Autoclave Cure of Composites: Validation of models using Dynamic Dielectric Analysis

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1. Background

Dielectric methods for monitoring thermoset cure have been developed recently and used to probe the different stages of resin cure in advanced composites processing [1-3]. The ultimate aim is to provide intelligent closed-loop control of RTM and autoclave processes. Changes in the dielectric behaviour of the resin under cure can give real-time and in-situ information on the advancement of the process parameters and the arrival at a desirable level of degree of cure.

This study concerns the development of a complex model scheme intended to combine the dielectric monitoring responses with models of thermoset cure. The essential features of this scheme are shown in Fig. 1. On the left hand side of the figure, mathematical models are used to convert the time-temperature profile of the cure process environment to the resin viscosity and the glass transition temperature, T_g. On the right hand side of the figure, real-time measurements from embedded dielectric sensors are used in combination with analytical dielectric models to predict the viscosity and the T_g of the resin at the vicinity of the sensors.

In this paper, each part of the overall scheme will be described separately, concentrating on the available study tools and giving selected examples of results obtained. It must be noted that at the present moment the different parts of the overall model are in different stages of development.

2. Elements of the overall model

2.1 Aspects of Heat Transfer

The heat transfer sub-model determines the time and the conditions needed to establish the required thermal history for the curing component. The fibre type, the lay-up characteristics, the tooling material and the component size are the main parameters affecting the characteristics of heat transfer from the environment (ie. the autoclave or the RTM mould) to the component during the cure cycle. This sub-model is most critical when a resin exotherm generates a significant proportion of the heat available to cure the resin. For typical aerospace applications, the thermal properties of the tooling are usually the determining factor.

Thick component curing provides the platform in which all the major modes of heat transfer are present. In this case, the temperature distribution across the thickness of the component (z direction) can be derived from an energy balance:

