

# MONITORING CURE IN GLASS FIBRE/VINYL ESTER PULTRUSIONS

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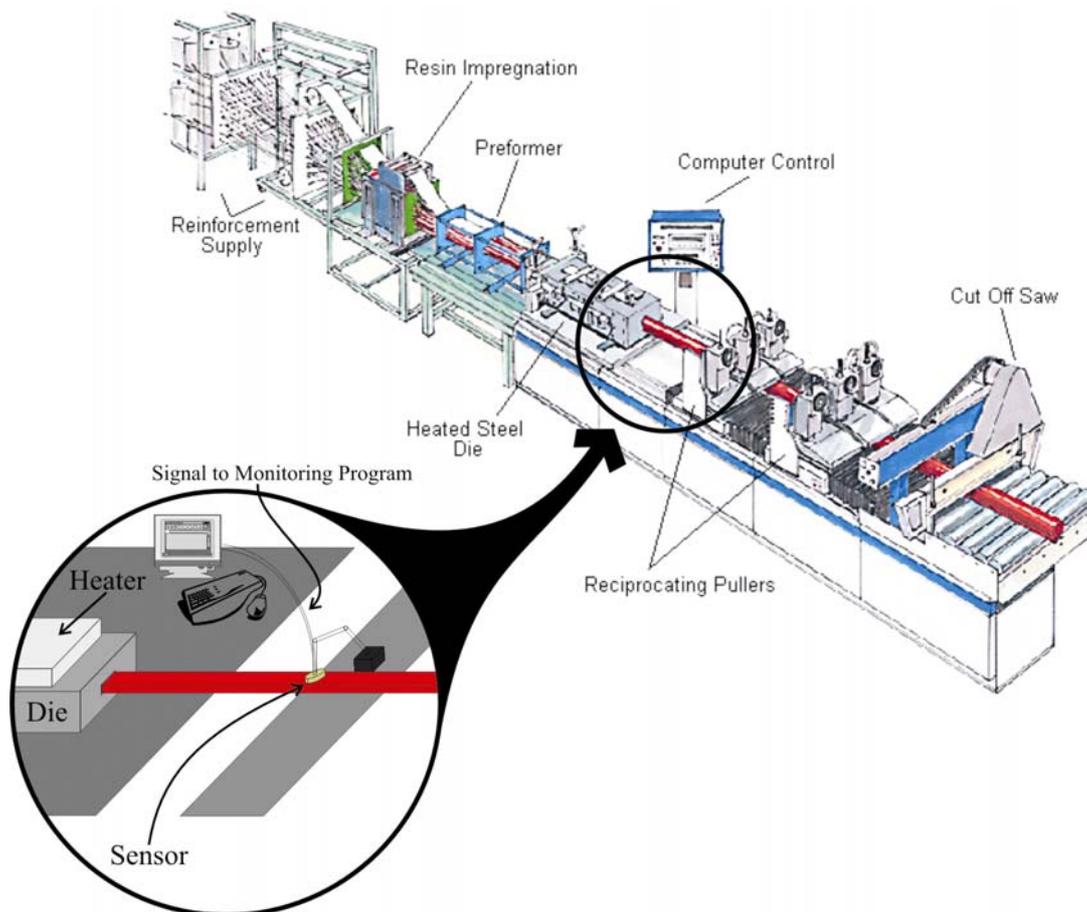
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## ABSTRACT

The paper describes the development of a material state model for a specific industrial Vinylester resin and its use in the context of process control of composite pultrusion. The application of thermoanalytical data to the modelling of chemical cure kinetics is outlined, together with a description of on-line, real time, cure monitoring. The cure monitoring signal is obtained by using a newly developed, robust, dielectric sensor and is presented in terms of changes in the complex impedance of the curing resin.

## 1. INTRODUCTION

The present paper concerns the development of cure monitoring and modelling tools with the aim of real time, on-line, monitoring of pultrusion. A typical pultrusion set up is illustrated in Fig. 1. Reinforcement fibres are drawn into a resin bath and then pulled through a pre-former into a heated die.



