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Exploring equivalence of information from dielectric and calorimetric measurements of thermoset cure—a model for the relationship between curing temperature, degree of cure and electrical impedance

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Abstract

The paper presents a phenomenological model, which accounts for the observed similarity between change in the imaginary electrical impedance maximum (IIM) during the cure of a commercial epoxy system, RTM6, and the cure reaction rate data collected by differential scanning calorimetry (DSC) experiments on the same resin. The model is developed by analysing the information content of dielectric cure monitoring signals and calorimetric cure monitoring signals under both isothermal and non-isothermal cure conditions. The absolute values of the coefficients in the model equation are shown to be indicative of the relative effects of the polymerisation reaction and of the temperature on the dielectric signal. The information presented here strengthens the suggestion that on-line dielectric measurements may be used to quantify the degree of cure in thermosetting resins in real time.

Keywords: Thermoset cure; Electrical impedance; Dielectric spectroscopy

1. Introduction

1.1. Background

Monitoring the cure of thermosetting polymers has been an active research area for over 20 years [1–10]. Cure monitoring is performed by measuring some physical quantity which corresponds directly or indirectly to the material state of the reacting system. One of the many techniques that fall under this general definition is dielectric spectroscopy. In dielectric cure monitoring, the electrical properties of the material are probed and analysed, by using complex permittivity [4,6,10] or complex impedance representation [7–9], although other forms of translating the dielectric signal are also possible [11,12]. Complex permittivity, ε^*, is a material property and hence considered more appropriate to characterise reactive systems on a molecular level. Complex impedance, Z^*, is better suited to describe systems with high levels of electrical conductivity, where the influence of ionic species in the dielectric signal overwhelms any other contributions. The two variables contain equivalent information and are related through the following expression [11]:

$$\varepsilon^* = \frac{1}{j\omega C_0 Z^*} \tag{1}$$

In the above equation j is the imaginary unit ($j^2 = -1$), ω is the angular frequency of the applied field and C_0 is the air capacitance which is a function of the geometrical features of the dielectric sensor.

Work in the authors' laboratory has concentrated on the application of dielectric spectroscopy as an on-line (real time) cure monitoring technique [13].

There have been various attempts to relate the changes in the dielectric signal with rheological and cure kinetics data [5,12–16]. Phenomenological models relating the electrical conductivity of the curing system to the degree of cure have been produced, based on versions of DiBenedetto [14], Mafezzoli [17] and Williams–Landel–Ferry (WLF) [12] equations. The use of conductivity in these studies is rationalised by the argument that the conductivity is a measure of the mobility of the various molecular species in

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the reactive system. Although the above argument has been proved valid for some systems (at least up to the gelation point), Gallone and co-workers have shown that there are polymeric systems that behave in a completely opposite way; with the electrical conductivity increasing as the reaction advances [16].

In a recent publication Skordos and Partridge have proposed a new way of using dielectric cure monitoring data as an in situ indicator of the progress of the polymerisation reaction [18]. They used the point of the maximum in the imaginary impedance spectrum (IIM) as the dielectric signal and showed that its first derivative with respect to time exhibits cure time dependence very similar to the reaction rate curves obtained by classical differential scanning calorimetry (DSC) (Fig. 1). The important suggestion made from the observed similarity between the dielectric and the calorimetric signals is that it should be possible to use the dielectric signal as a direct quantitative means of monitoring the material state.

1.2. Complex impedance representation of dielectric cure monitoring data

Mijovic and Yee have established an electrical equivalent circuit model that describes the three prominent phenomena present in a typical epoxy resin at frequencies up to the MHz region—electrode polarisation, charge migration and dipole polarisation and relaxation [7].

Electrode polarisation, being a relatively slow process, occurs at low frequencies; typically below 100 Hz. It is related to the accumulation of ‘free’ charges on the surface of any dielectric sensor [4]. Mobile charged molecular species are present in most thermosetting systems. They originate either from the manufacturing process (small ions, leftovers from the raw materials used for producing the thermoset [4,5,7]) or are products of the polymerisation reaction mechanism [7–9]. Dipolar molecules also exist in thermosets either as permanent dipoles or as induced dipoles [2]. When the resin is in its uncured liquid state the frequency of dipolar relaxation f_{dip} is in the range of GHz. As the cure progresses f_{dip} decreases rapidly and can be picked up in the MHz region. In the fully cured thermoset f_{dip} can fall below 1 Hz [4,10]. The frequency of dipolar relaxation is also affected by temperature. For a specific material state (for example when the material is fully cured) f_{dip} increases as the temperature increases. In the imaginary impedance spectrum the effect of dipole polarisation manifests itself as a shoulder in the MHz region.

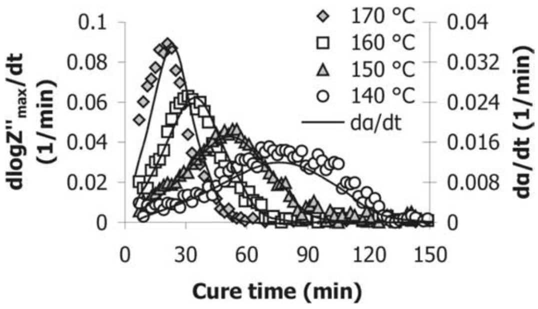

Fig. 1. Comparison between the IIM time derivative calculated from the dielectric data (in symbols) and the reaction rate curves obtained from DSC measurements (lines). The data are taken from four different isothermal cures of RTM6 resin, in the temperature range relevant to resin transfer moulding processing of composites made with this resin.

