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Feasibility study on Temperature Modulated Dynamic Dielectric Analysis

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Overall outcome of the project

The project concerned the development of a novel measurement and analysis tool, designed to aid the study of cure in thermosetting polymers. Cure is the irreversible process whereby an initially liquid (unreacted) resin turns into a rubbery solid and eventually into a rigid crosslinked glass. The process usually requires the application of heat to proceed to completion. The changes in structure are reflected in changing mobilities of electrically charged species in the resin and dielectric signals can therefore be used to monitor the progress of cure. In this project, the normal heating–up of the resin was accompanied by a superimposed sinusoidal temperature variation of +/- 1°C. Deconvolution of the resulting dielectric signal into its reversible and irreversible components made it possible to distinguish between the signal contributions arising from the temperature change alone and from those directly contributable to the irreversible chemical chain extension and crosslinking. This proves the original hypothesis put forward in the proposal.

The new ideas generated during the course of the project enabled us to obtain significant follow-on funding from the EPSRC. A new dielectric cell has been designed, which will be used in attempting to track particle dispersion in thermosetting nanocomposites.

Essential Background

Temperature modulation techniques have been introduced in the last decade to study thermo-physical properties of curing thermosets. The technique was first implemented in calorimetric studies [1-4] and later in dilatometry [5-6]. An extensive review of all current techniques that involve temperature modulation can be found in [7]. The basic idea behind any temperature modulated technique is to superimpose a sinusoidal temperature profile onto a standard temperature-time regime. The use of this complicated thermal profile provides important advantages – primarily the introduction of a characteristic time defined by the modulation period, which enables the separation of phenomena that respond on significantly different timescales.

Basic Dynamic Dielectric Analysis has been used recently by several groups worldwide to follow resin cure in-situ and in real time [8-10]. A small alternating electrical field is applied to the sample and its response is monitored, typically via embedded interdigitated electrodes (see Fig.1).

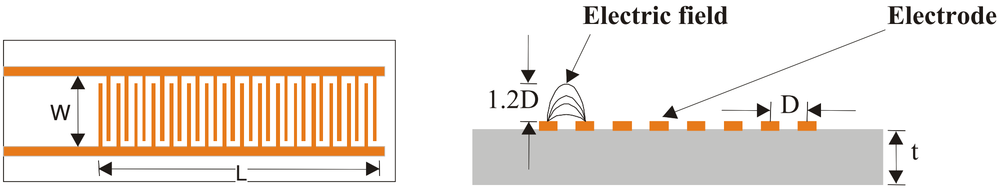

Fig. 1: Typical geometry of an interdigitated dielectric sensor. The field penetration is proportional to the inter-electrode spacing. For the sensor used in the study (GIA sensor by Pearson Panke Ltd) the following geometry values were measured: D = 300 μm, t = 100 μm, W = 0.5 cm and L = 2.5 cm

The frequency of the alternating current introduces a characteristic time. Phenomena that respond in time intervals shorter than or close to the characteristic time can be sensed. Commercially available data acquisition hardware provides multi-frequency measurements enabling the monitoring of phenomena that have characteristic times that can vary over several orders of magnitude or phenomena where the characteristic time changes during cure.

An example of such a phenomenon is vitrification. Temperature plays an important role in the magnitude and the time of the manifestation of these phenomena in the dielectric signal. In general, phenomena that are related with the resin reaction advancement can be termed “irreversible” and phenomena that are not related with the epoxy reaction advancement can be termed “reversible”. The two terms are used in the following context: - If temperature changes from a $\boldsymbol{T_A}$ value to a $\boldsymbol{T_B}$ value, resin reaction advances further. This advancement cannot be “undone” if the temperature returns to $\boldsymbol{T_A}$. On the other hand, a similar temperature change will affect the movement of ionic species in the resin, which give rise to the dielectric response, but the effect will vanish if the temperature returns to the initial value.