Rate of Conduction + Rate of Heat Generation = Rate of Energy Change

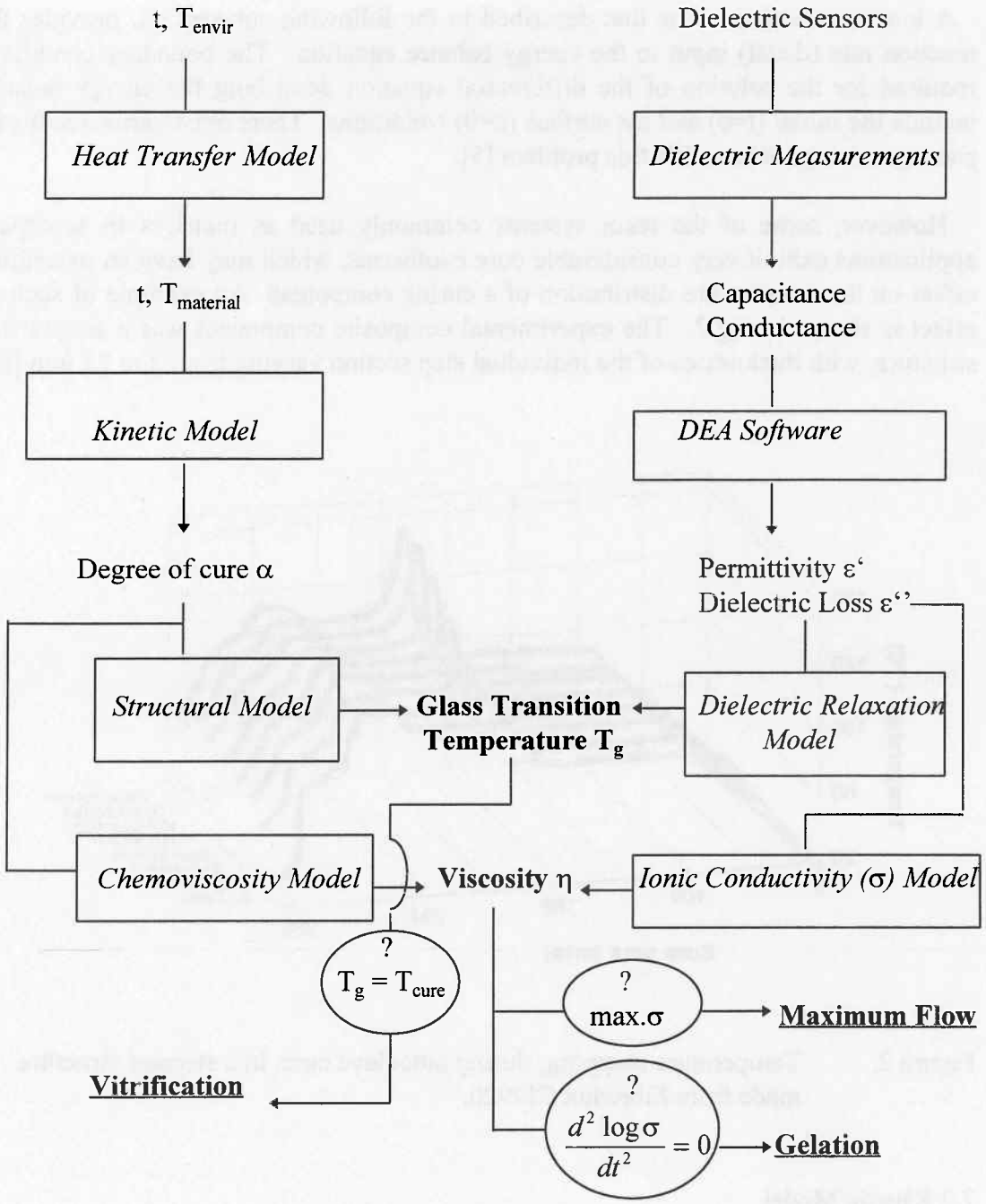

Figure 1. Flow diagram depicting the essential elements of an overall model of thermoset cure

which, for the case of a uniform thermal conductivity and uniform heat capacity, can be expressed as follows [4]:

$$\lambda \frac{\partial^2 T}{\partial z^2} + \rho \left(1 - \nu_f\right) \frac{d\alpha}{dt} H_R = \rho c_p \frac{\partial T}{\partial t} \qquad \text{(Eq.1)}$$

In Eq. 1 λ is the thermal conductivity, T is the absolute temperature, ρ is the density, v_f is the fibre volume fraction, α is the degree of resin cure, H_R is the total heat of reaction and c_p is the specific heat capacity.

A kinetic model, such as that described in the following sub-section, provides the reaction rate ($d\alpha/dt$) input to the energy balance equation. The boundary conditions required for the solution of the differential equation describing the energy balance include the initial (t=0) and the surface (z=0) conditions. There exist various software packages designed to tackle this problem [5].

However, some of the resin systems commonly used as matrices in aerospace applications exhibit very considerable cure exotherms, which may have an overriding effect on the temperature distribution of a curing component. An example of such an effect is shown in Fig.2. The experimental composite component was a simple step structure, with thicknesses of the individual step section varying from 2 to 25 mm [6].