The frequency regions, where these different phenomena manifest are usually well separated, as can be seen in Fig. 2. Out of the three phenomena, charge migration and dipolar relaxation are expected to be linked to the changes in the average mobility of the molecular species present in the system at any given state. In commercial thermoset systems charge migration is the dominant phenomenon in the dielectric signal [9]. The absolute value of the maximum in the imaginary impedance (IIM) spectrum at any given cure time is a measure of the mobility, concentration and type of charges [7,18]. There is an inverse relationship between the IIM and the electrical conductivity σ [7]:

$$\sigma \sim \frac{1}{Z''_{\max}} \tag{2}$$

During the polymerisation reaction of a thermoset, the frequency spectrum shifts continuously along both the imaginary impedance and the frequency axes. The extent of the shift depends on the temperature changes and on the reaction advancement in the system. The IIM point can thus be used for monitoring the shift of the spectrum and correlating it to material state parameters such as the degree of cure or the glass transition temperature [8]. The work presented here explores the use of this experimental parameter in the context of quantitative on-line cure monitoring.

2. Experimental

The resin used in this study is RTM6, supplied by Hexcel® Composites UK [19]. It is a pre-mixed aerospace grade epoxy/amine formulation, developed for use in

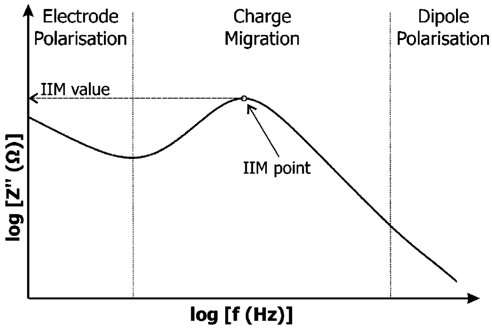

Fig. 2. Typical imaginary impedance spectrum for a thermosetting resin in the Hz–MHz frequency region. The position of the imaginary impedance maximum (IIM) point and value are also shown.

polymer matrix composite manufacture via resin transfer moulding and representative of the '180 °C cure' aerospace epoxy range. The chemical components of the system include a multifunctional epoxy resin and a mixture of amine hardeners of different functionalities [20]. Several different batches of the resin have been characterised previously in the authors' laboratory [18,20–22].

2.1. DSC experiments

Detailed evaluation of the chemical cure kinetics of RTM6 has been performed, using a TA Instruments 2920 heat flux DSC. Experiments were performed under nitrogen atmosphere, under isothermal and dynamic heating conditions, covering a temperature range from 100 to 210 °C (in 10 °C intervals) and heating rates from 0.2 to 20 °C/min. Standard aluminium pans were used, with liquid resin sample mass between 5 and 10 mg. In-house software was used to provide an in-depth analysis of the DSC data.

2.2. Dielectric experiments

Dielectric measurements were performed using a Solartron Analytical® 1260 Impedance Gain/Phase Analyzer, collecting data via a commercially available GIA dielectric sensor supplied by Pearson Panke Ltd. The geometric features and dimensions of the sensor are shown in Fig. 3. The sensor comprises of two copper comb electrodes on a porous polymer film substrate. The prong width is 30–35 μm and the average inter-electrode spacing is 350 μm. The excitation voltage on the sensor was 3 V. Twenty-five frequencies were scanned, logarithmically spaced over a frequency window of 1 Hz to 1 MHz. The total time for a frequency sweep was about 100 s, which is a short time compared to the duration of the polymerisation reaction (30 min at 210 °C, over 12 h at 100 °C).

The measuring cell is pictured in Fig. 4. It is a small glass test-tube, placed vertically within a hollow copper cylinder. Typical sample mass was 1 g.

In the isothermal experiments the cylinder was heated up to the dwell temperature before the glass tube with the resin was placed in the central hole, whereas in the non-isothermal experiments the sensor was immersed in the resin at 60 °C and the temperature ramp initiated. Heating elements (not shown in Fig. 4) surround the copper cylinder. A control and a monitoring thermocouple were placed in holes drilled in the copper cylinder, 1 mm from its inner surface. A third thermocouple was immersed in the resin in order to record the actual temperature experienced by the sample.

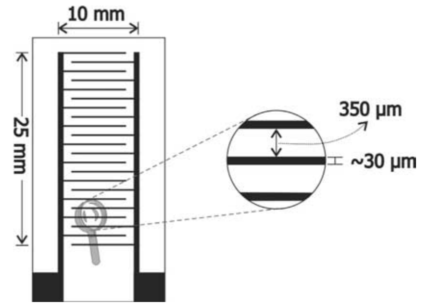

Fig. 3. Comb electrode GIA sensor used in the dielectric experiments (reproduced from Ref. [22]).

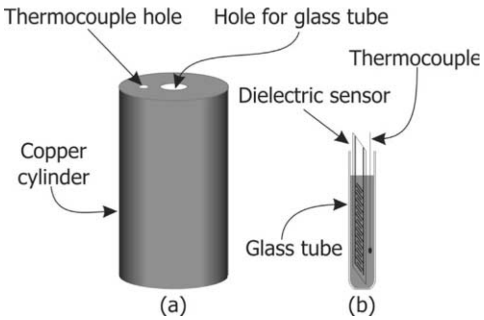

Fig. 4. Experimental configuration for dielectric experiments: (a) heated copper cylinder, (b) glass tube.

Temperature control was achieved through a Eurotherm® 2204e temperature controller. In house data acquisition software was used in order to simultaneously control the instruments, set-up the experiments and collect the data.

3. Results

3.1. Cure kinetics model

The raw data heat flow signals for the isothermal and dynamic cures of RTM6 are shown in Fig. 5. The curves exhibit a single peak under all experimental conditions, which is an indication of a single autocatalytic polymerisation reaction, typically observed in epoxy/amine formulations [1,20]. The opening of the epoxy ring in the DGEBA molecule by the presence of amines results in hydroxyl groups which act as catalysts and accelerate the reaction [1]. When the majority of the epoxy rings have opened, the number of available hydroxyl groups is reduced and the autocatalysis phenomenon gradually diminishes. In the later stages of cure, the resin approaches vitrification, which further reduces the reaction rate [1,23]. In Fig. 5(c) an extended shallow shoulder is observed at high temperatures. This shoulder is related to the devitrification of the sample which can occur when the heating rate is low [24].

