

Dielectric Cure Monitoring and Optimisation in RTM

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SUMMARY: This study demonstrates that the cure process of thermosetting resins can be followed in real-time and *in situ* by the use of the dielectric cure monitoring method. The method, which relies on the interrogation of fully wetted dielectric sensors, is capable of determining the significant points during isothermal cure reactions: the point of maximum flow, the gel time and the endpoint of the cure. The most appropriate property for this determination is the ionic conductivity. Based on the ionic conductivity signal, the cure process is divided into four distinct phases, taking into account non-isothermal curing. The temperature changes are either imposed by the process control environment or created from the exothermic nature of the process. The suitability of the technique for process control of the cure is discussed together with the application of the dielectric cure monitoring method in closed mould liquid composite moulding (RTM). At the present paper the system is tested for the RTM production using E-glass fibre reinforced polyester matrix.

KEYWORDS: Cure monitoring, Dielectric sensors, Polyester, RTM.

INTRODUCTION

Previous work [1] has shown that the cure process of thermosetting resins in an autoclave processing environment can be followed in real-time and *in situ* by the use of the dielectric cure monitoring method. The ultimate aim is to provide intelligent process control of composite manufacturing processes, including Resin Transfer Moulding (RTM). To achieve the process control, the dielectric monitoring response has to be combined with models of thermoset cure [1, 3]. These mathematical models convert the time-temperature profile of cure process environment to the resin viscosity ζ and the glass transition temperature T_g and reflect the kinetics and the molecular structure formation in the thermoset resin matrix. The importance of this approach is that on one hand the models are validated in real-world applications, but on the other hand the dielectric signal can provide reliably and in real-time the important process milestones, which are the point of resin maximum flow, the gel point and the vitrification time [2].

The dielectric method relies on the use of microelectrodes embedded into the monitored composite panels. They are flat capacitive interdigitated sensors producing a fringing electric field over their active surface [1]. The depth to which the electric field penetrates in the component varies from 30 to 300 μm depending on the sensor inter-digit spacing, D , as shown in figure 1. In case of conductive carbon fibres these are kept away from the active sensor surface by using a thin porous PTFE film. Multiple sensors can be embedded in different positions in a component and interrogated, in real time, during the cure process. AC Voltage of 1V rms is applied to the sensors via a Solartron 1260 impedance analyser and the resulting current intensity is compared to the voltage in respect to amplitude ratio and phase difference. The frequency of the measurements ranges from 1 Hz to 10 MHz. Capacitance and conductance throughout the frequency cycle are acquired, at fixed time intervals covering the whole cure cycle. Temperature readings can also be taken from thermocouples placed near the dielectric sensors. Data acquisition control is made using the DiAMon[®] software developed by INASCO UK Ltd. for manufacturing applications. The software transforms the

capacitance and conductance measurements to permittivity ϵ' and dielectric loss ϵ'' using sensor specific calibration equations and simultaneously calculates the resin viscosity and glass transition temperature from the relevant thermoanalytical models discussed previously. The RTM mould was instrumented appropriately to allow the use of the dielectric sensors. The wires carrying the electric signal from and to the analyser pass the mould plates through a custom-made channel. The length of cables is compensated by separate measurements directed by the control software. The temperature readings are taken simultaneously to the dielectric readings via an independent measurement circuit.

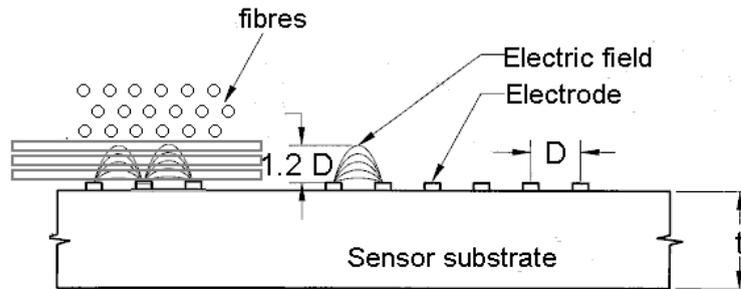


Figure 1. The dielectric sensor geometry, the produced electric field and the position of the sensor within the cure environment.

