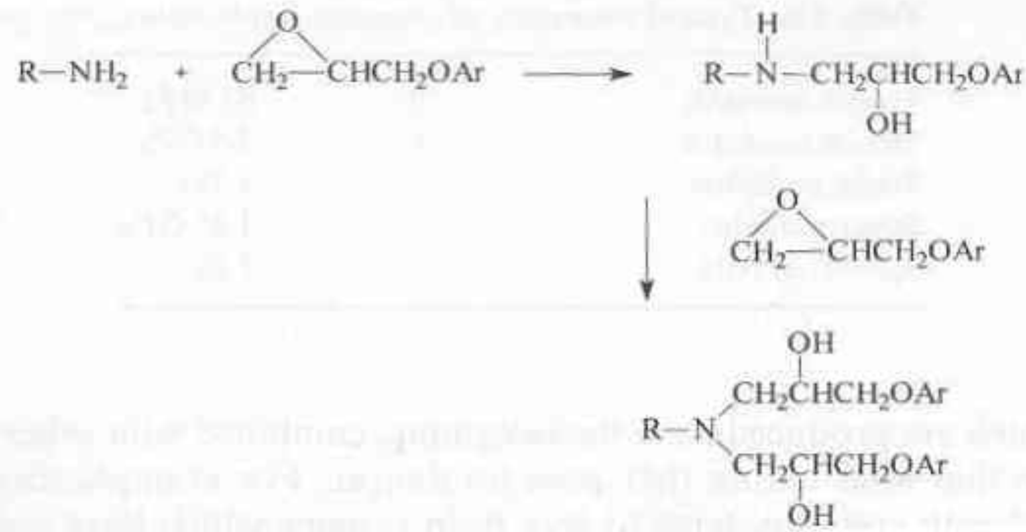


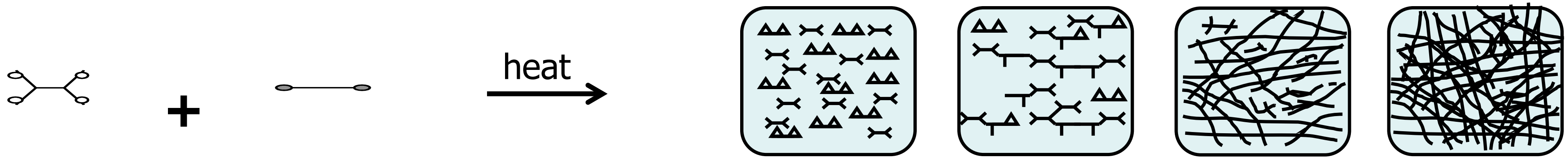
- The **curing reaction** of the resin is a critical process in composites manufacturing.
- Physico-chemical effects can be followed by process monitoring techniques, such as **dielectric sensing**