The total heat of reaction is calculated by integration of the heat flow curve of the dynamic experiments, using a sigmoid baseline. The results are given in Table 1. The calculated average heat of reaction is 429 ± 10 J/g, in agreement with previous measurements on other batches of the same material [20,21].

The reaction rate was calculated using the following equation:

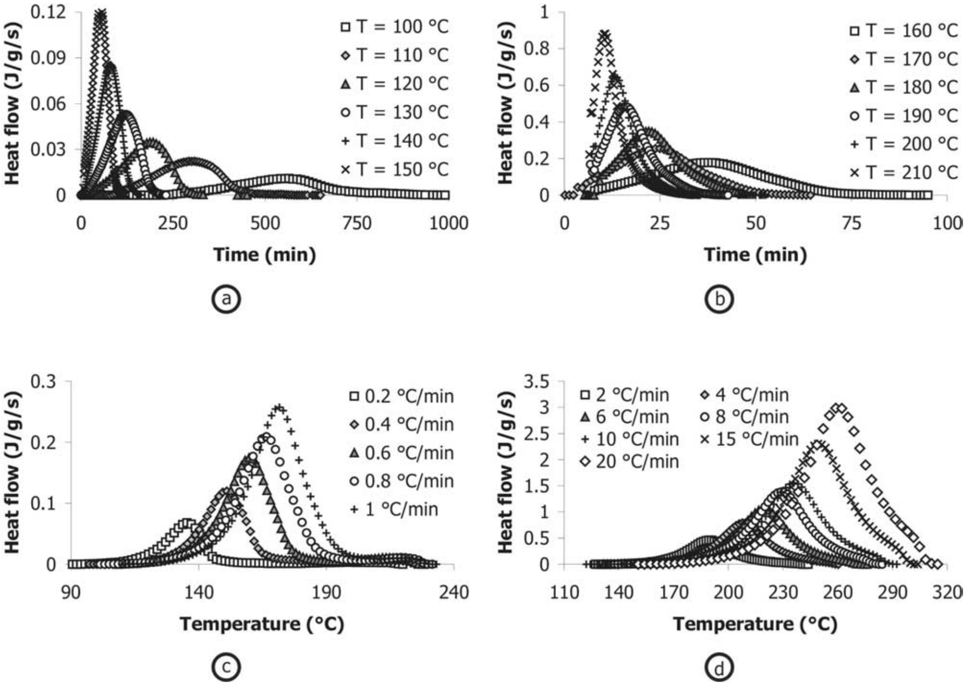

Fig. 5. Results from DSC cure experiments: (a) and (b) isothermal cures, (c) and (d) dynamic cures.

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{1}{H_{\mathrm{total}}} \frac{\mathrm{d}H}{\mathrm{d}t} \tag{3}$$

where a is the degree of cure or conversion (NB, both terms are considered equivalent and will be used interchangeably in the text), H is the heat of reaction, H_{total} is the total heat of reaction (429 J/g) and t is the time.

The cure kinetics model was built up using a non-parametric technique introduced and described in detail by Skordos and Partridge [21]. The data from all the experiments form a surface in the time–temperature–reaction rate space, shown in Fig. 6.

In regions marked as A and B on Fig. 6, no data can be collected. Region A is the plane, where the reaction rate is zero because the imposed cure temperature is too low for the reaction to proceed. Region B is bordered by the two light grey lines, one in the conversion–reaction rate plane and the other signifying the limit of the experimental window. In this region temperature is so high that the reaction starts before the actual set temperature has been achieved. Therefore, low conversion data cannot be collected at the specified temperatures.

Table 1
Total heat of reaction obtained from DSC experiments on RTM6

Heating rate (°C/min)	Heat of reaction (J/g)
0.2	420
0.4	427
0.6	444
0.8	430
1	432
2	449
4	429
6	424
8	429
10	411
15	425
20	428

The model of any given cure temperature profile is obtained by direct interpolation on the 3D surface shown in Fig. 6. Comparison of model results thus obtained with experimental results is presented in Fig. 7. For each modelled temperature profile the experimental data corresponding to that profile was excluded from the model database. The coincidence of model lines in Fig. 7 with the experimental data is near perfect, under all cure conditions within the region investigated.

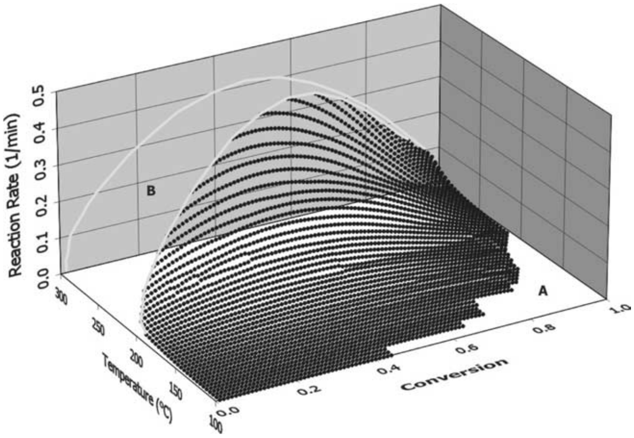

Fig. 6. Reaction rate surface for RTM6 in the conversion (degree of cure)–temperature–reaction rate space.