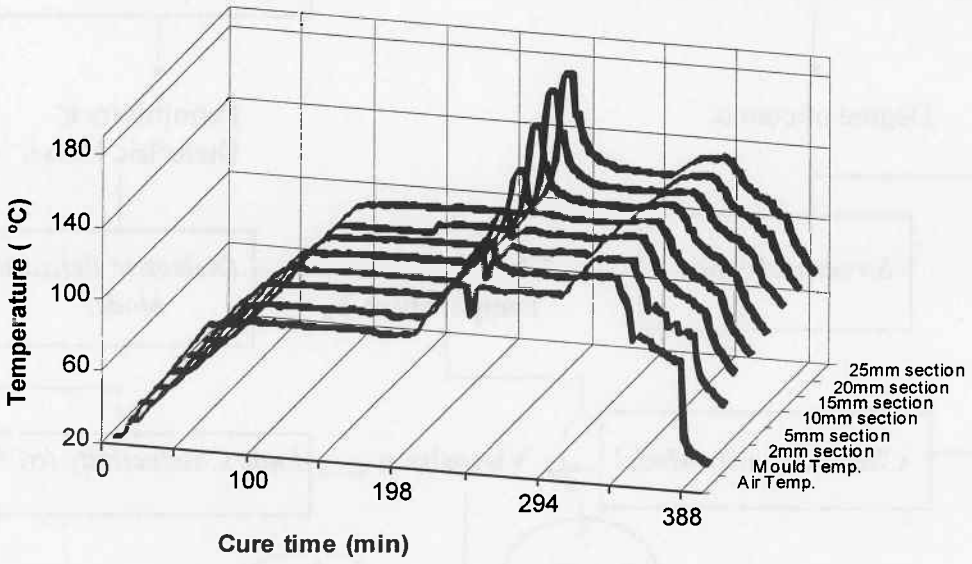

Figure 2. Temperature mapping, during autoclave cure, in a stepped structure made from Fibredux CF/920.

2.2 Kinetic Model

Kinetic models of cure are commonly used to estimate the reaction rates and the degree of cure of the resin, for a given thermal history. For the case of most epoxy resins, the kinetic model is a combination of a simple nth order reaction and of autocatalytic effects arising from the reactivity of the hydroxyl groups generated during the cure. In general, cure reactions of thermosets carried out under isothermal conditions can be expected to be incomplete. This observation is explained in terms of diffusion control effects on the cure reaction rates, which are significant after the liquid-to-rubber transformation has been reached and result in almost negligible reaction rates after the rubber-to-glass transformation.

A specific model, recently developed at Cranfield, combines the nth order kinetics, the autocatalytic and the diffusion control aspects to achieve a very good fit to the isothermal cure behaviour of RTM6 resin [7] (see Eq.2 and Fig.3).

$$\frac{d\alpha}{dt} = k_1 \cdot (1-\alpha)^{n_1} + k_2 \cdot \alpha^m \cdot (1-\alpha)^{n_2} \qquad \text{(Eq.2)}$$

In Eq.2, k_1 and k_2 are the reaction rate constants which include diffusion control and m, n_1 and n_2 are reaction orders.

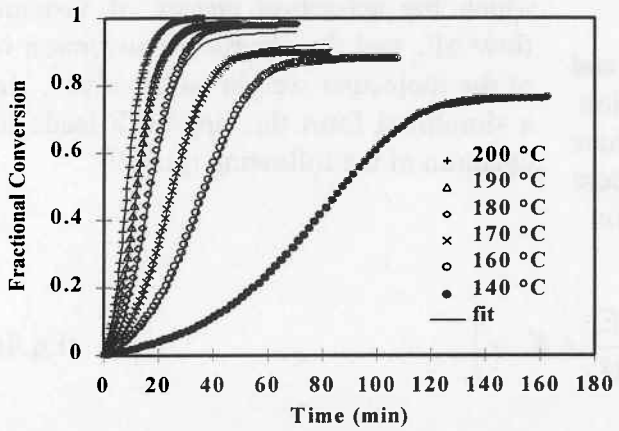

Figure 3. Comparison of model fit and experimental data from DSC measurements, for isothermal cures at different temperatures, of unreinforced RTM6 resin.

2.3 Structural Model

The parameter that is most sensitive to the advancement of the cure process and indicative of the thermoset network density is the glass transition temperature T_g,. The fact that T_g increases non-linearly with the degree of cure makes it more sensitive in the later stages of the cure when the reaction rates are low and T_g is close to the cure temperature.

A structural model relates the values of 'degree of cure' to T_g. Provided that the kinetic scheme is such that the crosslinking characteristics of the molecular network depend only on the level of chemical conversion and not on the thermal history of the cure process, there is a unique one-to-one relationship between T_g and conversion. In this context, Di Benedetto's [8] empirical relationship was derived from entropic considerations of a simple system consisting of monomer and fully reacted network:

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0}) \cdot \lambda \cdot \alpha}{1-(1-\lambda)\cdot\alpha} \qquad \text{(Eq.3)}$$

In Eq.3 , T_{g0} and $T_{g\infty}$ are the glass transition temperatures of the monomer and the fully reacted network respectively and λ is a structure dependent parameter.