DIELECTRIC MONITORING SYSTEM

The dielectric monitoring system can be divided into three subsystems: the hardware, the control software and the sensors. The division is both perceptual and functional. Each subsystem is described separately, but there are strong interdependencies as far as the monitoring operation is concerned.

Hardware

The heart of the monitoring hardware is the impedance analyser or frequency response analyser. This equipment applies AC voltage (usually 1V rms) over the circuit and monitors the resulting current intensity. The frequency of the AC signal ranges from 1 Hz to 1 MHz. By the comparison between the outgoing and incoming signals (amplitude gain and phase difference), the electrical properties of the circuit are measured (capacitance and conductance) and the properties of the material in the vicinity of the dielectric sensors are obtained, as described later in this section. The interrogation of multiple sensors requires the use of an external multiplexer in direct connection to the dielectric analyser, as shown in Fig.2.

The wires carrying the electric signal from and to the analyser pass the autoclave shell by purpose-built copper connections. The overall length of the cabling from the analyser to the connections on the sensors depends on the autoclave size, but typically is around 3 meters. The effect of the cabling on the overall signal is compensated by separate measurements directed by the control software. The monitoring hardware uses a separate circuit for temperature measurements controlled and multiplexed by the Thermocouple box shown in Fig.2.

Dielectric Sensors

The dielectric monitoring method relies on the use of microelectrodes embedded into the monitored composite panels, as shown in fig. 2. The dielectric sensors are flat interdigitated capacitive electrodes and they consist of an insulating substrate and a conductive grid forming the active surface. The electric field produced when AC voltage is applied has a fringing shape over the active surface [4].

The depth to which the electric field penetrates in the component varies depending on the sensor inter-digit spacing, D , as shown in Fig. 1.

There are two commercial dielectric sensors used in this study and their particular characteristics are given in Table 1. It can be seen that the sensor with the PTFE substrate has a coarser grid than the sensor with the polyimide substrate resulting in a more disperse electric field and lower air capacitance (sensor background measurement) values. Effectively, the sensor protection acts as a filter allowing the resin to approach the sensor surface leaving the fibres out of the electric field. The chemical changes traced by the monitoring technique occur in the resin (matrix) phase and the effort is made to isolate any other medium with capacity of interfering with the resin electrical properties without affecting the cure chemistry and reaction mechanism.

Trade name	Material (conductor/substrate)	Thickness t (mm)	Interdigit spacing D (μm)	Sensing Area (mm) (W x L)	Cost	Distance: Sensing to soldering
Dek-Dyne	Cu/Polyimide	0.1	30	11 x 20	Medium	Very short
GIA	Au/PTFE	0.1	300	5 x 25	Low	Medium-Long

Table 1. Characteristics of the two dielectric sensors used in this study.