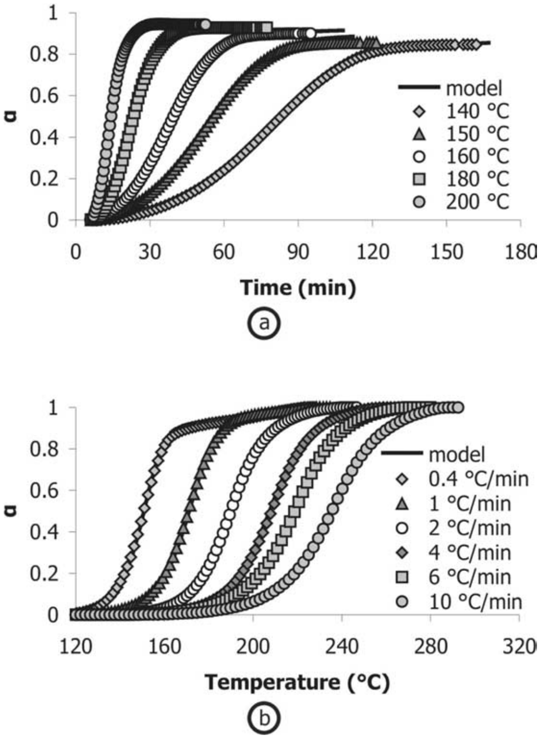

Fig. 7. Application of the non-parametric cure kinetics model to (a) isothermal and (b) dynamic cure temperature profiles.

3.2. Dielectric cure monitoring experiments

The imaginary impedance evolution under isothermal (160 °C) and dynamic (0.6 °C/min) cure conditions at various frequencies is shown in Figs. 8 and 9, respectively. The results showed a high level of reproducibility, both in the time development and in the absolute values of impedance. The shapes of the curves are typical of thermosetting polymers and have been analysed by various research groups in the past [7,9,23]. The different features in the curves observed at different testing frequencies can be understood if the frequency spectrum of the imaginary impedance is considered at specific times (or at specific temperatures in the case of dynamic cure). Such an exposition is presented in Fig. 9, where the imaginary impedance evolution at two frequencies, 100 Hz and 10 kHz, is plotted together with plots of the frequency spectrum.

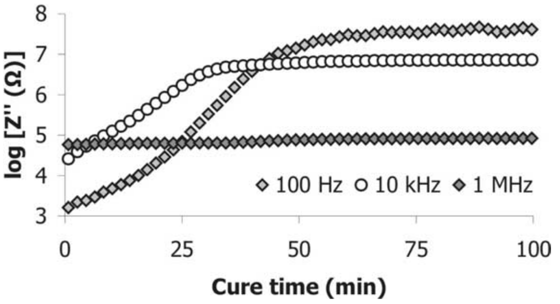

Fig. 8. Imaginary impedance evolution at various frequencies during the isothermal cure of RTM6 at 160 °C.

The frequency spectrum position shifts during the cure. At the initial stages of the cure the reaction has not started. Only temperature affects the dielectric signal. The spectrum shifts from its initial/starting position to higher frequencies and lower impedance values (points *a*–*e*). At later stages, as the effect of the curing reaction becomes dominant in the dielectric response of the resin, the spectrum movement reverses, the signal tending to lower frequencies and higher impedance values (points *e*–*g*). Finally, when the curing reaction is over, the imposed temperature is—as in the beginning—the only parameter that influences the signal, causing the imaginary impedance values to decrease (points *g*–*i*).

As can be seen from Fig. 9 the shape and information contained in the imaginary impedance curves depends on the frequency of observation. As the materials state changes, the phenomena that dominate the dielectric signal at a particular frequency may change.

In the resin systems considered here, the changes brought about by cure are reflected in the mobility of charged species [7,18]. Thus it is most convenient to follow the movement of the IIM point as defined in Fig. 2. The IIM evolution in the isothermal and dynamic experiments on RTM6 resin is shown in Figs. 10 and 11, respectively.

In the isothermal experiments the IIM evolution exhibits a trend similar to the evolution of the degree of cure (shown in Fig. 7(a)). The IIM starts from an apparently constant value ($\sim 10^4$ Ω) at the beginning of cure and then increases to a final plateau, between 10^7 and 10^8 Ω at typical cure temperatures.

The IIM curves in the dynamic experiments are rather more complicated, because of the competing effects of temperature increase and reaction progression on the dielectric signal. There is an initial stage up to about 90 °C, where all the curves superimpose. A change in the rate of decrease is also observed in the same temperature region, over a range of 10 °C. This phenomenon may be attributed to the melting and/or dissolution of crystalline hardeners/initiators within the resin, which would suddenly increase the concentration of ionic species in the material, hence lowering the impedance.

Beyond 100 °C the IIM values reach a lower plateau before rising again as the reaction progresses. The extent of the plateau is different for experiments carried out at different heating rates (shortest for the experiment at 0.2 °C/min) and the curves begin to diverge. All curves attain a maximum point at a particular temperature, which increases as the heating rate used in the experiment increases. From these maxima, the downward slopes of the curves begin to superimpose once more. The two regions, where these curves superimpose signify the phases, where either the reaction has not started (initial stage) or the reaction has finished (final stage) [18].