The structural model fitted from data on the isothermal reactions of RTM6 resin [7] is shown in Fig. 4. The structural parameter λ was found to depend on the temperature of the reaction.

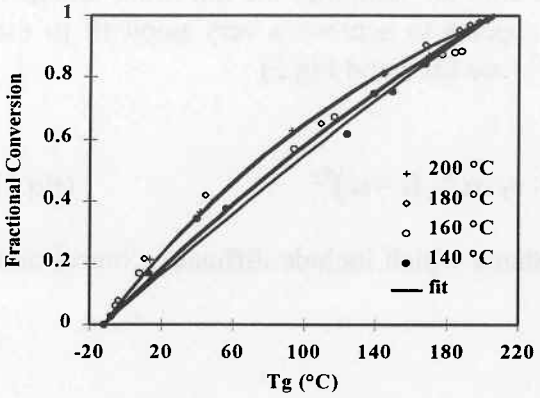

Figure 4. Relationship between T_g and the corresponding fractional conversion, as calculated from isothermal DSC runs on RTM6 resin, at different cure temperatures. Eq.3 was used for the fit.

2.4 Chemoviscosity Model

During the period in cure preceding gelation and vitrification, chemorheology principles can be expected to estimate viscosity as a function of the advancement of the cure. There are two general approaches. In the first, a branching theory is applied and a kinetic expression of viscosity can be derived, in which the activation energy of viscous flow ΔE_η and the chemical conversion α or the molecular weight are involved. In a simplified form this approach leads to equation of the following type [9]:

$$\eta = \eta_\infty \cdot \exp\left(\frac{\Delta E_\eta}{RT} + K \cdot \alpha\right) \qquad \text{(Eq.4)}$$

where K is the fitting constant and η_∞ is a resin specific integration constant.

In the second approach, the Williams-Landel Ferry equation is used to represent changes of viscosity with increasing T_g [10]. A comparison of the two approaches for a typical aerospace resin was made by Mijovic et al [11]. It was observed that the branching theory model follows more accurately the increase in viscosity near gelation both under isothermal and non-isothermal conditions. Current work at Cranfield concentrates on this aspect of the overall model development [12].

2.5 Dielectric Monitoring of Thermoset Cure

The dielectric method relies on the use of embedded microelectrodes. They are flat capacitative interdigitated sensors producing a fringing electric field over their active surface. The depth to which the electric field penetrates in the component varies from 30 to 300 μm depending on the sensor inter-digit spacing. In the composite component conductive carbon fibres 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 an 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 by in-house produced software. The software transforms the capacitance and

conductance measurements to permittivity ε′ and dielectric loss ε″ using sensor specific calibration equations. Changes in the frequency dependent dielectric loss, monitored during the course of an autoclave cure of a Fibredux CF/924 composite coupon, are shown in Fig. 5. The features exhibited in this plot are typical of those observed in all epoxy based resin systems.

2.6 Dielectric Relaxation Model

The dipolar portions of the permittivity and dielectric loss can be utilised to trace the advancement of the cure process. The dipole contributions to permittivity and dielectric loss can be separated from the ionic and interfacial components [13]. The widely used Cole-Cole equation describes the frequency dependence of the dipolar dielectric properties:

$$\varepsilon_d^* = \varepsilon' - i\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + (i\omega\tau_0)^\beta} + \varepsilon_\infty \qquad \text{(Eq.5)}$$

In Eq.5, ω is the angular frequency, ε_∞ is the infinite frequency permittivity, ε_0 is the static permittivity and β is the parameter representing the distribution of dipole relaxation times around the average value τ_0.