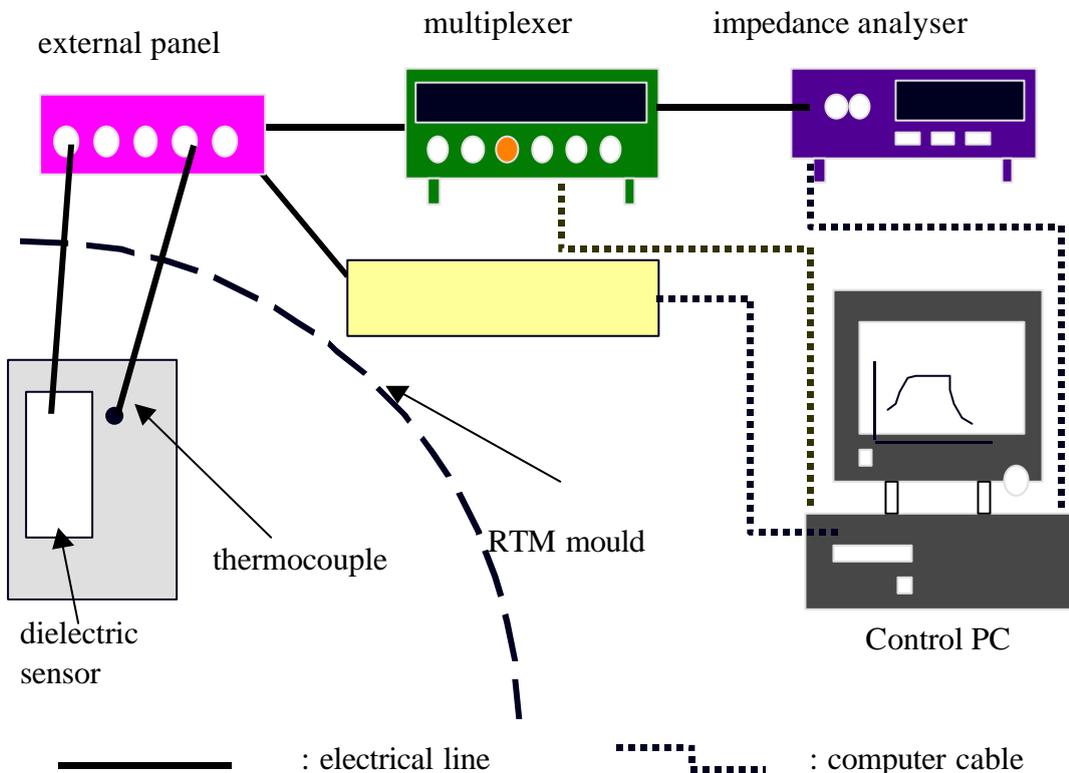


Figure 2. The components of the dielectric monitoring system for composites processing as attached to an autoclave.

Control Software

In the dielectric monitoring system sketched in Fig.2 the real-time data acquisition and analysis is made using purpose made software licensed by INASCO UK Ltd. The data acquisition is controlled by the software, which commands the multiplexer, the dielectric analyser and the thermocouple line. There are distinct readings of dielectric properties at selected time intervals. The sensors are interrogated as the multiplexer connects them one at a time. Typically a single cycle is made within 20 seconds, which is short enough for any considerable reaction to happen. The real-time determination of ionic conductivity, the significant points during the cure and the output from material science models are within the improvements planned for the new version of the cure monitoring software prepared by INASCO UK Ltd. The recording of the significant points in a sensor knowledge base [3] is also considered for inclusion in the new modules.

DIELECTRIC RESPONSE OF THERMOSET MATERIALS

The dielectric response of thermosets and of polymers in general arises from the presence of ions, dipoles and interfaces in the material and their behaviour in the applied electric field can be distinguished and separated [8]. In the following analysis each species will be examined separately and the basic features of the dielectric response will be highlighted. A complete analysis of the dielectric response and of the relevant models can be found in Senturia and Sheppard [5] and Maistros and Bucknall [8].

IONS IN THERMOSETS

Thermosets are inherently chemically impure materials and the presence of ions between the electrically charged species is predominant. The ionic effects become apparent in the dielectric loss signal from which the ionic conductivity is estimated. The ionic component of the measured dielectric loss, ϵ''_c , shows a reciprocal dependence on the test frequency, f :

$$\epsilon''_c = \frac{\mathbf{s}}{2\pi f \epsilon} \quad (1)$$

In Eq.1, \mathbf{s} is the conductivity in S/m, f is the test frequency in Hz and ϵ is the permittivity of free space (8.85 pF/m). The ionic conductivity is proportional to the ion concentration and to the ion mobility. As the resin viscosity reflects the mobility of the chain segments in the growing network of the curing thermoset, a very useful relationship exists between viscosity and ionic conductivity. The dielectric measurements during the cure process use the ions as a probe of the segmental mobility of the macromolecules, thus the relationship between viscosity and conductivity. It is proposed in [9] that the viscosity, \mathbf{h} , is inversely proportional to the ionic conductivity, \mathbf{s} :

$$\mathbf{h} = K \cdot \mathbf{s}^{-b} \quad (2)$$

where K and \mathbf{b} are resin specific and temperature dependent constants. For most resin systems the exponent \mathbf{b} takes values close to 1 [9]. This relationship is of great importance in the cure monitoring, since it is possible to measure, *in-situ*, the dielectric loss and thus the conductivity, but not viscosity. Senturia and Sheppard [5] observed that the conductivity does not fall to zero as viscosity tends to infinity after gelation. Therefore, it is expected that eq. 2 will begin to break down as gelation is approached ($\mathbf{h} > 10^4$ Pa's). The time in the resin cure when $d^2(\log \mathbf{s})/dt^2 = 0$ is the first evidence of a gelled system [1].