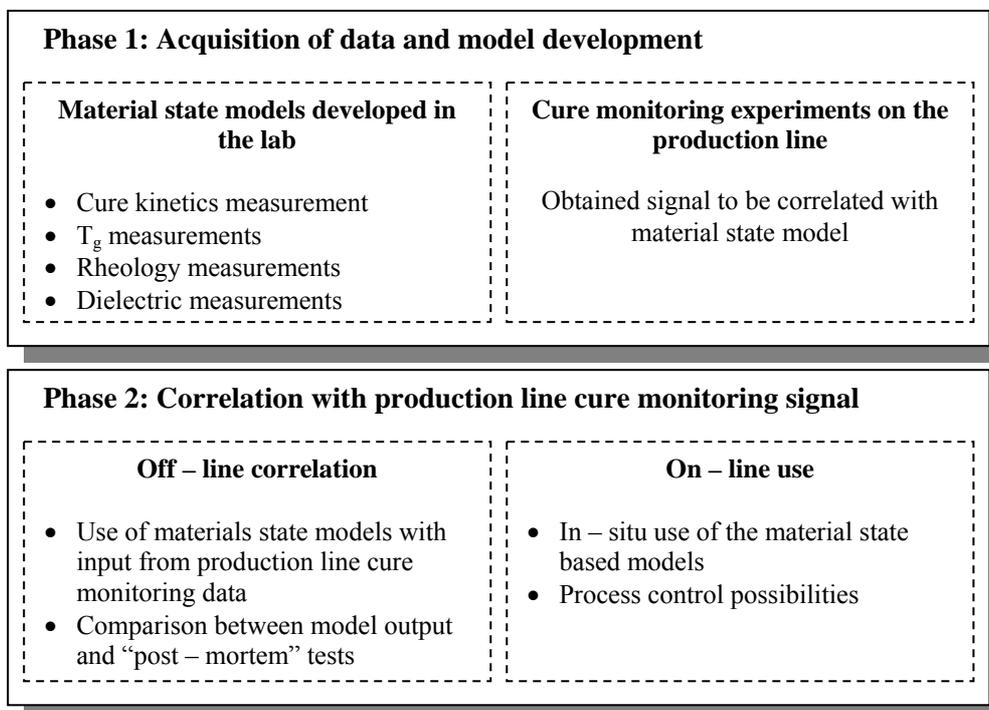
**Fig. 1.** Schematic representation of the thermoset pultrusion process. The inset diagram shows the placement of the dielectric sensor

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The elevated temperature in the die initiates the curing reaction. Cross-linking results in the formation of a three dimensional network that gradually transforms the thermosetting material from a polymeric liquid to rubber and then to glass. The temperature of the heated die and the pulling speed define the process outcome. Control of these variables requires the utilisation of an appropriate monitoring technique and the corresponding interpretation tools [1 – 3]. Dielectric cure monitoring has been identified as such a technique in the context of process control in composites manufacturing [1]. The work reported here focuses on the application of dielectric cure monitoring to the pultrusion of glass fibre/vinyl ester composites. A new, robust and abrasion resistant dielectric sensor has been developed by partners in GIRD-CT-2001-03010 ‘CONDICOMP’ project. The positioning of this sensor along the pultrusion line is indicated in Fig.1.

## 2. BACKGROUND TO PROCESS MONITORING

The general methodology for successful in-situ, real time, monitoring lies in the feasibility of establishing robust relationships between the monitoring signal and material state models produced in laboratory experiments. Fig.2 outlines the required elements of a monitoring/control scheme.



**Fig. 2.** Methodology for material state based, in – situ and real-time, cure monitoring

In Phase 1 an experimental database is produced. Elements of the database are then linked into validated (semi-empirical) models. The material state is usually defined by the reaction conversion,  $\alpha$ . Chemical cure kinetics models seek to relate  $\alpha$  with cure time  $t$  and cure temperature  $T$ , in a general form [2, 4]. When the correlation can be expressed as an analytic function we write:

$$a = f_1(t, T) \quad (1)$$

When dielectric measurements are utilised as the monitoring technique [5, 6] a relationship similar to Eq. (1) is sought:

$$S = f_2(t, T) \quad (2)$$

where  $S$  is the (generic) dielectric signal. The dielectric signal can be expressed in many formats: Complex permittivity, Complex impedance, Complex admittance etc [6]. The two relationships are then coupled to produce a material state model based on the dielectric signal:

$$a = f(S, T) \quad (3)$$

It is usually the case that either Eq. (1) or Eq. (2) (or both) cannot be expressed analytically. In such cases regression analysis is performed on calorimetric and dielectric data collected under the same temperature conditions and material specific relationships are obtained.

Once Eq. (3) has been established for a particular material, the next step is to validate it against experimental data acquired from the production line. The model validation is the passing point from Phase 1 to Phase 2 in the methodology diagram shown in Fig.2. When the model validation is established, the model can be implemented on the production line and used for real time monitoring.

