

FRAMEWORK FOR PROCESS-RELATED RESIN SELECTION AND OPTIMISATION FOR THE RESIN TRANSFER MOULDING (RTM) OF COMPOSITE MATERIALS

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ABSTRACT

A framework for process-related resin selection and optimisation for the resin transfer moulding (RTM) of composite materials is proposed in the context of research and development for industrial applications. The proposed framework and the associated test and analysis methodologies are applied to three epoxy resin systems which are assessed against different RTM process requirements.

1 INTRODUCTION

Industrial applications require intensive research and development in the area of RTM process optimisation for a new product, scaling up of production or changes in materials. As a result, an engineering methodology to reduce the number of experiments and set up of complex processing simulations is highly desirable. The aim of this study has been to assemble a framework for process-related resin selection and optimisation for a given RTM mould and fibre reinforcement. In this framework, set requirements may be modified regarding mechanical and other properties of the RTM composite product, filling length and filling time, total cycle time, demould time and post-cure time.

2 MATERIALS AND MATERIALS CHARACTERISATION

The three different epoxy based systems investigated were: (a) Resin A and cure agent AA; (b) Resin B and curing agent BB; (c) Resin C and curing agent CC.

NMR and FTIR studies concluded that all resins were similar in their bulk resin make up, the differences being in their relative ratios and the twinned curing agent.

3 REACTION KINETICS

The reaction kinetics for catalytic (1) and autocatalytic (2) reactions in epoxy systems are described by the following equations where equation (3) depicts the Arrhenius temperature dependence:

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \quad (1)$$

$$\frac{d\alpha}{dt} = K\alpha^m(1 - \alpha)^n \quad (2)$$

$$K = Ae^{-Ea/RT} \quad (3)$$

Differential scanning calorimetry (DSC) studies were carried out to determine the reaction type (catalytic or autocatalytic) and reaction kinetics parameters for all resin systems; Figure 1(a) shows an example of such DSC analysis for resin system A/AA. The measured exotherms in Figure 1(a) were 516, 548, 494, 559 and 465 Jg⁻¹ at the imposed temperature ramp rates of 5,7.5,10,12.5 and 15 Kmin⁻¹, respectively. Figure 1(b) presents the fit lines to determine the activation energy, Ea, in equation (3) according to two different methods, where it was determined that Ea = 60.0 kJ/mol (Kissinger method [1]) and Ea = 63.4 kJ/mol (Ozawa method [2]) where the pre-exponential factor A = 22.5x10⁶ min⁻¹. A catalytic reaction of equation-type (1) fitted the curves of Figure 1(a) after the peak exotherm, hence, the need for an autocatalytic reaction of equation-type (2) was evident for the A/AA epoxy system: a numerical fit of equation (2) to the experimental data yielded m = 0.15 and n = 0.80, as is presented in Figure 1(c). The so determined reaction kinetics parameters were inputted in equations (2) and (3) to predict the extent of reaction versus time for the isothermal DSC at 85 °C and these predictions compare very well with the corresponding experimental data for system A/AA as is shown in Figure 1(d).