Temperature Modulated Dynamic Dielectric Analysis (TMDDA)

The novel idea tested this program is the combination of temperature modulations with electric field oscillations, giving rise to Temperature Modulated Dynamic Dielectric Analysis (TMDDA). The two basic equations of TMDDA are given below:

$$\text{Excitation field: } V_{excitation}\left(\omega_V, t\right) = V_{DC} + A_V \sin\left(\omega_V t\right) \quad (1)$$

$$\text{Temperature profile: } T_{cure}\left(\omega_T, t\right) = T_0 + rt + A_T \sin\left(\omega_T t\right) \quad (2)$$

Here V_{DC} is the bias voltage, A_V is the excitation amplitude, ω_V is the excitation frequency, T_0 is the starting cure temperature, r is the heating rate, A_T is the modulation amplitude, ω_T is the modulation frequency and t is time.

The dielectric signal is expected to comprise of two superimposing components: One component that follows the resin cure and a second part that follows the temperature modulation. The first component should be identical to the signal obtained from traditional Dielectric cure monitoring experiments. Previous work by the PI’s group shows that there is a one-to-one relationship between the dielectric signal and the polymerization reaction conversion [10]. Unpublished work by the group has shown that the relationship between the dielectric impedance Z'', the extent of the curing reaction α and the curing temperature T_{cure} can be described by the following equation:

$$Z''\left(a, T_{cure}\right) = \left(c_1 + c_2 T_{cure}\right) a + c_3 T_{cure} \quad (3)$$

where c_1, c_2 and c_3 are appropriate coefficients which can be determined from isothermal dielectric cure monitoring experiments. For the resin used in this study (RTM6) we have:

$$c_1 = 9.3, \quad c_2 = 4.4\times10^{-2}\frac{1}{°C}, \quad c_3 = 3.8\times10^{-2}\frac{1}{°C} \quad (4)$$

When the temperature profile of Eq. (2) is applied to the curing material the resulting dielectric signal is a superposition of an underlying component (similar to the signals of standard dielectric spectroscopy) and a modulated component. The amplitude $A_{Z''}$ and phase $\delta_{Z''}$ of the modulated component are as follows:

$$A_{Z''} = A_T \sqrt{\left(c_2 \frac{da}{dt} \right)^2 + \left(\left(c_3 + c_2 a \right) \omega_T \right)^2}, \quad \tan\delta_{Z''} = \frac{\left(c_3 + c_2 a \right) \omega_T}{c_2 \frac{da}{dt}} \qquad (5)$$

The experimental parameters of the TMDDA experiments are :-modulation period $P \sim 1 min$ → $\omega_T \sim 0.1\ rad/s$) and the reaction rates recorded in most thermosetting systems indicate a maximum $da/dt \sim 10^{-1}\ min^{-1}$. Under these conditions the amplitude of the modulation is directly related to the reaction conversion.

The main experimental challenges of TMDDA were considered to be (i) precise temperature control of the heating and cooling cycles and (ii) the appropriate choice of experimental parameters. Temperature control was achieved using a Eurotherm® 2408 temperature controller capable of controlling temperature with accuracy ± 0.1°C. The temperature control had to be fine tuned with the dielectric measurements conducted using a Solartron Analytical® 1260 Gain/Phase Analyzer. For this reason in-house software was developed to control and coordinate the measurements of the temperature and of the dielectric signal. The experimental setup is shown in Fig. 2. The following signals are involved in the measurement:

1. Set temperature point to be followed according to the modulated temperature profile
2. Set frequency and voltage amplitude for the dielectric measurement
3. Heat/cool experimental cell according to temperature set-point
4. Control thermocouple
5. Send excitation to the dielectric sensor
6. Read sensor response
7. Store dielectric measurements
8. Record cell temperature and resin temperature
9. Store temperature readings

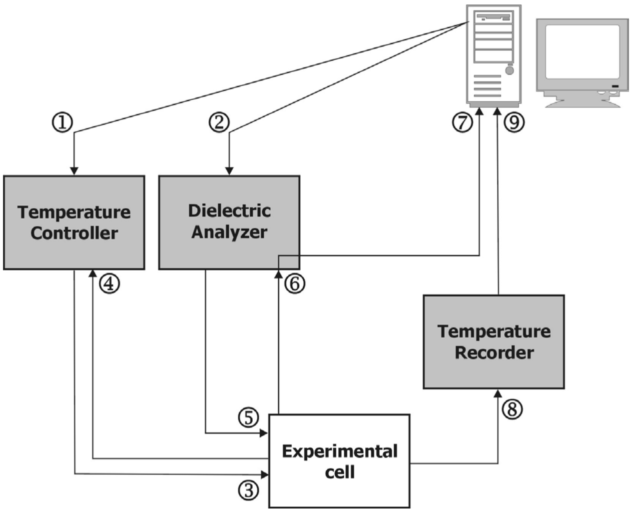

Fig. 2: Experimental setup for TMDDA measurements

The experimental parameter values adopted for the TMDDA measurements are given in Table I. The difference in the values of ω_V and ω_T is crucial because it defines the number of experimental points within one temperature period. Numerical studies in Modulated Differential Scanning Calorimetry (MDSC®) have shown that a number of ~10 experimental points are needed for successful data analysis [4].