At the early stages of the thermoset cure, when the glass transition temperature (T_g) of the resin is a lot lower than the cure temperature (T), the temperature dependence of the viscosity is described by the Arrhenius equation:

$$\mathbf{h}_r = A \cdot e^{-E_a/RT} \quad (3)$$

where A is the pre-exponential factor, R is the universal gas constant and E_a is the activation energy in J/(mol.K). From Equations 2 and 3, it is derived that the ionic conductivity, \mathbf{s} , also

follows the Arrhenius temperature dependence.

DIPOLES IN THERMOSETS

As mentioned above, the ionic species are dominant in thermoset materials and they are responsible for the high values of dielectric loss exhibited by thermosets. The dipolar portion of the dielectric loss is swamped by the ionic losses as will be shown later. Therefore, only the permittivity values can be used to extract information on the number and the mobility of dipoles. The dipole contributions to permittivity can be separated from the ionic and interfacial components [8] and can be described by the widely used Cole-Cole equation:

$$\mathbf{e}'_d = \text{Re}(\mathbf{e}^*) = \text{Re}\left(\frac{(\mathbf{e}_0 - \mathbf{e}_\infty)}{1 + (i\omega\mathbf{t}_0)^b} + \mathbf{e}_\infty \right) \quad (4)$$

In Eq.4, ω is the angular frequency, \mathbf{e}_∞ is the infinite frequency permittivity, \mathbf{e}_0 is the static permittivity and b is the parameter representing the distribution of dipole relaxation times around the average value \mathbf{t}_0 .

By examining the evolution of the permittivity during isothermal cure reactions of epoxy resins, it was observed that [1]:

- (i) the infinite frequency permittivity \mathbf{e}_∞ is independent of cure time and temperature and ranges between 2 and 4;
- (ii) the static permittivity \mathbf{e}_0 is linearly dependent on the degree of cure (\mathbf{a}) and decreases with increasing temperature

$$\mathbf{e}_0 = \frac{D_1}{T} + D_2 - D_3 \cdot \mathbf{a} \quad (5)$$

where D_1 , D_2 and D_3 are resin specific constants;

- (iii) the changes in the average relaxation time \mathbf{t}_0 reflect changes in the resin T_g according to the following equation:

$$\log \mathbf{t}_0 = \log \mathbf{t}_A + c \cdot T_g^2 \quad (6)$$

INTERFACES IN THERMOSETS

The low frequency response of thermosets, especially at early stages in the cure process, is dominated by the accumulation of blocking charge at the electrode surface. This effect is called electrode polarisation. The blocking charge is formed by mobile ions situated permanently on the electrode surface capable of travelling between the alternating polarity electrode fingers. The net effect is a permittivity component, $\Delta\mathbf{e}'_c$, modelled by Day et al [10] and expressed by the following equation, simulating a capacitor with electrode spacing L and blocking layer of thickness t_b :

$$\Delta\mathbf{e}'_c = \mathbf{e} \left(\frac{S^2(B-1)}{S^2 + B^2} \right) \quad (7)$$

where $B = L/2t_b$, $S = \mathbf{e}'/\mathbf{e}'' = \tan\delta = \mathbf{d}/\mathbf{e}\mathbf{e}_0\omega$, and \mathbf{e}' and \mathbf{e}'' are the permittivity and dielectric loss of the bulk dielectric.

When the fibre reinforcement is kept outside the electric field, it is believed that there is no contribution to the dielectric signal from heterogeneous interfaces arising from the fibres. The same way interfacial polarisation attributed to the creation of a second phase within the thermoset matrix [11] is thought to be negligible compared to the blocking electrode polarisation and dipole relaxation components of the dielectric signal.