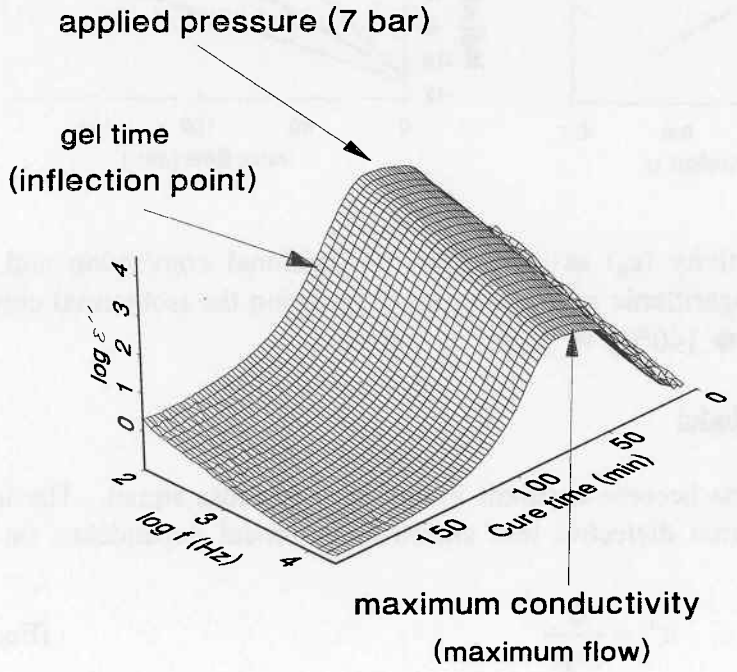

Fig.5 Changes in dielectric loss ε″ against test frequency and cure time for Fibredux CF/934 composite cured in an autoclave at 160°C.

By examining the evolution of the permittivity and dielectric loss values during isothermal cure reactions of epoxy resins, it was observed that [13]:

(i) the infinite frequency permittivity ε_∞ is independent of cure time and temperature and ranges between 2 and 4;
(ii) the static permittivity ε_0 is linearly dependent on the degree of cure and decreases with increasing temperature

$$\varepsilon_0 = \frac{D_1}{T} + D_2 - D_3 \cdot \alpha \qquad \text{(Eq.6)}$$

where D_1, D_2 and D_3 are resin specific constants;
(iii) the changes in the average relaxation time τ_0 reflect changes in the resin T_g according to the following equation:

$$\log \tau_0 = \log \tau_A + c \cdot T_g^2 \qquad \text{(Eq.7)}$$

In Eq. 7, τ_A and c are the resin specific and the fitting constants respectively. For a constant cure temperature, the changes in the logarithmic relaxation time exhibit a linear relationship with cure time (see Fig.6)

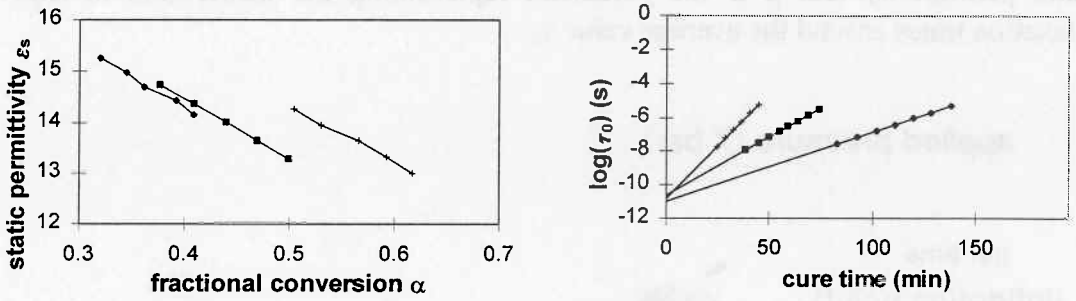

Fig. 6. The static permittivity (ε_0) as a function of fractional conversion and the changes in the average logarithmic relaxation time (τ_0) during the isothermal cure of Fibredux 924 **resin**. Key: ◆ 140°C, ■ 160°C, + 180°C