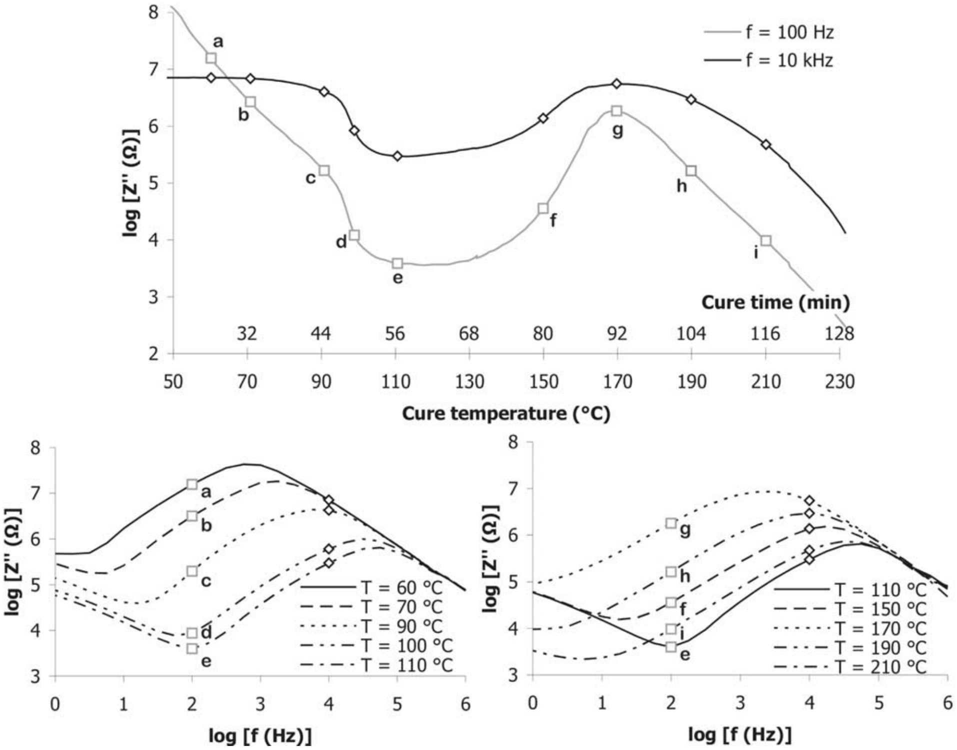

Fig. 9. Analysis of imaginary impedance curves according to the shift of the frequency spectrum during the dynamic cure of RTM6 at 0.6 °C/min. Small letters (in alphabetical order) denote the same experimental points as viewed in the time and in the frequency domains for the case of 100 Hz measurement frequency.

4. Analysis

4.1. Isothermal experiments

The correlation between the dielectric signal and the degree of cure in the isothermal cure of RTM6 resin is shown in Fig. 12. The degree of cure was calculated by utilising the real temperature profile of the dielectric cure monitoring experiment within the cure kinetics model described in Section 3.1.

There is a log-linear relationship between the IIM (in logarithmic units) and the degree of cure for $\alpha > 0.1$ at all temperatures up to 170 °C (in the run at 180 °C the linear region limits for $\alpha > 0.3$):

$$\log Z''_{\max} = c_1\alpha + c_2, \quad \alpha > 0.1 \tag{4}$$

Results from linear regression on all the experiments shown in Fig. 12 are presented in Table 2.

The regression coefficient R^2 is close to unity for all experiments except for that carried out at 180 °C. (This experiment represents the upper limit of realistic cure conditions for this resin and will not be considered in the subsequent analysis).

The intercept c_2 is relatively constant in all experiments ($5.81 \pm 0.08 \log(\Omega) \approx 650 \pm 50\ \mathrm{k}\Omega$). This does not mean that the reaction starts at a specific IIM value, since in the early cure stages the log–linear relationship between the IIM and the degree of cure does not hold. However, it is an indication that the IIM value at the beginning the polymerisation reaction does not depend strongly on temperature. The average impedance value at the reaction onset for all isothermal experiments (experimental points corresponding to $\alpha = 0$ in Fig. 12) is $5.62 \pm$

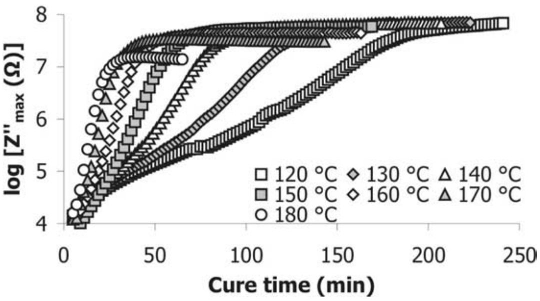

Fig. 10. IIM evolution during the isothermal cure of RTM6.

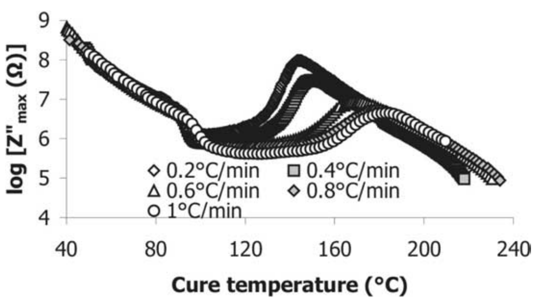

Fig. 11. IIM evolution during the non-isothermal cure of RTM6 resin.

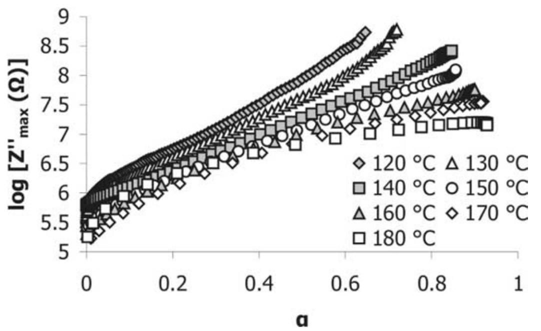

Fig. 12. Correlation between the dielectric signal (IIM point) and the degree of cure in the isothermal cure of RTM6 resin.

$0.16 \log(\Omega) \approx 420 \pm 65\ \mathrm{k\Omega}$. This value will be used for the coefficient c_2 since, it is closer to the physical meaning implied by Eq. (4)—coefficient c_2 reflects the impedance of the resin before the polymerisation reaction onset.

Coefficient c_1 exhibits a linear dependence on the cure temperature. Linear regression of the c_1 values in Table 2 results in the following relationship:

$$c_1 = c_{11} + c_{12}T \tag{5}$$

Here T is the cure temperature. The coefficients c_{11}, c_{12} and the regression coefficient are given in Table 3.