Table I: Experimental Parameter values used in TMDDA experiments

Excitation field:	$V_{DC} = 0$ Volt	$A_V = 3$ Volt	$\omega_V = 1 - 10$ kHz
Temperature profile:	$T_0 = 30$°C $r = 0.5 - 1$°C/min	$A_T = 1$°C	$\omega_V = 10 - 40$ mHz

Construction of an experimental cell

In order to impose steady temperature modulations on the curing material, a new experimental cell was designed and constructed. The main design objective was to achieve a quick thermal response to the imposed temperature profile. This objective led to the following considerations/guidelines for the manufacturing of the cell:

- Small amount of metal so that heat could be transferred to the resin quickly
- High surface to volume ratio for rapid cooling of the resin, which led to the use of fins

The cell is pictured in Fig. 3. The base material was copper which provides good thermal response and is easy to process. The curing resin was placed in disposable copper tubes which are fitted in the centre of the cell.

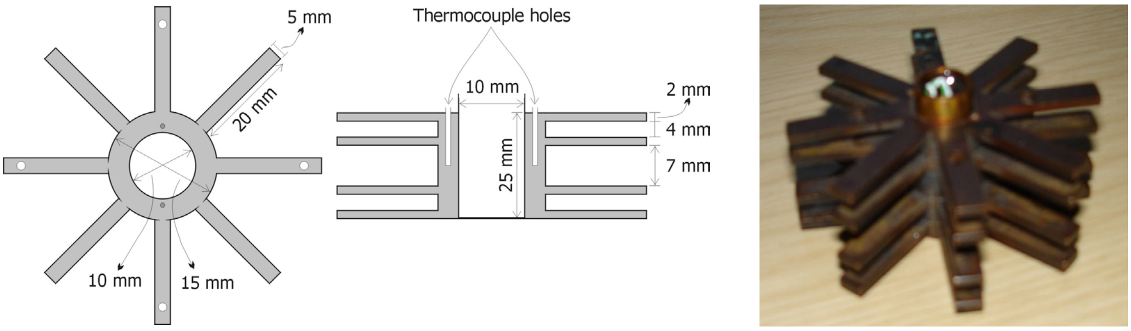

Fig. 3: Schematic design (left) and a photograph (right) of the experimental cell used in TMDDA experiments

Heating was provided using a Ni/Cr alloy wire purchased from Omega Engineering Inc (www.omega.co.uk). Appropriate PTFE sleeving was used in order to isolate the current from the heating wire. The whole cell was earthed during the measurements.

Experimental results and analysis

A well studied commercially available resin system was used for the initial TMDDA experiments. RTM6 is an aerospace grade one – component system used in Resin Transfer Moulding processes. Representative TMDDA results are presented in Fig. 4. The imaginary impedance signal oscillates, following the temperature modulation.

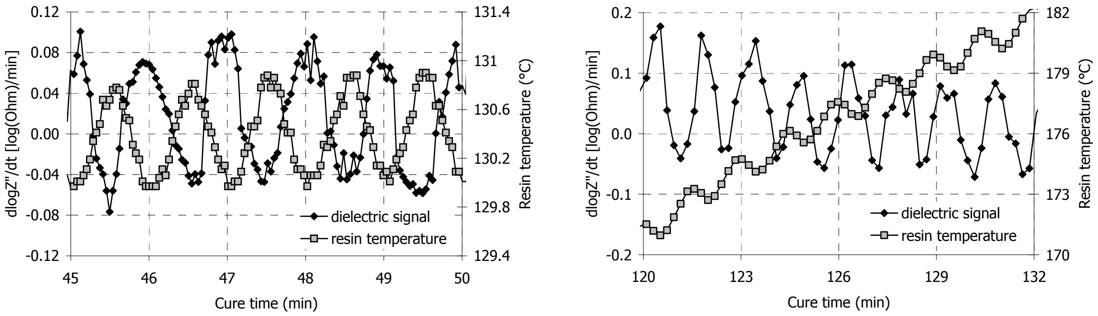

Fig. 4: Representative results from quasi-isothermal (left plot) and dynamic (right plot) TMDDA experiments. Experimental parameters: (i) Quasi-isothermal experiment ($T_0 = 130°C, A_T = 1.5°C, P = 1\ min$), (ii) Dynamic experiment ($A_T = 1.5°C, P = 1.5\ min, r=1°C/min$)