Thermosetting resins and cure reaction

Resin chemistry complex and usually unknown

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

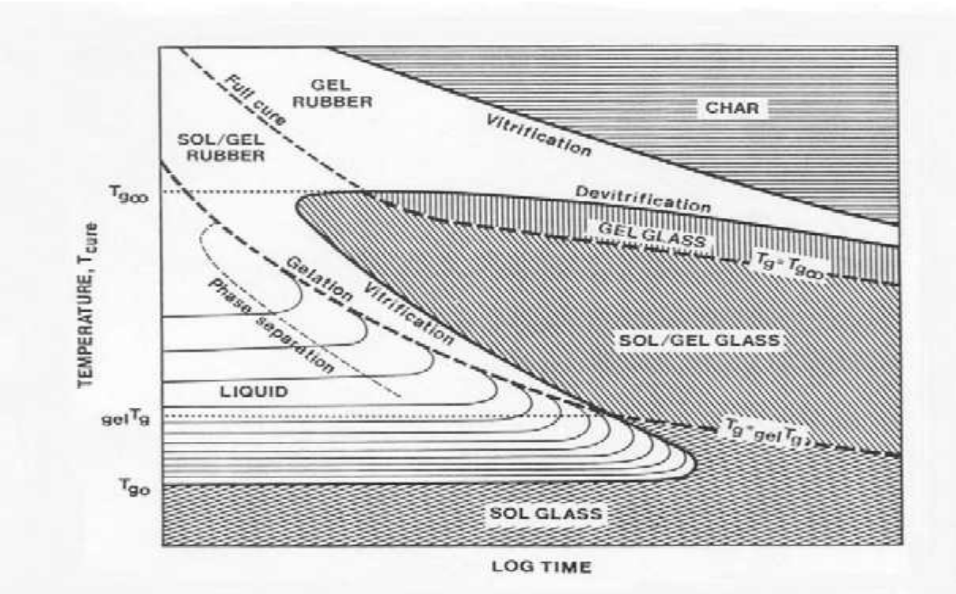


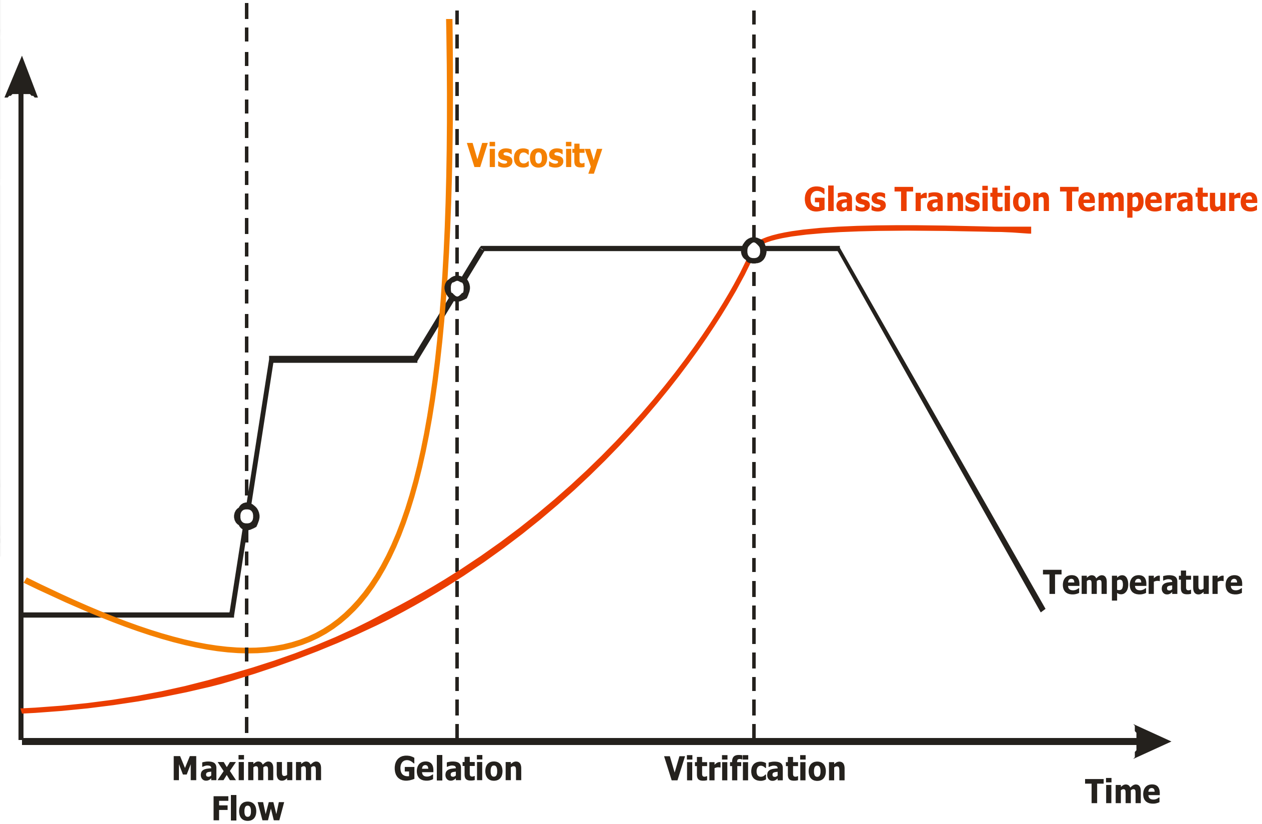


Unreacted resin	Curing reaction	Gelation	Vitrification
Liquid	**Liquid**	**Rubber**	**Glass**

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

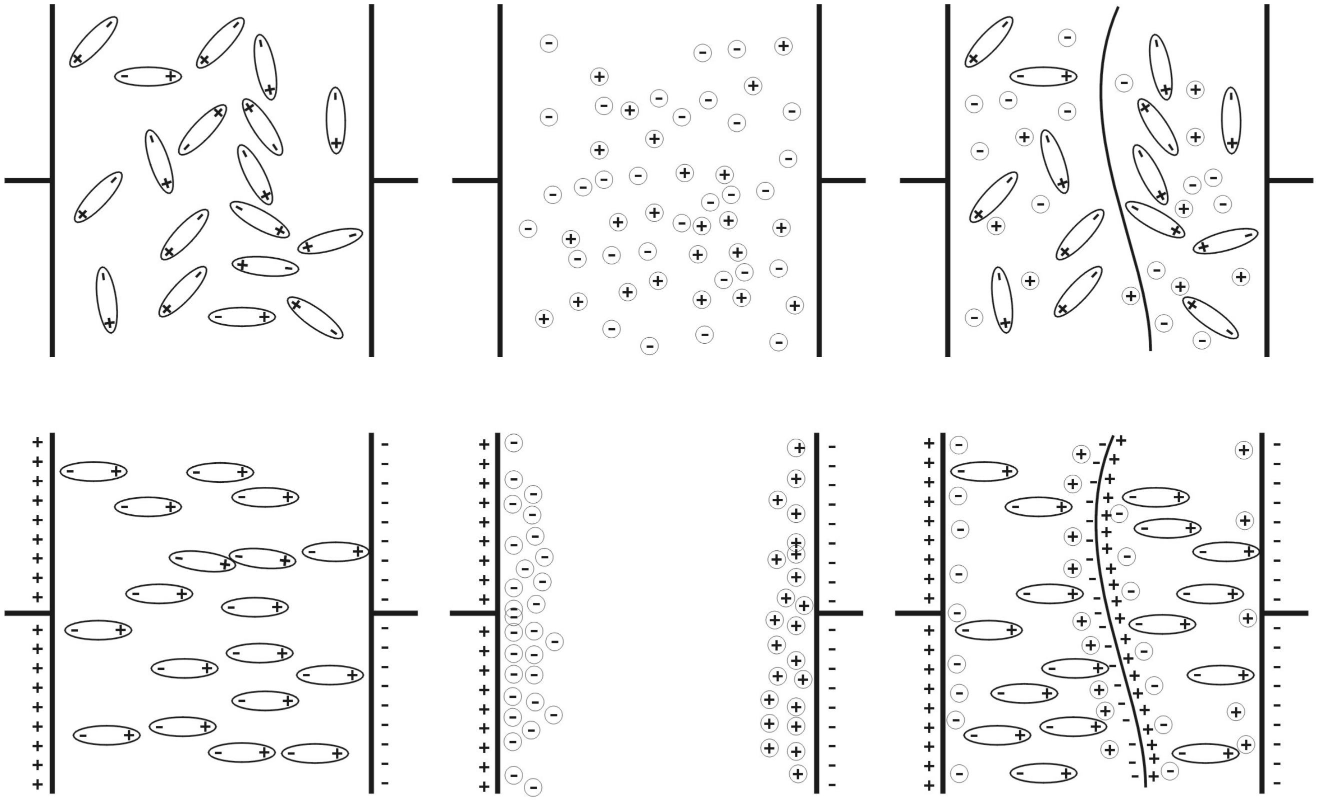
- **Vitrification**

  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



No field, E=0

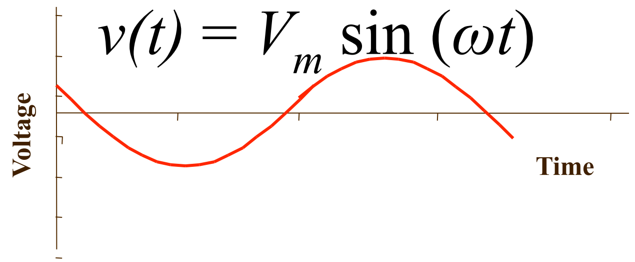
Main contributions in resin systems: from ions and interfaces