Substituting Eq. (5) into Eq. (4) results in a simple expression that relates the dielectric signal to the cure temperature and the degree of cure:

$$\log Z''_{\max} = (c_{11} + c_{12}T)\alpha + c_2 \tag{6}$$

The model represented by Eq. (6) is plotted against experimental data in Fig. 13. Conversion was calculated using the cure kinetics model and the temperature profile from the dielectric experiments. The model lines reproduce the experimental data with high accuracy.

A direct comparison between the dielectric and the calorimetric experimental results has been presented in Fig. 1. The model expressed by Eq. (6) predicts the similarity between the dielectric and calorimetric signals. The derivative of the IIM with respect to time, using Eq. (6), yields the following expression:

Table 2
Linear regression analysis for the correlation between IIM and the degree of cure in the isothermal cure dielectric experiments

Cure temperature (°C)	c_1 (log (Ω))	c_2 (log (Ω))	R^2
120	4.04	5.95	0.9949
130	3.56	5.89	0.9965
140	3.09	5.77	0.9989
150	2.78	5.69	0.9984
160	2.23	5.78	0.9838
170	1.97	5.78	0.9831
180	1.35	6.04	0.9505

Table 3
Regression analysis for c_1

c_{11} (log (Ω))	c_{12} (log (Ω)/°C)	R^2
9.2	−0.043	0.9947

$$\frac{\mathrm{d}\log Z''_{\max}}{\mathrm{d}t} = \frac{\partial \log Z''_{\max}}{\partial a}\frac{\mathrm{d}a}{\mathrm{d}t} + \frac{\partial \log Z''_{\max}}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}t} \Rightarrow \frac{\mathrm{d}\log Z''_{\max}}{\mathrm{d}t} = \underbrace{(c_{11} + c_{12}T)\frac{\mathrm{d}a}{\mathrm{d}t}}_{\text{Term A:Reaction rate term}} + \underbrace{c_{12}ar}_{\text{Term B:Heating rate term}} \tag{7}$$

In the above equation r is the heating rate, defined as the time derivative of the cure temperature. Out of the two terms on the right hand side of Eq. (7) the heating rate term is zero for the isothermal cures ($r=0$). What remains is 'Term A', which is the product of a constant (c_1) and of the reaction rate. The agreement between the two sets of data shown in Fig. 1 indicates the proportionality between the two derivatives implied by Eq. (7). This proportionality is the result of the linear correlation between the dielectric signal and the degree of cure, which can be observed in Fig. 12.

4.2. Non-isothermal experiments

The relationship between the dielectric signal and the degree of cure data for non-isothermal experiments is shown in Fig. 14. At any given heating rate, the dielectric signal increases from the reaction onset and reaches a maximum at conversions above 80%, corresponding to the maximum of the appropriate peak shown in Fig. 11. Thereafter, the effect of the temperature increase is much stronger than the effect of the remaining reaction and, therefore, the IIM decreases.

The temperature profiles of the non-isothermal experiments were used for the calculation of the IIM values through Eq. (6). The resulting model curves are plotted alongside corresponding experimental data in Fig. 15. The IIM data calculated using Eq. (6) follow the non-isothermal experimental data despite the fact that none of these experimental data were used for the determination of the coefficients c_1 and c_2 in Eq. (6).

An analysis of the numerical factors that determine the

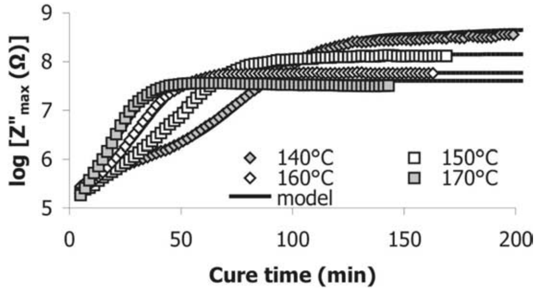

Fig. 13. Modelling of isothermal IIM data using Eq. (6).

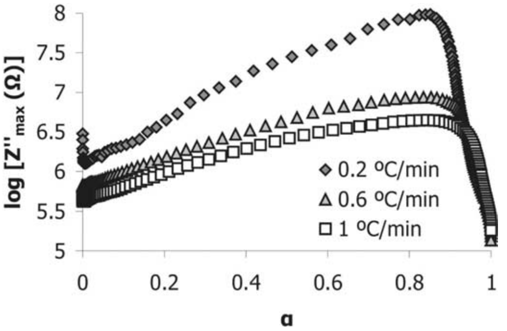

Fig. 14. Relationship between the dielectric signal (IIM point) and the degree of cure in the dynamic cure of RTM6 resin.

IIM value calculated by Eq. (6) demonstrates the reason for this agreement. The interplay between the two terms of the right hand side of Eq. (6) is as follows—initially, before the reaction onset, only the value of constant c_2 is reflected in the model since, $\alpha=0$.

$$\log Z''_{\max} = (c_{11}+c_{12}T)\alpha + c_2 \xrightarrow[\alpha=0]{\text{Prior to cure}} \log Z''_{\max} = c_2 \tag{8}$$

As the polymerisation reaction progresses the degree of cure increases and the first term of Eq. (6) begins to have an impact on the shape of the model curves. Although the value of c_1 decreases as the temperature increases (Eq. (5)), the accelerated change (increase) in the degree of cure, consequence of the autocatalytic nature of the polymerisation reaction, causes the IIM values to increase. At the end of the reaction the changes in the degree of cure are very slow whilst the value of c_1 continues to drop with increasing temperature. The resultant is a decrease in the IIM values. Finally, when $\alpha=1$, IIM exhibits an exponential dependence on temperature.

$$\log Z''_{\max} = (c_{11}+c_{12}T)\alpha + c_2 \xrightarrow[\alpha=1]{\text{Full cure}} \log Z''_{\max} = (c_{11}+c_{12}T) + c_2 \Leftrightarrow Z''_{\max} = Ae^{bT} \tag{9}$$

where A, b are calculated from c_{11}, c_{12} and c_2.