In both experiments we can observe that the dielectric signal is out-of-phase with the imposed temperature modulations. The experimental value for $\delta_{Z''}$ was ~89°. The dielectric signal was analysed using standard Fast Fourier Transform deconvolution techniques. The analysis of the signals from the two experiments presented in Fig. 4 is shown in Fig. 5. From the power spectrum we can see that the dielectric response of the curing material to the temperature modulation is linear (only one peak at the modulation frequency appears in the spectrum). The high values obtained at periods close to zero are due to the dominating non-modulating component.

Inverse Fourier Transformation of the power spectrum can be used in order to separate the modulated and underlying parts of the dielectric signal. Standard numerical analysis [4] can be then applied to the modulated part of the signal in order to calculate the amplitude of the modulation and consequently the reaction conversion. Such calculation is shown in Fig. 6 where the reaction conversions determined using TMDDA and DSC are plotted. The 'TMDDA conversion' is not sensitive at the beginning of cure. In this region the effect of temperature roughly balances the effect of the curing reaction. Towards the end of cure, where the material approaches vitrification, the 'TMDDA conversion' is sensitive to the small changes in conversion because these changes translate to significant changes in the internal structure of the material (T_g increases rapidly).

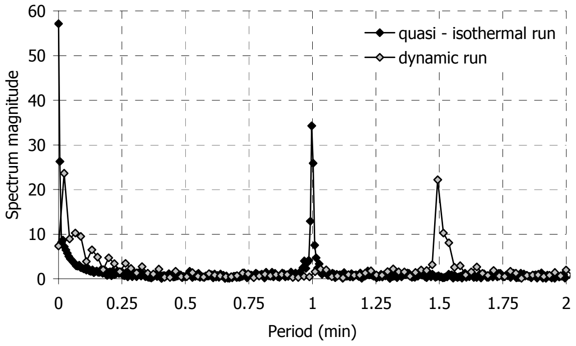

Fig. 5: Fourier Transform analysis of the TMDDA experiments shown in Fig. 4

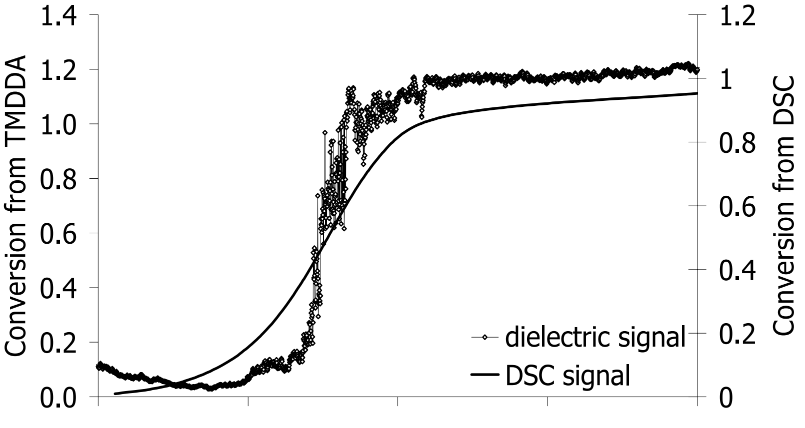

Fig. 6: Reaction conversion calculated from the TMDDA experiment (A_T=*1.5°C, P=1.5 min, r=0.4°C/min*). The reaction conversion obtained from DSC is also plotted for comparison.

The result shown in Fig. 6 suggests for the first time that information about the polymerisation reaction can be extracted and separated from the effect of temperature in the dielectric signal. Early indications from experiments on other types of (commercial) resins such as Vinylester and thermoset/thermoplastic blend are that the above indicated methodology is applicable.

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