DIELECTRIC CURE MONITORING RESULTS

The primary dielectric properties, permittivity and dielectric loss, measured in real-time are frequency and time dependent. The most convenient and comprehensive way to represent the

changes these properties undergo during cure is a 3-D surface plot, where the dielectric property is placed on the z-axis, while time and frequency make the x-y plane [6]. The dielectric cure monitoring system has been installed at the National Technical University of Athens (Figure 3) and tests are being performed in a flat circular mould and in a more realistic box-type part with fibre glass preforms and unsaturated polyester without any additional heating. The unsaturated polyester needs an initiator in order the curing cycle to be initiated. However, at the present case, lower percentage of initiator (0.8 %) than usual (1.5%) has been used on purpose to avoid exactly the premature start of the gelation and the curing phase.



Figure 3. The dielectric cure monitoring system (left) and the RTM mould (right).

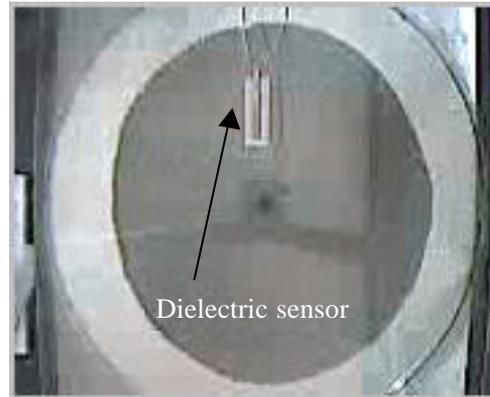


Figure 4. The circular transparent mould with the dielectric sensor partially filled with polyester (central gating).

Figure 5 shows a 3-D plot of permittivity with respect to frequency and processing time for the cure of the polyester in the RTM mould using the PTFE dielectric sensor.

RTM processing on circular test-bed

Polyester with 0.8 phr initiator and 38.5% fabric

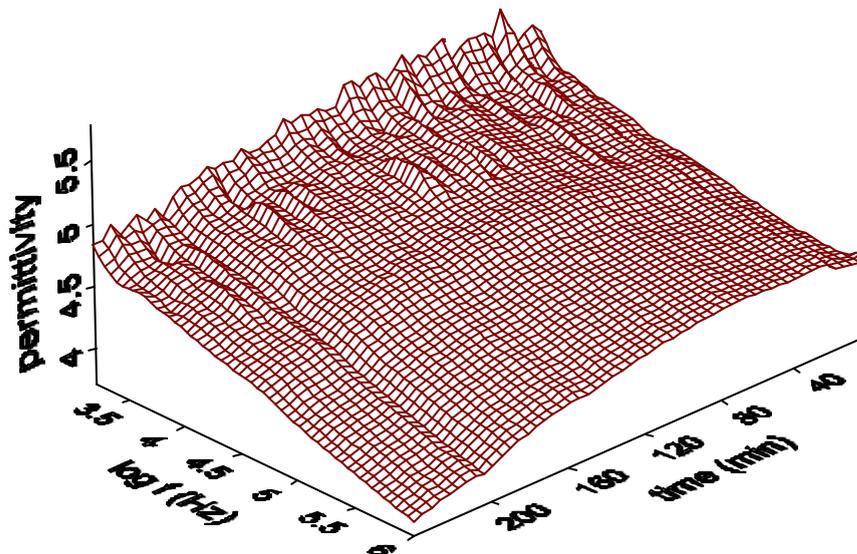


Figure 5. The 3-D representation of the changes of permittivity against logarithmic frequency and time for the cure profile of unsaturated polyester.

The permittivity data reflect clearly the changes in dipole mobility during the polyester cure reaction. It is evident that the reaction proceeds right from the start of monitoring and the crosslinking is progressing even at the end of the monitoring. The gradual change of the permittivity values is indicative of the drop of the static permittivity (ϵ_0 in Eqs. 4 and 5) as the degree of cure α is increasing. The strong frequency dependence of the permittivity at the final time slot (change of more than 1 unit across the frequency spectrum) indicates the presence of a relaxation process. The modelling of the observed relaxation by means of average relaxation time and relaxation time distribution function requires the regression analysis of Eq. 4 and the determination of τ_0 and β .