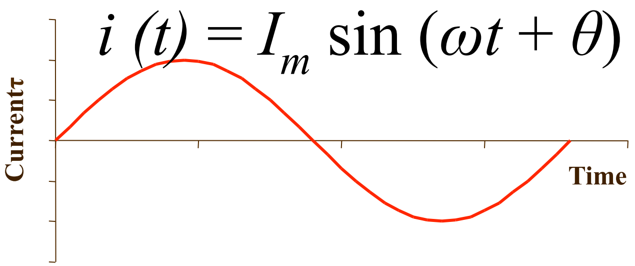
Applied field, E>0

The charged species respond differently at various frequencies in the spectrum

Dielectric measurements

Signal analysis and property derivations





$$v(t)/i(t) = |Z|, \theta$$

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

Circuit analysis

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

C-R parallel circuit analysis

$$R_p, f, geometry \rightarrow \varepsilon''$$

$$C_p, \varepsilon'', f, geometry \rightarrow \varepsilon'$$

Interdigital sensor calibration

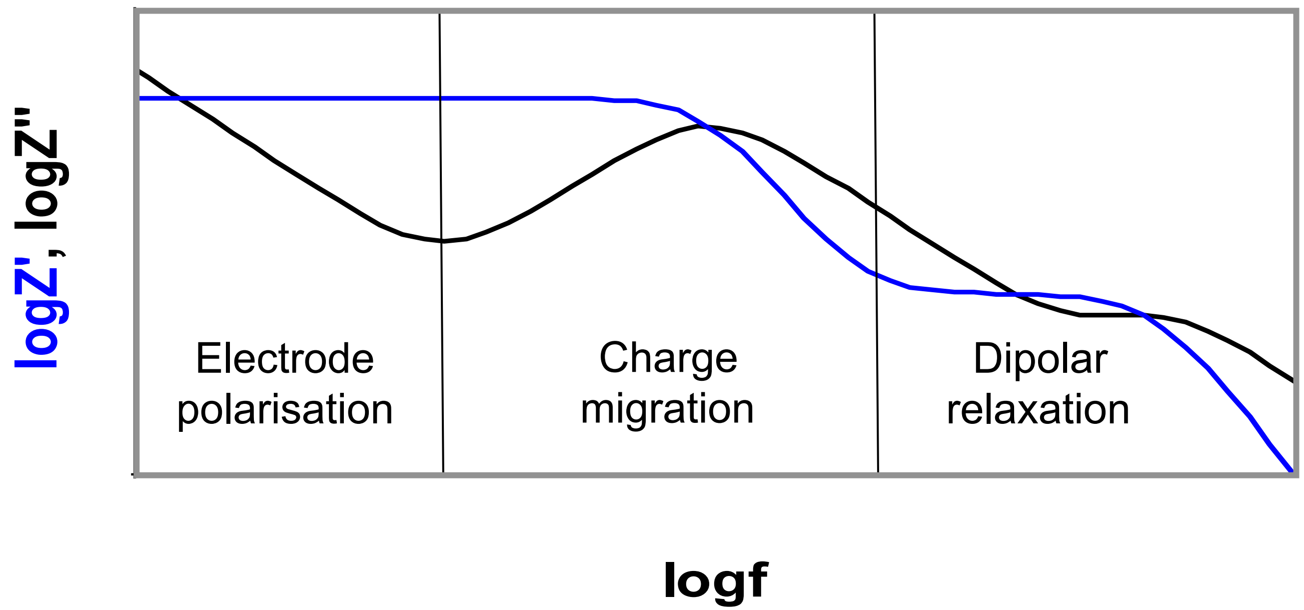
$$C_p, R_p \rightarrow \varepsilon', \varepsilon'' \rightarrow \varepsilon', \sigma$$

Derivation of conductivity

Moving from circuit properties to material properties

Dielectric cure monitoring

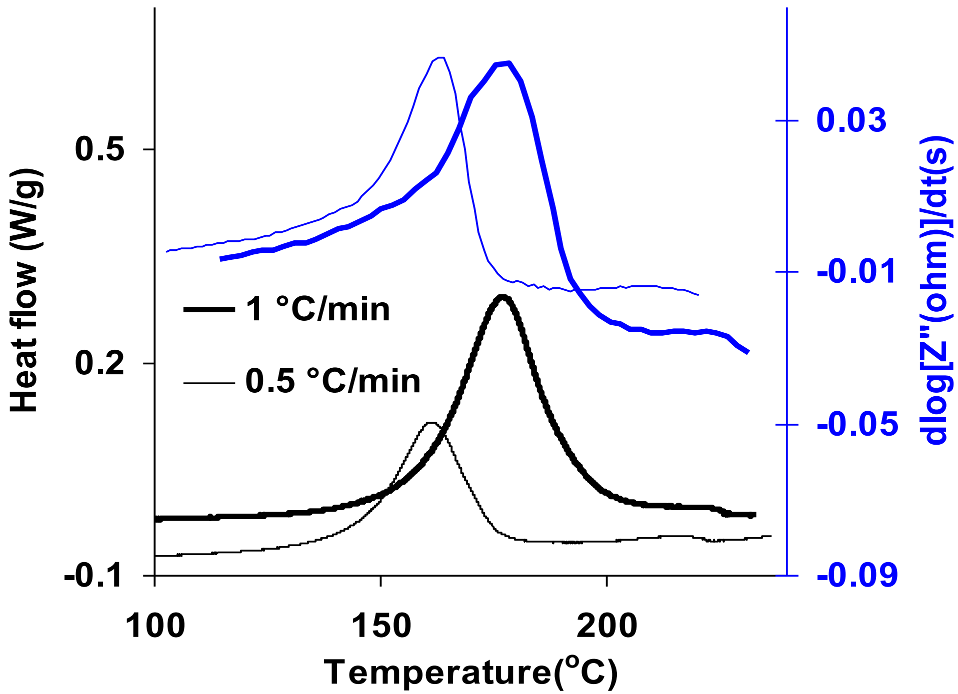
Impedance representation

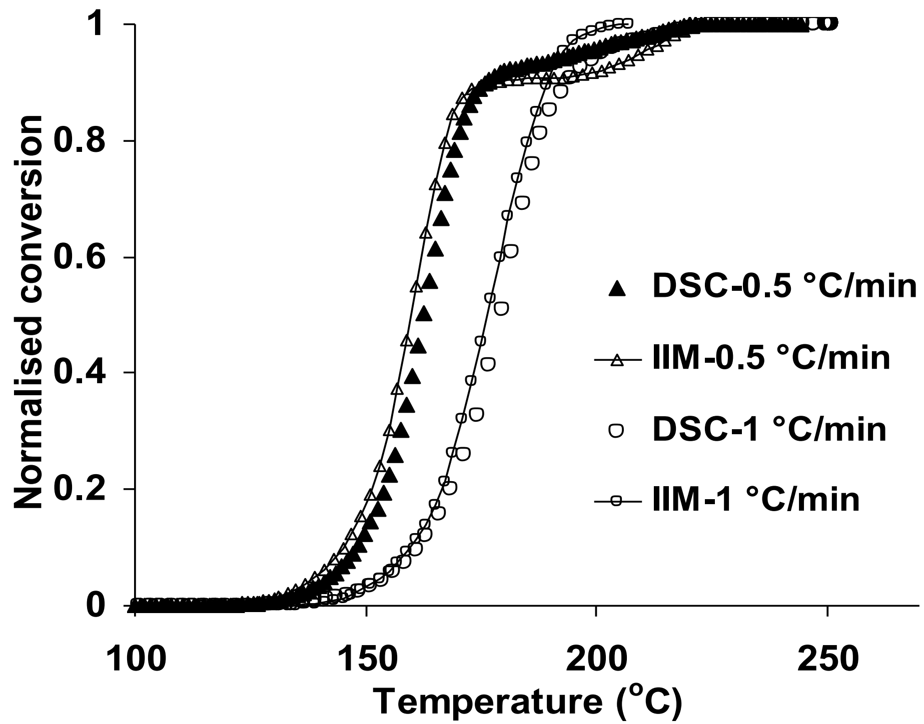


- Minimum, maximum and shoulder in the imaginary impedance spectrum
- Two plateaus in the real impedance spectrum