### 3. RESULTS FOR SELECTED ELEMENTS OF THE SCHEME

The results presented here involve the determination of a material state equation for a Vinylester system used by Fibreforce Composites Ltd. in pultrusion applications [7]. Details of the system formulation and components can be found elsewhere [8]. The cure kinetics model was built on calorimetric measurements performed on a TA Instruments Ltd 2920 DSC. The dielectric measurements were performed on a Solartron Analytical 1260 Gain/Phase Analyzer. The prototype reusable dielectric sensor, specifically developed for thermoset cure monitoring, was used.

Calorimetric results from isothermal and dynamic cure of the Vinylester resin system are shown in Fig.3.

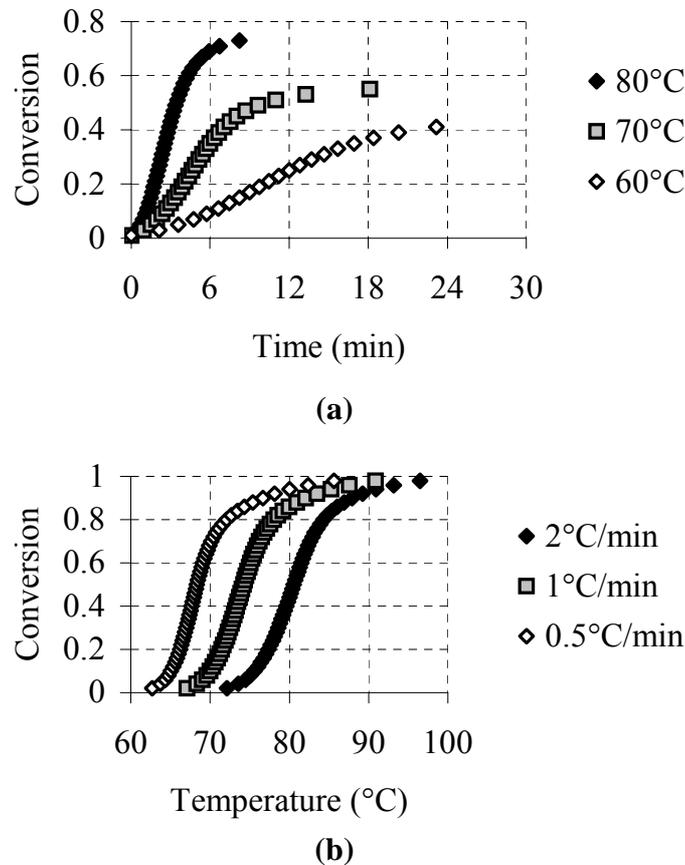


Fig. 3: Isothermal (a) and dynamic (b) calorimetric data from the cure of Vinylester

The curing reaction of Vinylester is autocatalytic. There are two different reaction mechanisms in the Vinylester cure which dominate in different temperature ranges [8]. The cure kinetics equation which models the main reaction is the following:

$$\frac{da}{dt} = ka^{n_1} (a_{\max} - a)^{n_2} (a_{\max})^{-m} \quad (4)$$

where

$$k = Ae^{-\frac{E}{RT}}$$

$$a_{\max} = a_{\max i} + N(T, 360, 10)(1 - a_{\max i})$$

$$a_{\max i} = 1.1 \times 10^{-2} T - 3.4 - (3.6 \times 10^{-3} T - 1.46) N(T, 343, 0.5)$$

and  $N(T, \mu, \sigma)$  is the cumulative normal distribution function:

$$N(T, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^T e^{-\frac{(T-\mu)^2}{2\sigma^2}} dT$$

All the parameter values are given in Table 1.  $a_{\max}$  is the maximum conversion obtained at a specific temperature. Eq. (4) models all isothermal and dynamic cure cycles up to 140°C. A full cure kinetics model which models the cure up to 180°C can be found in [8].

“Table 1. Parameter values for the chemical cure kinetics model.”

A (min <sup>-1</sup> )	E (kJ/mol)	n <sub>1</sub>	n <sub>2</sub>	m
1.7x10 <sup>11</sup>	77	1.1	0.73	1.4

Dielectric cure monitoring results are presented in Fig. 4. The value at the maximum point of the imaginary impedance  $Z''_{\max}$  has been chosen as the monitoring parameter.  $Z''_{\max}$  is related to the movements of the charged species present in the curing system [5].