Figure 6 shows a 3-D plot of dielectric loss for the cure of the polyester in the RTM mould using the PTFE dielectric sensor. The basic features of this dielectric loss diagram are:

- the dominance of the ionic contribution at low frequencies ($f < 1$ kHz), as shown by the straight-line dependence (of slope -1) between $\log e''$ and $\log f$, and
- the increase of dielectric loss at high frequencies resulting from dipole contribution to the signal. There is correspondence of this observation to the strong frequency dependence of permittivity at the same period in the process. The dielectric loss signal tends to level off at all frequencies at the end of the monitored process, thus indicating the drop in the reaction rate.

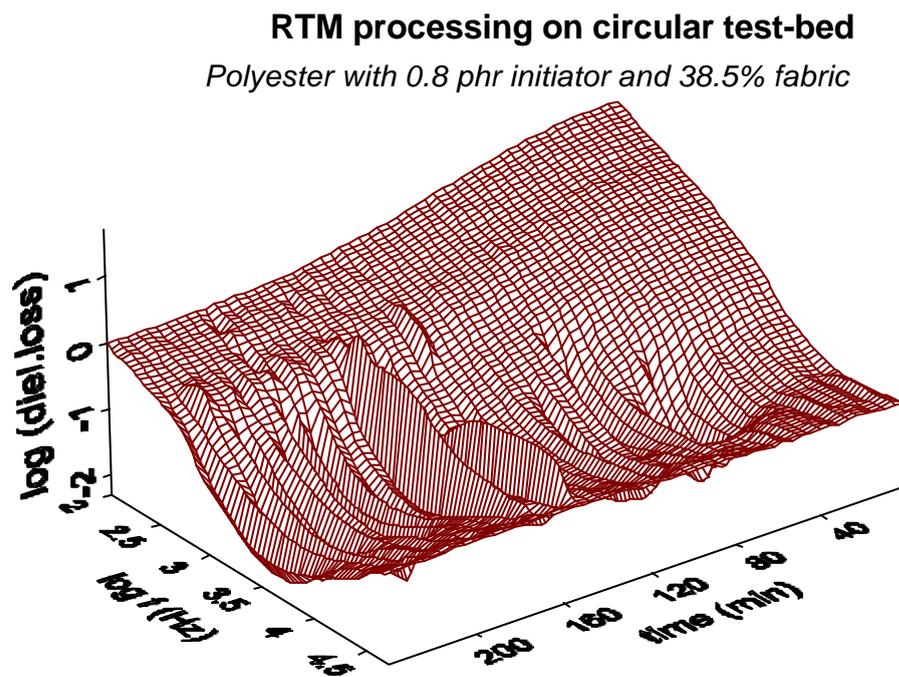


Figure 6. The 3-D representation of the changes of logarithmic dielectric loss with respect to frequency and time.

The most descriptive dielectric property is the ionic conductivity [13]. The main advantage lies in its frequency independence. The ionic conductivity, \mathbf{s} , is derived from the frequency dependence of dielectric loss as expressed in Eq. 1. Another advantage for the composites processing is that \mathbf{s} reflects the changes of viscosity \mathbf{h} in a direct way. The dielectric sensor acts as an *in situ* rheometer in the heart of the processing environment when it measures values of \mathbf{s} in real-time and relates these changes to changes of resin viscosity. Consequently, the point of resin maximum

flow is near the occurrence of maximum conductivity while gelation occurs just before the point where $d^2(\log S)/dt^2 = 0$ [7] (Figure 7). It has been shown [8, 12] that when the cure reaction slows down the conductivity levels off. In reality, the conductivity continues to drop at a very slow rate even after the end of cure because this property is very sensitive even to minute changes in the mobility of ions.