Dielectric cure monitoring

Degree of cure estimation under dynamic conditions



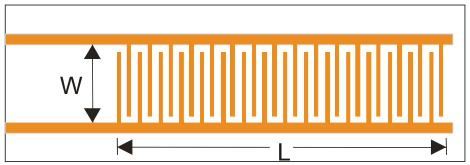


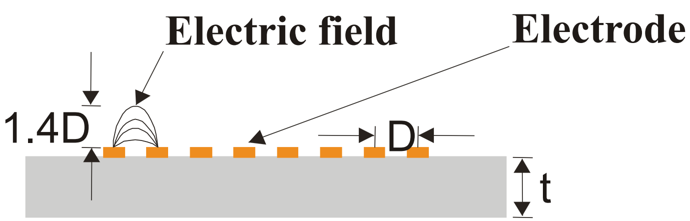
Commercial epoxy

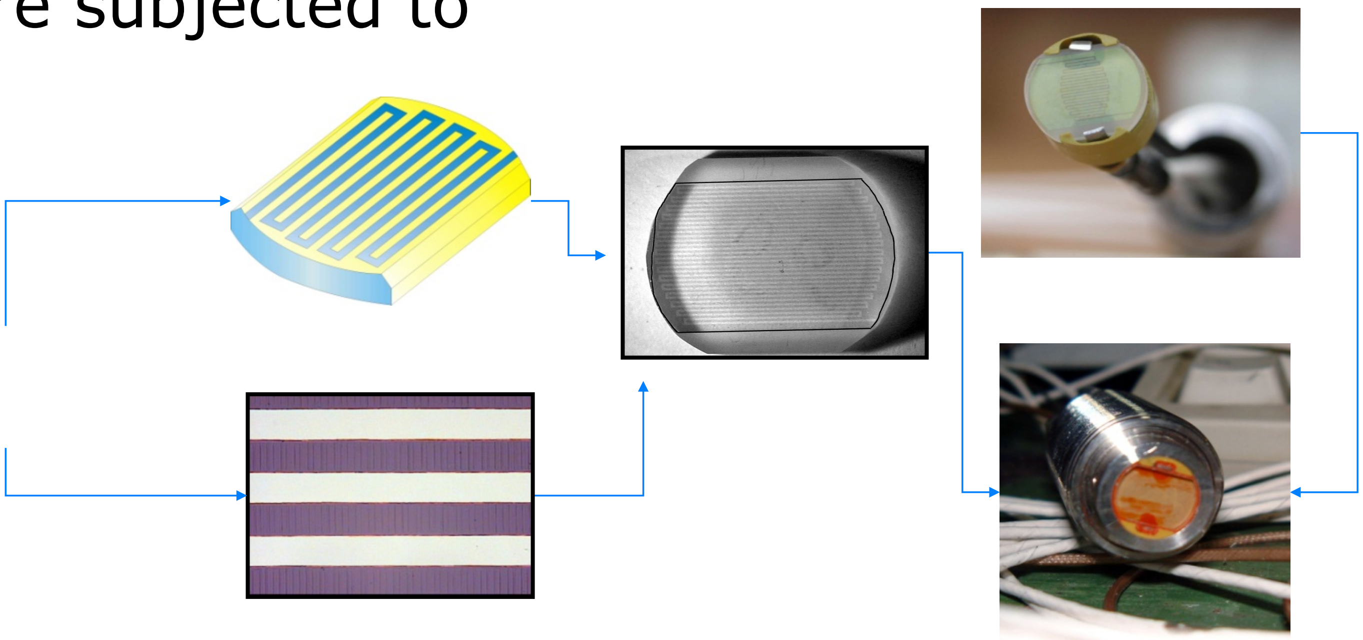
Sensor development

<u>Dielectric sensor</u>: 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







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

Always require protection against shorting out on conductive fibres

Application to composites processing

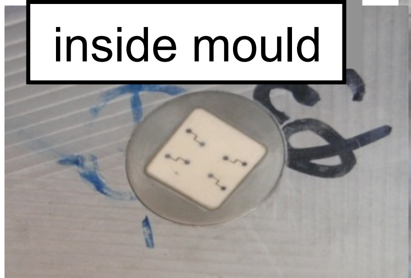
Installation of monitoring system in composite processing tools

RTM moulds

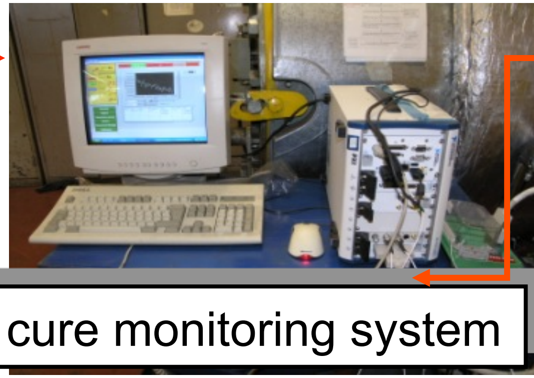
(IAI, Israel)

underside of mould

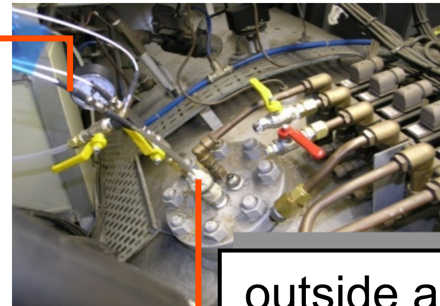
inside mould



autoclave (Bombardier UK)



cure monitoring system

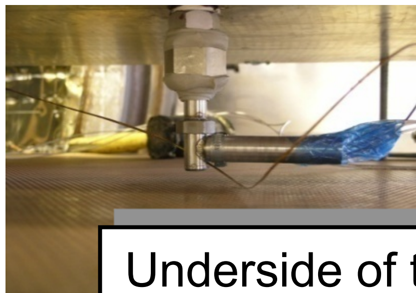


outside autoclave

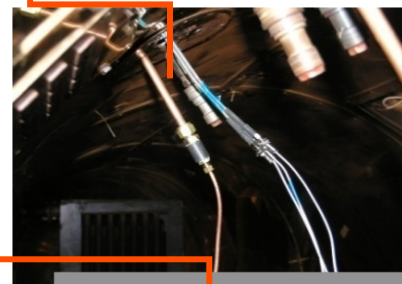
Sensor at die exit

pultrusion

(Excel, UK)