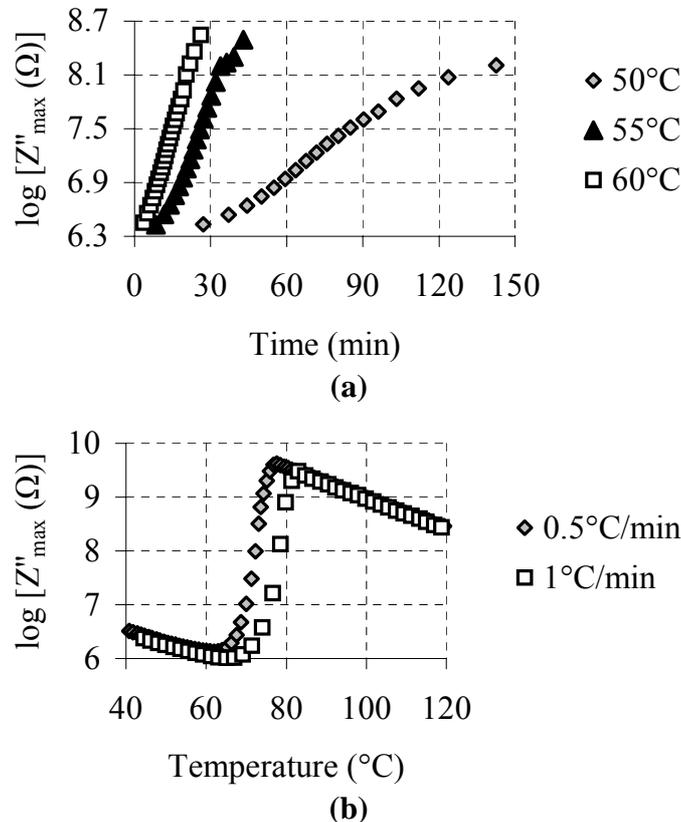


Fig. 4. Isothermal (a) and dynamic (b) dielectric data from the cure of Vinylester

In the isothermal experiments the dielectric signal increases as the cure progresses. At some point (not shown in Fig. 4a) the dielectric signal levels out and further increase is negligible. In the dynamic experiments the dielectric signal decreases exponentially (note:  $Z''_{max}$  is plotted on logarithmic scale in Fig. 4) at low temperatures where the reaction has not started, showing effect of temperature alone. The polymerisation reaction causes  $Z''_{max}$  to increase more than three orders of magnitude. When the reaction is complete the behaviour is similar to that observed before the reaction onset; the signal decreases exponentially with increasing temperature.

The correlation between the calorimetric and the dielectric curves was performed in three steps:

1. The temperature recorded in the dielectric cure monitoring experiment is fed into the cure kinetics model (Eq. (4)). The conversion profile for the specific temperature profile is calculated.
2. The conversion data are plotted against the dielectric data for the specific experiment.
3. Regression analysis for the conversion – dielectric signal data is performed simultaneously for a range of temperature conditions.

In the case of the Vinylester, the following equation adequately describes the experimental data for temperatures not exceeding 70°C.

$$a = (c_1 + c_2 T) \log Z''_{max} + (c_3 + c_4 T) \quad (5)$$

The coefficient values are given in Table 2. At temperatures higher than 70°C the reaction was too fast to monitor with dielectric sensors and the accompanying exotherm prevented accurate control of temperature.

“Table 2. Parameter values for the material state equation.”

$c_1$	$c_2$ (1/°C)	$c_3$	$c_4$ (1/°C)
-0.50	$1.3 \times 10^{-2}$	2.6	$-7.4 \times 10^{-2}$

The application of Eq. (5) in modelling the experimental data is shown in Figs. 5 and 6 for isothermal and dynamic conditions respectively. The average error of the estimation is ~3% in isothermal cure and ~8% in non-isothermal cure.

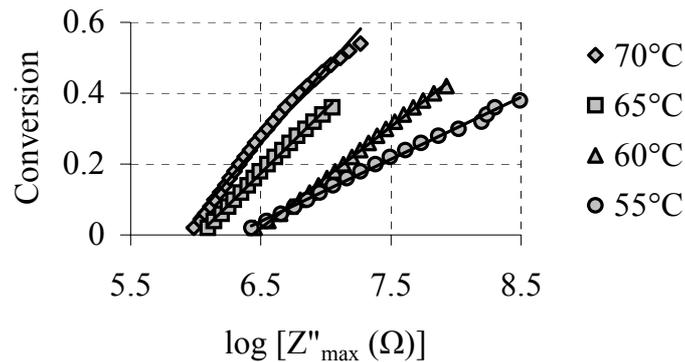
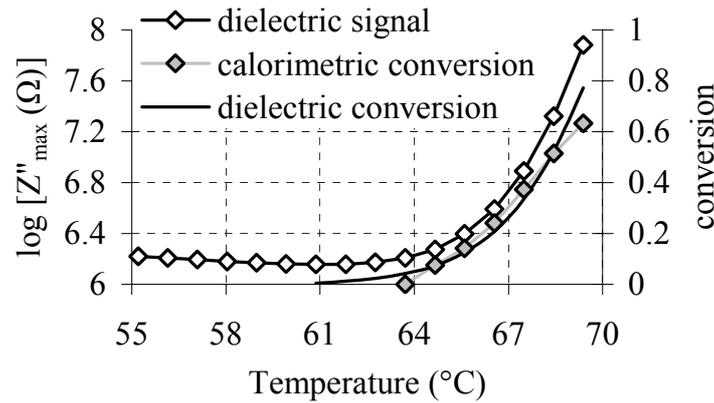