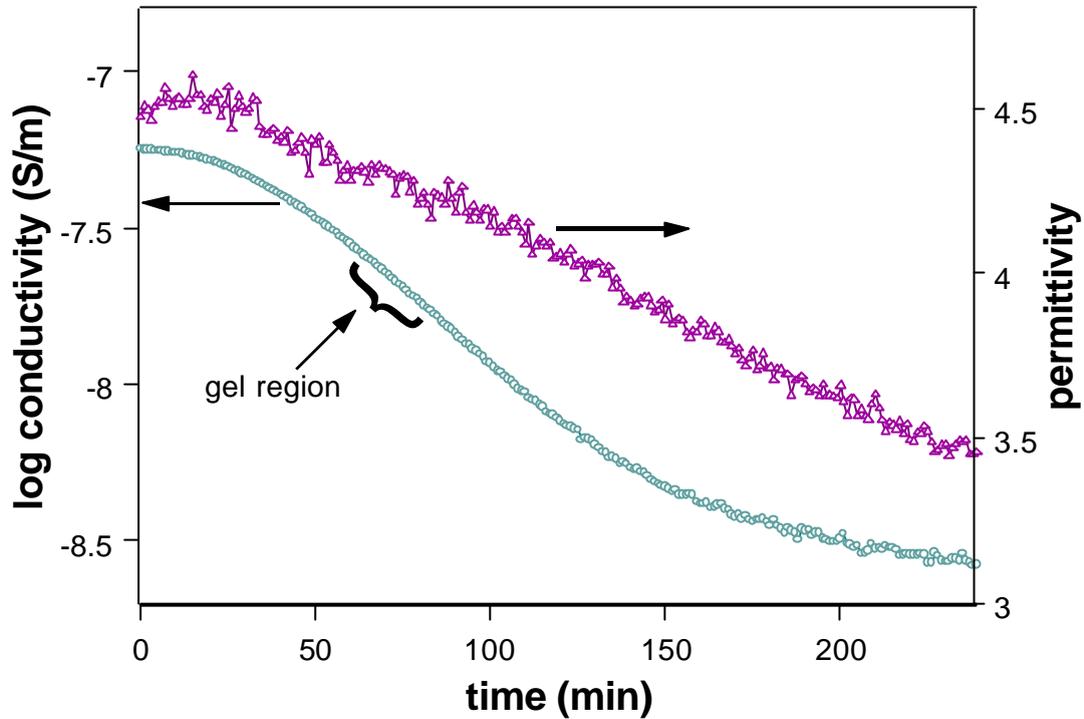


Figure 7. Conductivity and permittivity changes against time alongside the indication of the gel region. Permittivity values are measured at frequency $f=100$ Hz.

From the conductivity plot in Figure 7 and Eq. 2, it is evident that the resin viscosity is increasing as soon as the monitoring begins at the completion of the mould filling stage. To derive quantitative data on viscosity from the conductivity curve, the chemorheology model has to be developed and integrated with the dielectric results. However, it is obvious that the gel region for the polyester resin in the sensor vicinity is between 60 and 80 minutes into the monitoring. To pinpoint the gelation event with the dielectric monitoring the temperature data have to be considered and the temperature effects to be removed from the conductivity signal. Finally, it is obvious that the reaction rate drops significantly at the end of the monitoring period, as the conductivity values level off and the ionic mobility stops changing. The permittivity data reflect the same event as observed from the mobility of the dipoles. The permittivity values, which exhibited a steady drop during the cure process, approach the infinite frequency permittivity value (ϵ_{∞} in Eq.4) between 3 and 3.5. This value approximates the square of the resin refractive index.

The basic features of the conductivity signal are the time locations of the maximum value, of the inflexion point during the drop (around gel point) and of the levelling off at the end of cure. These points are expected to change in the case of polyester resin cure with the catalyst concentration or with the part thickness, parameters affecting the heat transfer characteristics of the RTM process.

CONCLUSIONS

Concluding, the ionic conductivity is a property with a potential for process control of the composites cure. The dielectric signal provides information on the resin viscosity changes and provides a sensor independent platform on which the main material transitions are determined. Further work is carried to tune chemorheology and kinetic models of polyester resins to the real-time dielectric signal.

Furthermore, the optimum control of the curing phase either through optimal heating or through optimal mixing of the percentage initiator is the ultimate target of using dielectric cure monitoring and will be the main topic in the next years for the presented system.

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