Underside of tool

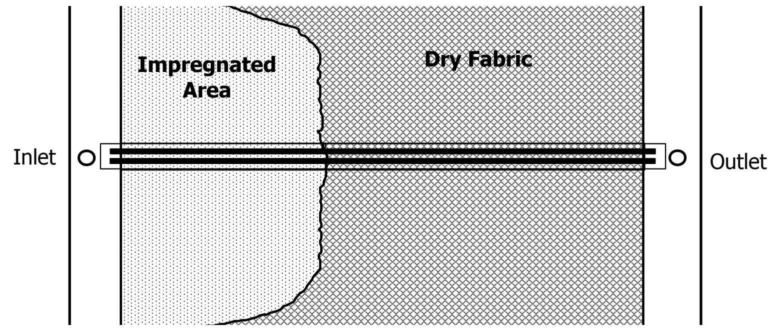


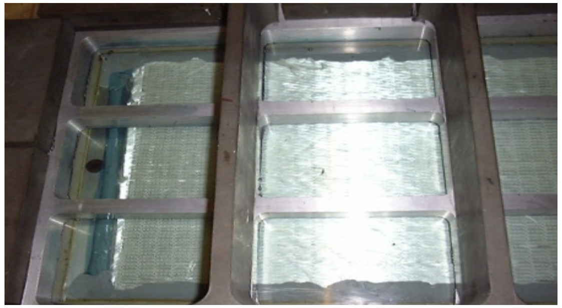
Inside autoclave

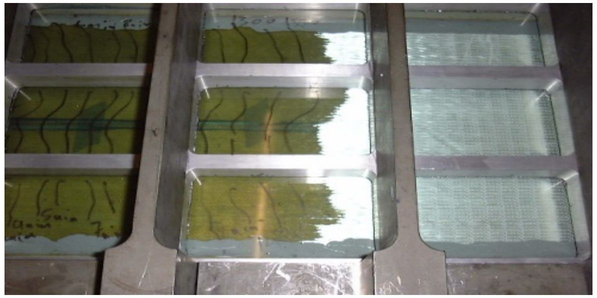
(Images supplied by INASCO)

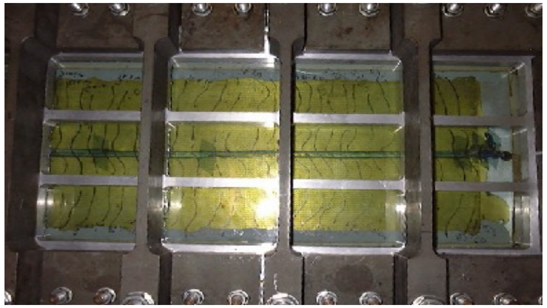
Resin flow monitoring in Resin transfer moulding

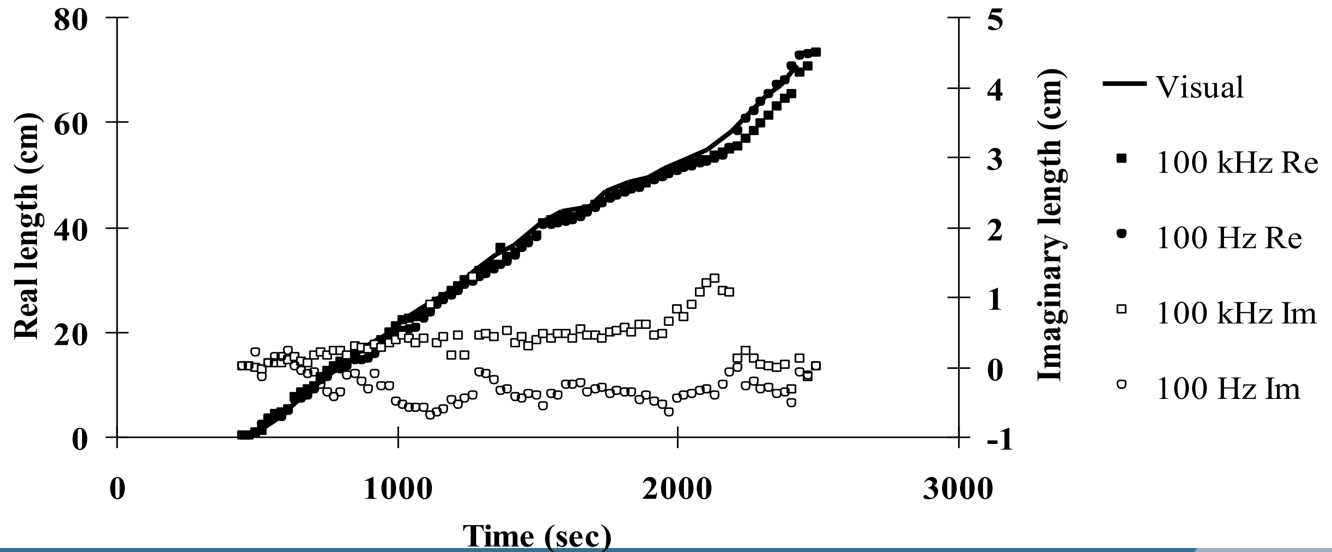
Dielectric lineal sensor in non conductive reinforcement