Fig. 5. Correlation between calorimetric and dielectric data for the isothermal cure of Vinylester. Data from four separate isothermal experiments are shown. The black line represents the model predictions.



**Fig. 6.** Correlation between calorimetric and dielectric data for the dynamic cure of Vinylester at 0.5°C/min.

#### 4. DISCUSSION

The successful application of any cure monitoring technique in-situ in a manufacturing process is subject to many factors, the most important being:

- the quality of the models that will be used for predicting the state of the material ; and
- the performance of the dielectric sensor and of the accompanying monitoring system on the production floor.

In the case study presented here, the imaginary impedance maximum has been chosen as the monitoring parameter and the reaction conversion has been chosen as the material state parameter. A close correlation between these two parameters has been established under experimental conditions that could be reproduced in the lab.

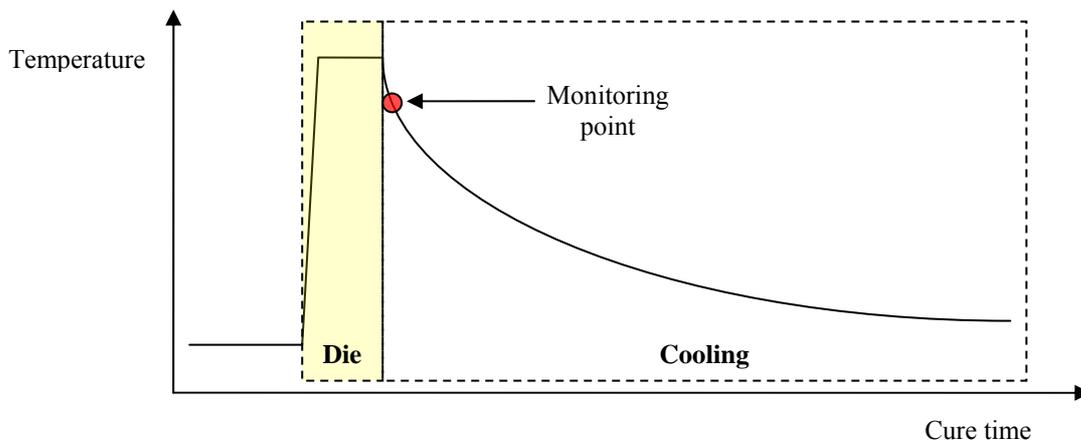
The development of a prototype reusable sensor, specifically designed for monitoring thermoset composite cure, solved many practical issues faced by the industry in previous attempts to employ cure monitoring in composite manufacturing. The new sensor configuration is shown in Fig. 7 as it was tested on the pultrusion line at Fibreforce Composites Ltd. [7].



**Fig. 7.** Dielectric cure monitoring for pultrusion. (a) Sensor configuration, (b) Real – time monitoring system developed by INASCO Hellas [9]. The red arrows note the direction of movement of the pultrusion line

The sensor surface has been designed for high wear resistance which allows continuous monitoring to be carried out at a selected point of the pultrusion line without the need of regular replacement. This point is usually after the heated dies, as shown in Fig. 1, because of

the inherent manufacturing difficulties in fitting the sensor to the inside surface of the die. At that point, the polymerisation reaction has either stopped or been completed and the material is cooling down, as can be pictured in Fig. 8, where the imposed temperature profile during the pultrusion process is shown.



**Fig. 8.** Typical temperature profile experienced by the curing material during the pultrusion process. The positioning of the sensor is noted with a red circle. The monitoring point is after the die (see also Fig. 1)

In this case, the dielectric signal information is related to the finalised material state of the product. This information can be correlated with material state parameters such as the glass transition temperature ( $T_g$ ) or the maximum reaction conversion attained under specific temperature conditions ( $\alpha_{max}$ ).

Whilst the subject of dielectric cure monitoring is not new, the exploitation of the potential of the technique in complex manufacturing processes such as pultrusion continues to present a number of challenges. This paper has shown how some of the issues may be addressed and represents significant progress towards a real manufacturing application.

## ACKNOWLEDGEMENTS

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