2.7 Ionic Conductivity Model

Ionic conductivity effects become apparent in the dielectric loss signal. The ionic component of the measured dielectric loss shows a reciprocal dependence on the measurement frequency:

$$\varepsilon''_c = \frac{\sigma}{2\pi f \varepsilon} \qquad \text{(Eq.8)}$$

In Eq.8, ε''_c is the conduction part of the dielectric loss, σ 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 their mobility. As resin viscosity reflects the mobility of the chain segments in the growing network, a very useful relationship exists between viscosity and ionic conductivity. It is proposed [13] that viscosity is inversely proportional to ionic conductivity:

$$\eta = A \cdot \sigma^{-\beta} \qquad \text{(Eq.9)}$$

where A and β are resin specific and temperature dependent constants.

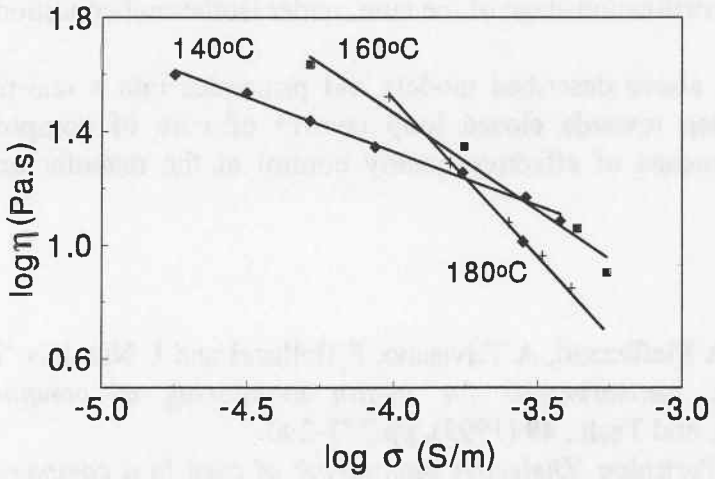

Fig.7 Linear relationships between the logarithmic viscosities and conductivities of Fibredux 924 **resin**, at different isothermal cure temperatures. Key as in Fig.6.

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 [14] observed that the conductivity does not fall to zero as viscosity tends to infinity after gelation. Therefore, it is expected that Eq. 9 will begin to break down as gelation is approached and the time during the resin cure when $d^2(\log \sigma)/dt^2 = 0$ is the first evidence of a gelled system. The relationship between viscosity and conductivity during isothermal cure reactions of Fibredux 924 resin is shown in Fig. 7.

3. State of development of the model

The overall model as described in Fig.1 is designed to validate the models on the left half of the figure. These models require time and temperature as inputs and are derived from thermal analysis tests on the unreinforced resin system and on the composite. The achievable level of accuracy in the predictions of resin states (ie. the T_g, the viscosity, and the arrival at maximum flow, gelation and vitrification) from the models is expected to be determined by the nature of the resin system and the type of cure process(es) involved. So far, the kinetic and the structural models have been developed fully only for one specific resin system. The chemoviscosity studies [12] and the heat transfer model application studies are ongoing.

It is the monitoring side of the overall model which has been the primary subject of our studies in recent years. The dielectric sensors can be adapted to suit a particular application and the powerful monitoring software provides the real-time capability of the technique. Several different types of thermosetting systems have been studied by the dynamic dielectric analysis and the dielectric models have been derived for simple two-component resins as well as for complex commercial aerospace resins [13,2]. The relationships of the dielectric properties to material transformations have been shown to obey some generic rules:

(i) the maximum in the resin conductivity coincides with the point of minimum viscosity under isothermal or dynamic (thermal) conditions;
(ii) the inflection point in the drop of the logarithmic ionic conductivity after the point of maximum flow provides the first evidence of a gelled material;
(iii) the extrapolated maximum in the dipolar loss, at the frequency of 1 Hz , correlates well with the arrival at the vitrification stage of the cure, under isothermal conditions.

The incorporation of the above described models and principles into a real-time monitoring system is a step towards closed loop control of cure of composite materials and promises a means of effective quality control at the manufacturing stage.

4. References

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