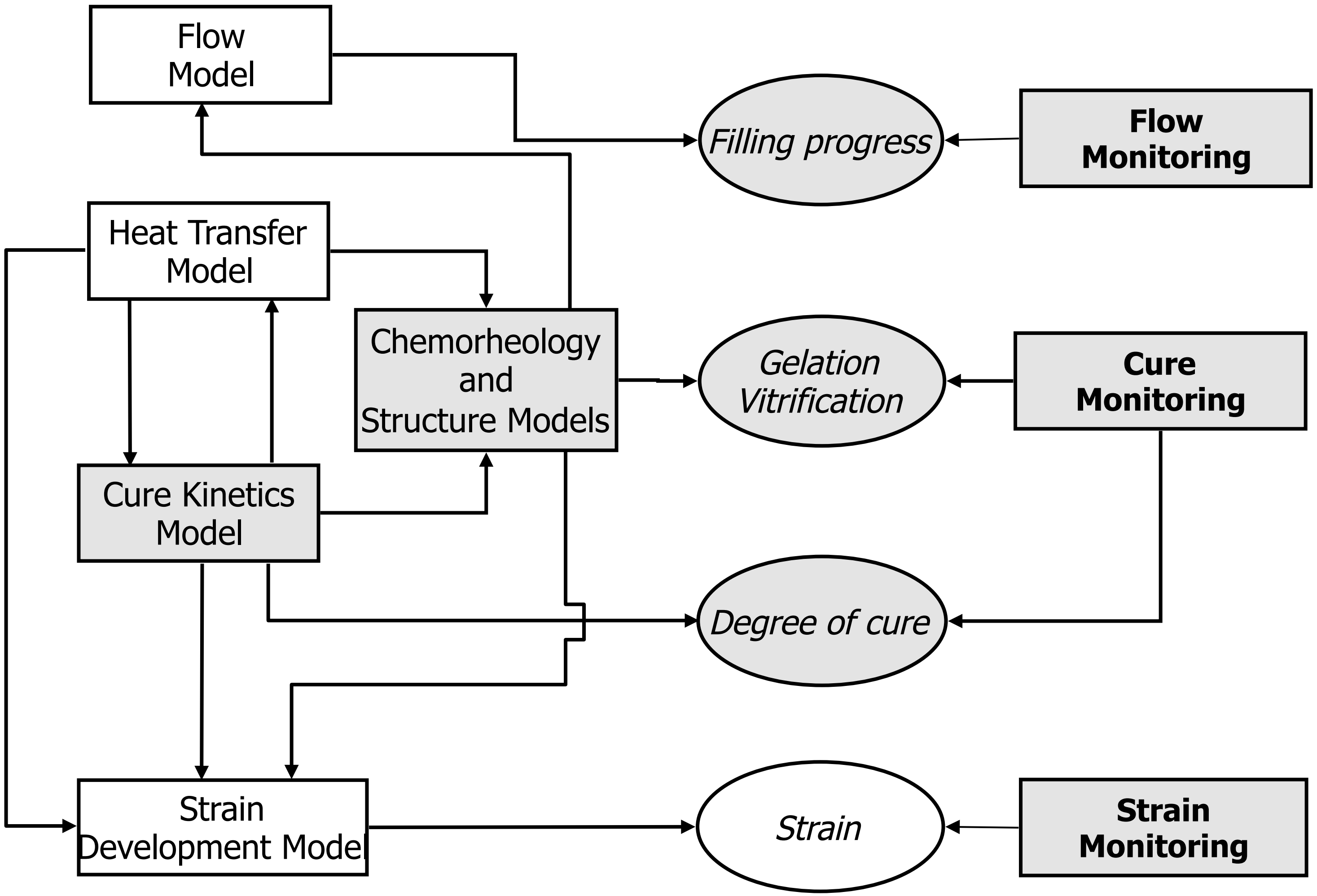








Modelling and monitoring



Towards feedback loop control

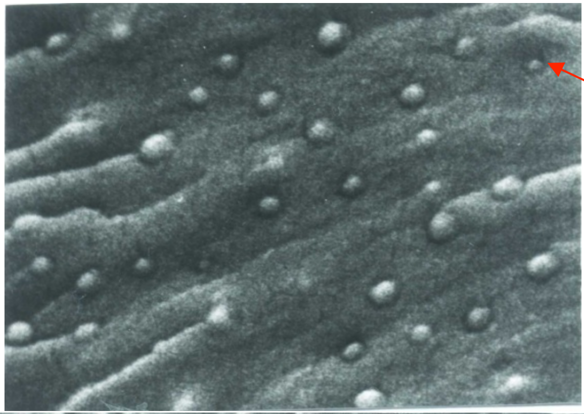
Cure monitoring system also controls the oven heating/cooling.
Material properties in current database:

- **Degree of cure**
- **Viscosity advancement**
- **Tg advancement**

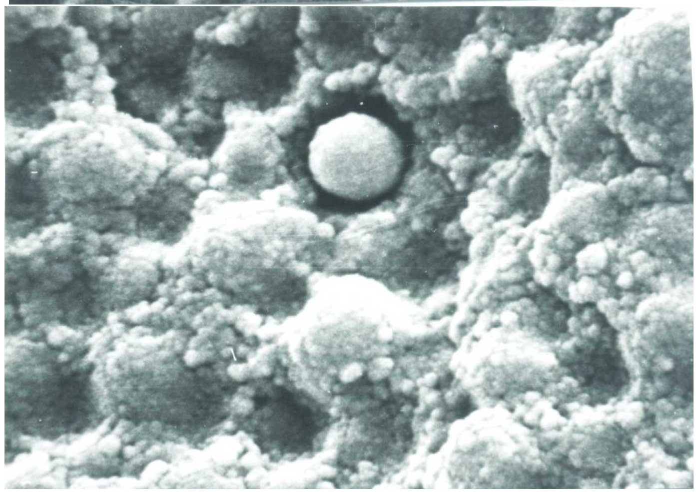
User defined cure cycle
Material property evolution in real time.

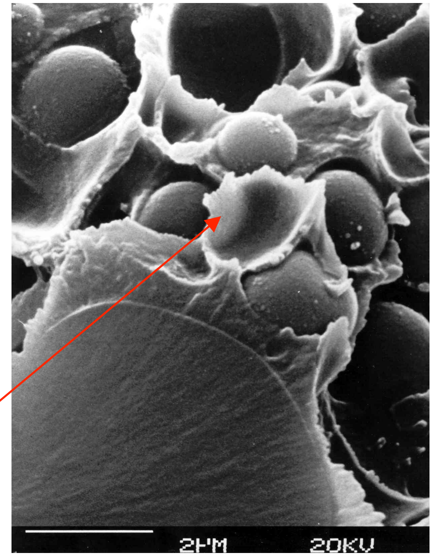
INASCO dielectric cure monitoring equipment and controlled oven, Airbus UK/National Composites Centre