The comparison between the dielectric (symbols) and the calorimetric data (lines) for the different non-isothermal cures of RTM6 is shown in Fig. 16. Compared to the isothermal case (Fig. 1), the two sets of data are less coincident. The presence of 'Term B' in Eq. (7), which by default has zero value in the isothermal case, designates the lack of proportionality between the dielectric and the calorimetric signals in the non-isothermal case. However, as Fig. 16 shows, despite the influence of the heating rate term the time derivative of IIM still approximates the reaction rate signal to a reasonable degree.

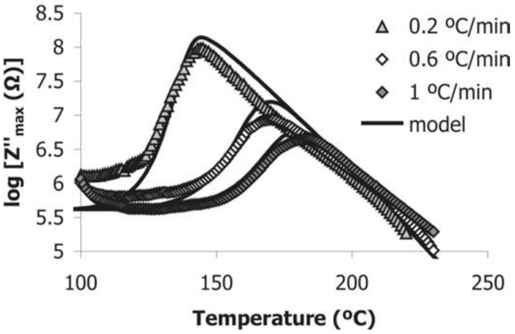

Fig. 15. Modelling of non-isothermal IIM data using Eq. (6)—comparison with experiment.

5. Discussion

The build up of the model Eq. (6) was based on the observation that the dielectric and the calorimetric signals are linearly correlated under isothermal cure conditions. The successful application of the same model to non-isothermal experiments leads to the conclusion that Eq. (6) is not just an empirical equation. The linear relationship between the two sets of data is to be expected when one assumes that both experimental techniques measure some parameter which is affected in the same way by the same phenomenon; in this case the polymerisation reaction. This assumption is not straightforward since, dielectric measurements provide information about the movements of molecular entities in the curing material, whereas in calorimetric experiments the exothermic heat produced by the polymerisation reaction is being measured. There is no obvious reason for the mobility of small charged species (quantified as the IIM value) to be expected to be affected in the same way as the number of reacting molecules or functional molecular sites (reflecting the amount of heat being released at a given time), apart from the experimental evidence at hand and a few other studies [7–9]. Answer to this open issue is likely to come from experimental and molecular simulation studies on model thermosetting systems, where the polymerisation reaction and the amount and properties of the charged species can be measured and controlled.

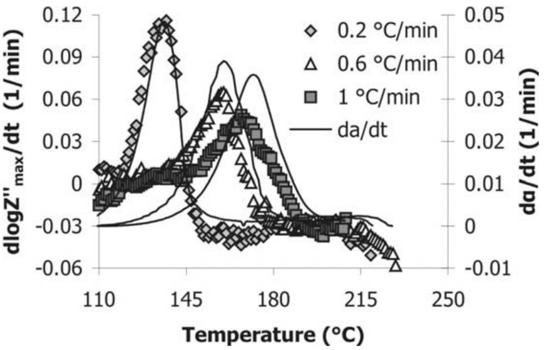

Fig. 16. Comparison between the IIM time derivative (symbols) calculated from the dielectric data and the reaction rate curves obtained from DSC measurements (lines), for three different non-isothermal cures of RTM6 resin.

In what follows, the performance of the model at the early stages of cure, its consistency at low, mid and high conversion values and the possibility of using dielectric experiments as a means of indirect calorimetric measurements are being discussed.

5.1. Early stages of cure

At resin conversion values below 10% the log–linear relationship between the IIM and the conversion does not appear to hold, compromising the validity of Eq. (4) and hence of Eq. (6)) in this range. A possible explanation for this discrepancy may lie in the subtle difference between the ways in which the isothermal cure experiments had to be conducted when using the different measuring techniques. In the DSC experiments, temperature was increased at a constant rate of 20 °C/min up to the desired cure temperature. Previously carried out analysis of the dynamic cure at 20 °C/min meant that it was possible to make an accurate calculation of the reaction conversion the resin had reached before getting to the temperature of the isothermal dwell. This value was used then as the initial conversion value for the calculation of the conversion profiles in the isothermal DSC experiments through Eq. (3). In the dielectric experiments, the resin was preheated to 60 °C in order to lower its viscosity, and poured into the experimental cell which had itself been preheated to the desired cure temperature in order to start the cure reaction at that temperature. This resulted in local heat up rates of the resin sample as high as 70 °C/min. A new miniaturised dielectric cell is currently under construction, designed to widen the range of thermal profiles available for the dielectric experiments. It will be used to make a more rigorous assessment of the validity of the model in the early stages of cure.

5.2. Applicability of a single model

The structure of Eq. (6) reflects the existence a complex interplay between the effect of the polymerisation reaction itself and the effect of temperature during the cure. The effect of temperature at different instances in the polymerisation reaction can be studied by plotting iso-conversional curves using Eq. (6). Such curves are shown in Fig. 17 together with experimental data from both isothermal and non-isothermal experiments.