Matrices for high performance composites



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

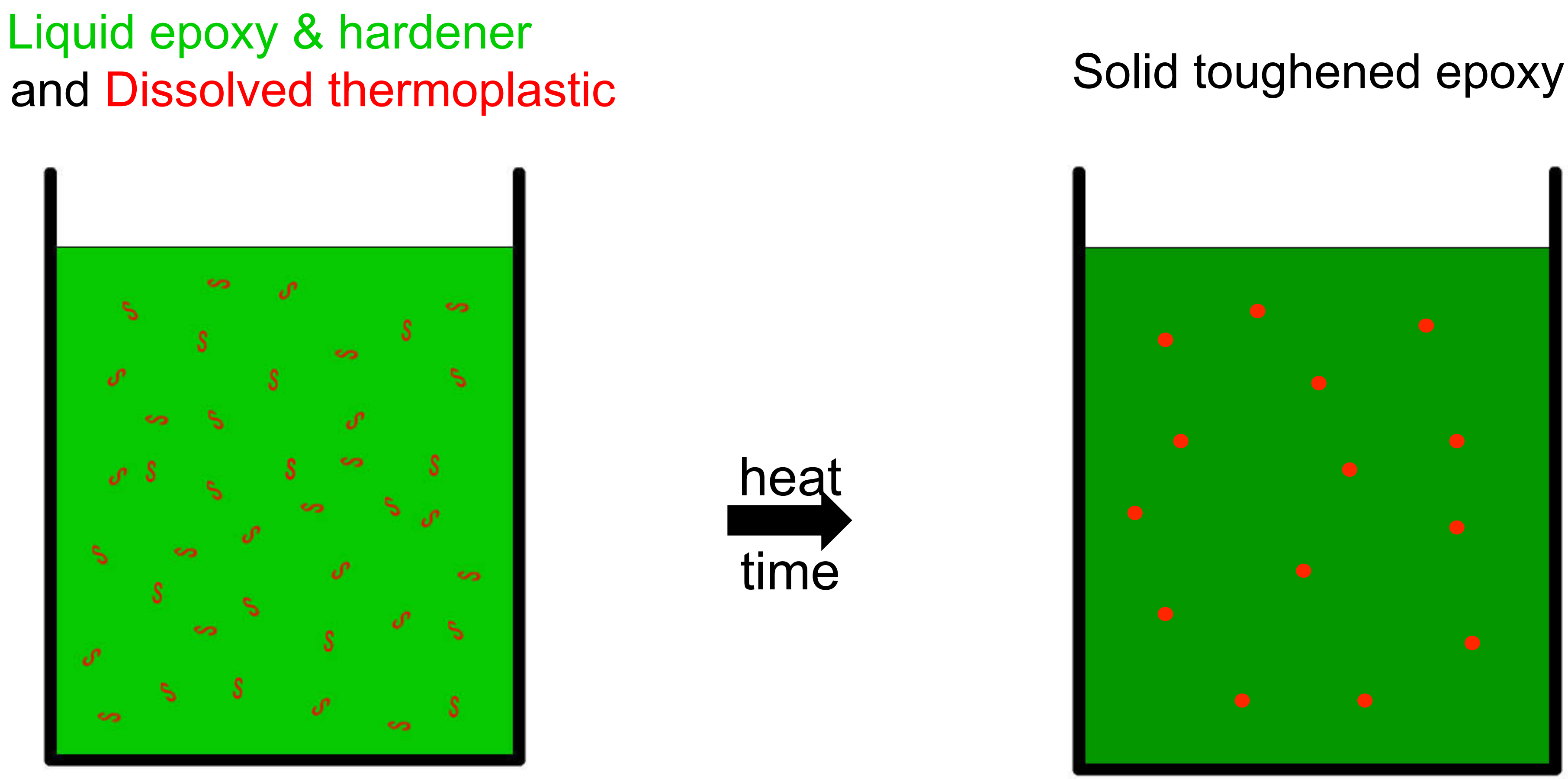




Or 'phase inverted' structure such as in TGDDM epoxy/ PEI thermoplastic

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



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

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School of Industrial and Manufacturing Science, Cranfield Institute of Technology, Cranfield, Bedford MK43 0AL, UK
(Received 30 April 1991; revised 23 January 1992; accepted 13 March 1992)

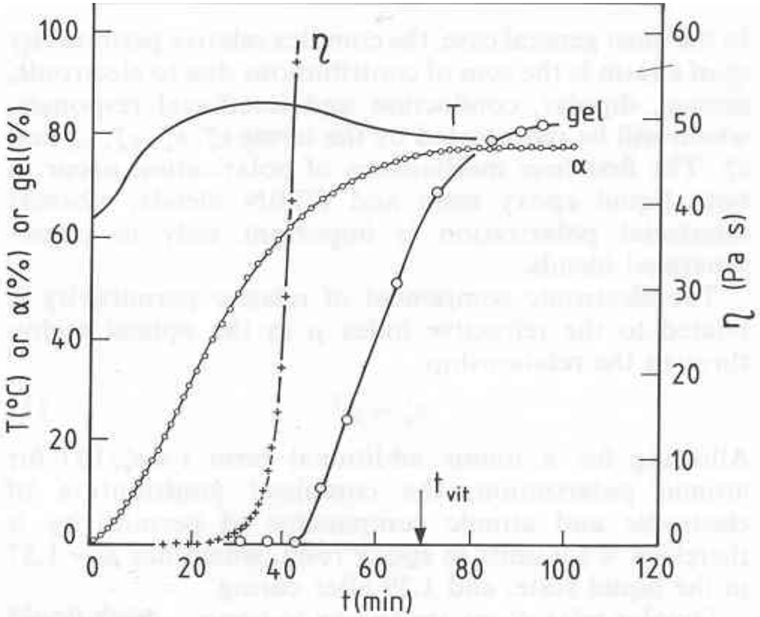


Figure 1 Variation in temperature T of the dielectric sample cell during cure of the neat resin at an oven temperature of 80°C, compared with conversion α, gel fraction and viscosity η for the same system, also at a nominal cure temperature of 80°C. The cure time, t_{vit}, to reach T_g was obtained from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

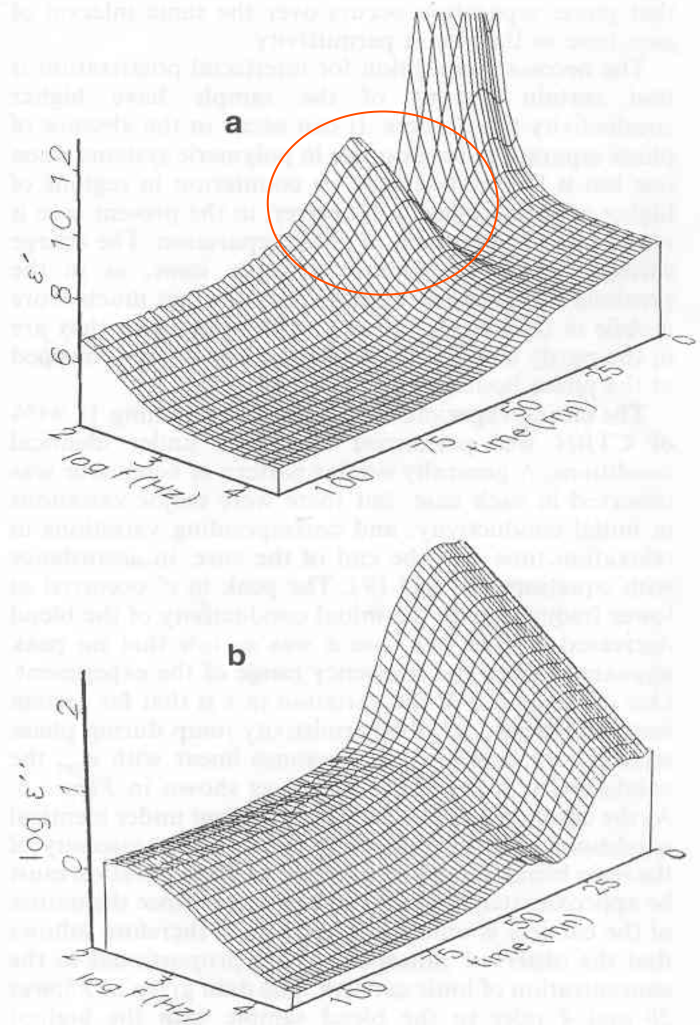
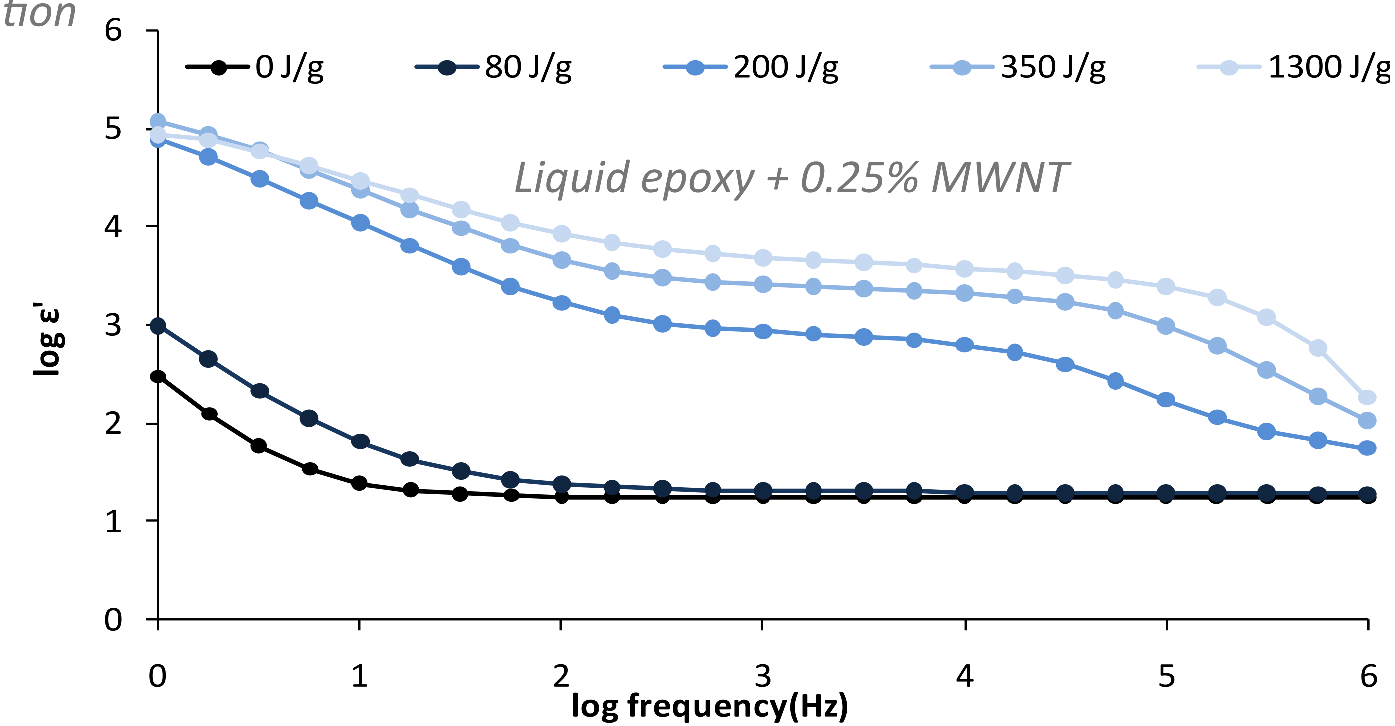
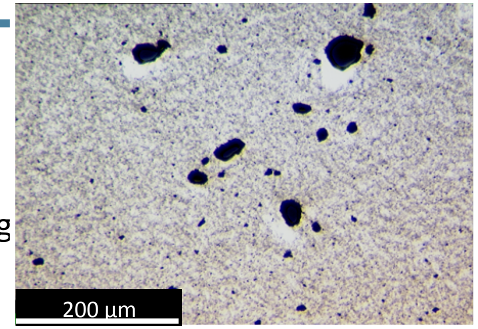


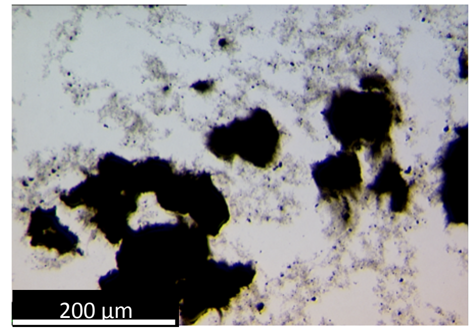
Figure 4 Dielectric data on the blend of epoxy resin and hardener with 15 wt% CTBN rubber, cured at 80°C. Plots of: (a) relative permittivity ε', and (b) dielectric loss ε'', against frequency and cure time. Sample contains highest concentration of adventitious mobile ions (see *Figure 5*). Note that scales for ε' and ε'' are different from *Figure 3*

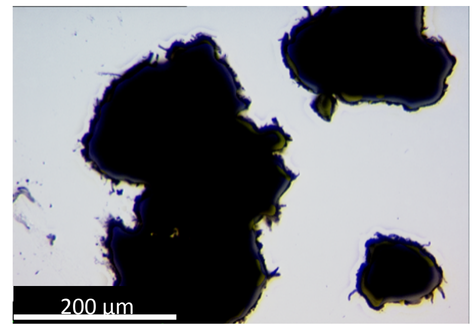
Dispersion monitoring in epoxy/CNT

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 University

Future applications ?

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…….