The model predicts that the effect of temperature on the cure will become more pronounced as the polymerisation advances. The theoretical slope of the iso-conversional curves starts from zero at $\alpha = 0$ and increases as α increases, reaching the maximum value equal to c_{12} at $\alpha = 1$. The experimental data confirm this prediction, except at the very beginning of cure, where the data suggest that the IIM value has a non-zero temperature dependence. This dependence was found to be related to the temperature dependence of the electrical impedance of the uncured resin at low temperatures (<90 °C). Least squares linear regression gives the relationship as:

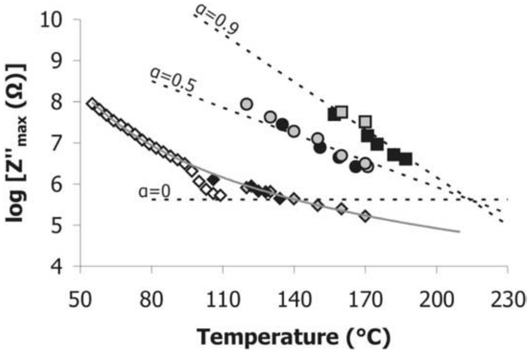

Fig. 17. Iso-conversional curves calculated from Eq. (6) and experimental data at 0, 50 and 90% conversion. The points correspond to the same degree of cure and come from isothermal (grey points) and non-isothermal (black points) experiments. The full grey line is the result of linear regression analysis on non-isothermal experimental data (open diamonds) in the temperature range 50–90 °C.

$$\log Z''_{\max}\big|_{\text{uncured, } T<90\ ^\circ\text{C}} = \frac{36}{T^{0.37}}, \quad R^2 = 0.9977 \tag{10}$$

It is interesting to note that that the assumed melting/-dissolution of one of the resin constituents in the 90–110 °C temperature range, indicated by the anomalous feature in Fig. 17 (Fig. 11), does not appear to restrict the application of Eq. (10) to temperatures below 90 °C, indeed the data for the uncured resin can be fitted by Eq. (10) up to 170 °C.

The results displayed in Fig. 17 indicate that the dielectric response of the resin is time-temperature path independent. The IIM value at a specific temperature and a specific conversion is the same whether it is measured isothermally or by using a heating ramp. This is the reason behind the applicability of a single closed form function model.

5.3. Equivalence between dielectric and calorimetric data

The influence of the two terms of Eq. (7) in the dielectric signal can be studied in Fig. 18, where data from the dynamic cure at 0.6 °C/min are superimposed onto plots of 'Term A' and 'Term B' from Eq. (7). 'Term A' follows the changes of the reaction rate, although the presence of temperature in the parenthesis of 'Term A' in Eq. (7) means that there is no direct proportionality between the dielectric and the calorimetric signals, as there is in the isothermal case. The low value of parameter c_{12}, however, reduces the impact of temperature on 'Term A'. This can be seen in Fig. 19, where 'Term A' is compared to the reaction rate for the dynamic experiment at 0.6 °C/min.

In the late stages of cure, above 200 °C, a second small peak in the reaction rate curve, likely to be the results of devitrification of the resin [24], is smeared out by the effect of temperature in 'Term A'. What remains is a faint shoulder, barely observable in Fig. 19.

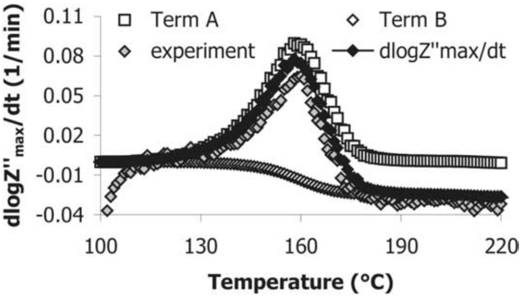

Fig. 18. Application of Eq. (7) to the dynamic cure of RTM6 at 0.6 °C/min.

The shape of 'Term B' is determined by the shape of the conversion curve, as can be observed in Fig. 18. However, its value is determined by the product $c_{12} \times r$, which is a constant. The presence of the heating rate r in 'Term B' means that at high heating rates the IIM derivative will be more skewed towards the end of the reaction and the peak less pronounced. This term acts as a baseline for the total dielectric signal and is the reason for the negative d log $Z''_{\max}$/dt values obtained towards the end of the reaction in the non-isothermal experiments.

6. Concluding remarks

The information content of dielectric cure monitoring signals has been analysed and compared to that of calorimetric cure monitoring signals, using RTM6 resin as a representative of the class of commercially available epoxy resins intended for use in the manufacture of aerospace grade continuous fibre reinforced structures. The phenomenological similarity observed between the dielectric and calorimetric signals led to the development of a model equation, which has been shown to apply under both isothermal and dynamic heating cure conditions. The model relates the absolute value of the dielectric signal to the instantaneous cure temperature and the instantaneous degree of cure. The relative values of the model coefficients can be considered an indicator of the relative influence of the polymerisation reaction and of the temperature on the dielectric signal.

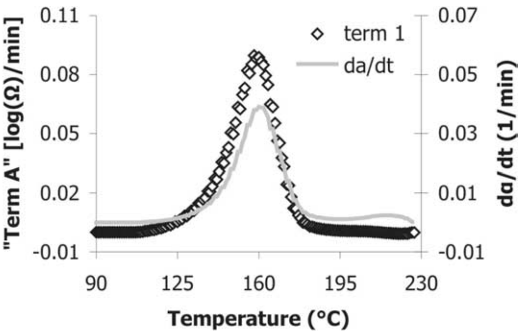

Fig. 19. Comparison of the reaction rate (obtained from DSC experiment) and 'Term A' of Eq. (7) for the cure of RTM6 at 0.6 °C/min. The correlation coefficient between the two data sets is 0.92.

The work presented in this paper has exploited our wide experimental database on just one representative resin system. Most recent work confirms the applicability of the findings in a generic fashion, in a range of thermosetting resins, including a 120 °C cure toughened epoxy prepreg system [25], a bismaleimide and a vinyl–ester resin [26]. Thus it seems likely that in situ, real time dielectric measurements from embedded micro-sensors may in future be used as a kind of 'in situ DSC'. The degree of accuracy to which the correlation between the two types of measurements needs to be established will depend on the application; the correlation established in this work for the mid-cure range in a commercial epoxy would be sufficient to satisfy the quality assurance issues in composites manufacture.

Acknowledgements

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