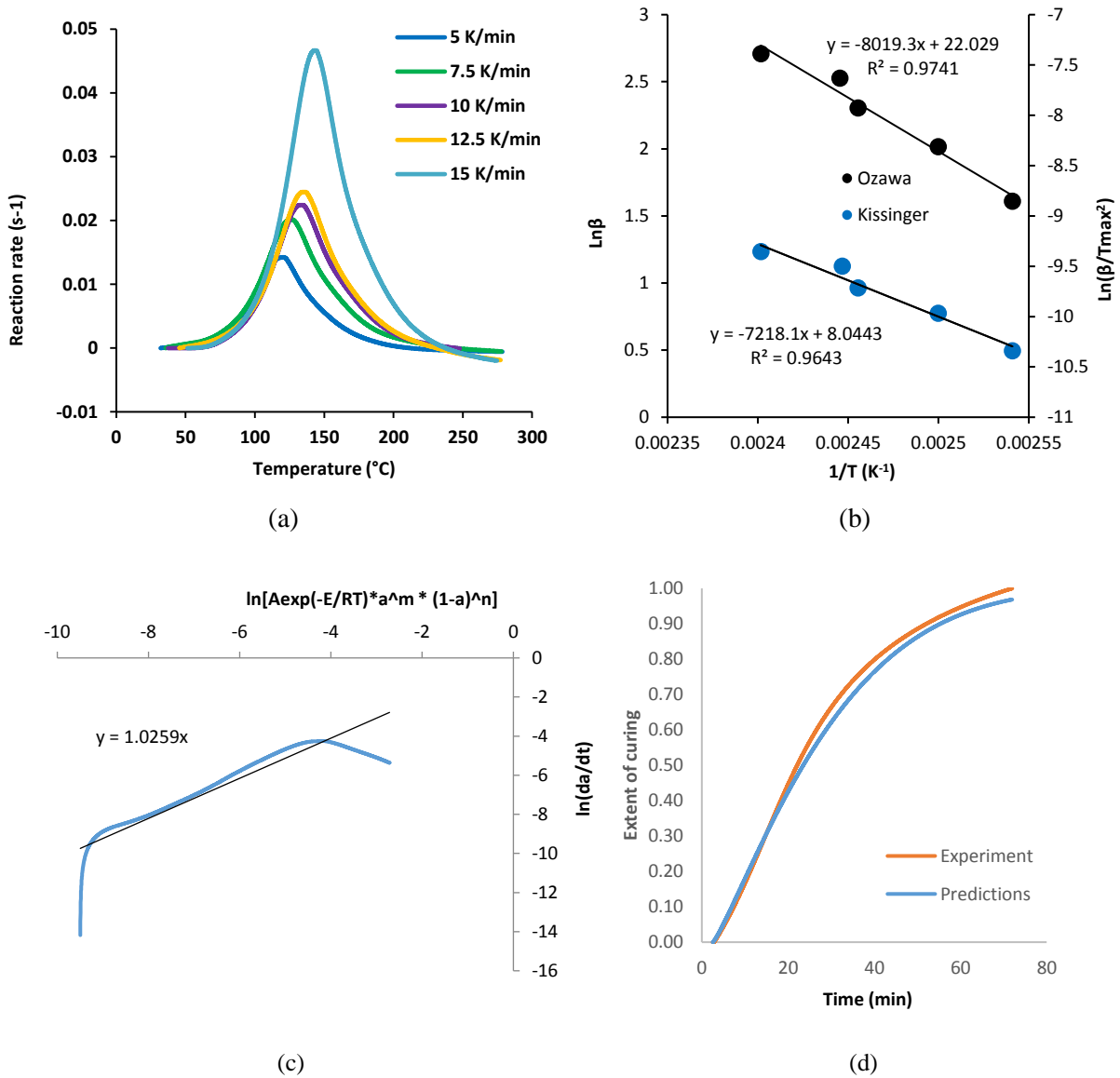


Figure 1: Examples of results from the DSC analysis and numerical fitting of experimental data for the A/AA epoxy system: (a),(b),(c) temperature scanning, (d) isothermal DSC at 85 °C.

Table 1 presents the results of the data fitting exercise for the reaction kinetics of curing. All three epoxy systems seem to follow autocatalytic reaction kinetics (equation (2)). System A/AA has the highest reaction constant at 85 °C. System C/CC has the lowest reaction constant at 85 °C allowing for a delayed gel point (Figure 3). However, the high values of m and n for system C/CC allow this resin system to reach high degree of curing after the gel point accompanied by a high storage modulus (Figure 4) which permits for early demould time.

Epoxy system	Reaction equation	A (min ⁻¹)	Ea (kJ/mol)	K _{85 °C} (min ⁻¹)	m	n
A/AA	(2)	22.5x10 ⁶	60.0	3.94x10 ⁻²	0.15	0.80
B/BB	(2)	18.8 x10 ⁶	60.2	3.11 x10 ⁻²	0.40	1.80
C/CC	(2)	7.99 x10 ⁶	58.1	2.65x10 ⁻²	0.40	2.5

Table 1. Reaction kinetics constants derived from the DCS analysis of the three epoxy/curing agent systems of this study

4 RHEOLOGY

The curing kinetics also affects the viscosity, μ , of the curing epoxy system as well as the mechanical properties. Two relations have been investigated in the experimental data fitting exercise [3-5]:

$$\mu = \mu_o e^{Ev/RT} \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{B+C\alpha} \quad (4)$$

$$\mu = \mu_o e^{Ev/RT} e^{B\alpha} \quad (5)$$

where α_g is the conversion at the gel point and under isothermal conditions at temperature T:

$$\mu_{oT} = \mu_o e^{Ev/RT} \quad (6)$$

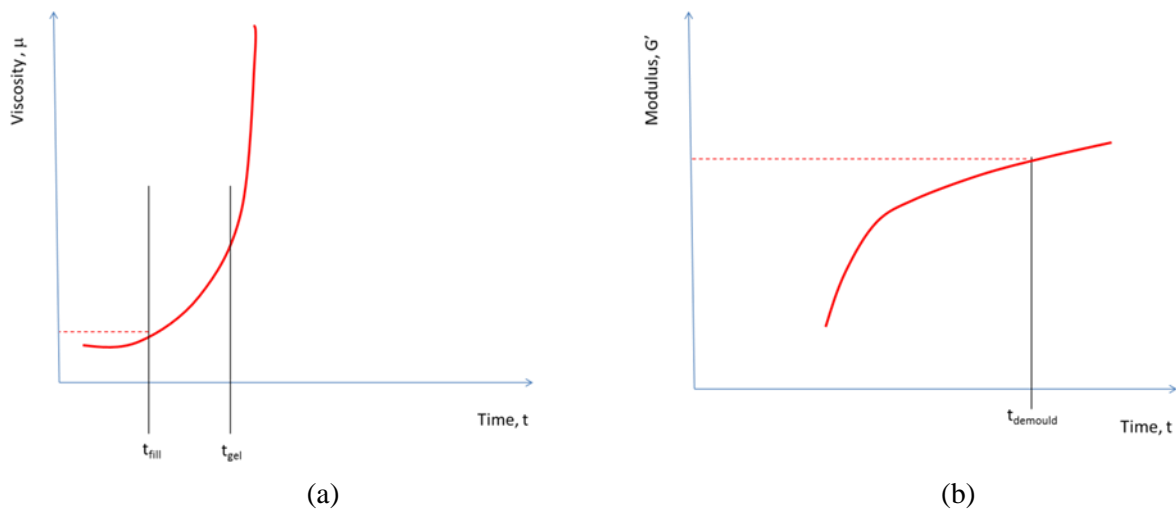


Figure 2. Diagram demonstrating the relation between process requirements and properties of the curing material system at (a) low frequency (e.g. 1 Hz) and (b) high frequency (e.g. 100 Hz)

Key factors for the process and product optimisation in RTM are: the filling time, the gel time, the curing time and the demould time. The filling and curing time may be associated with process requirements in terms of manufacturing cost, for example. Once the process requirements for the filling time, cycle time and demould time have been set for a particular RTM process, mould and fibre reinforcement, these can be related to exact values of viscosity or shear elastic modulus as illustrated in Figure 2. So a set filling time corresponds to a viscosity for the resin, which means that different resins may be considered for that RTM process, mould and reinforcement provided that their viscosity until the set t_{fill} is below the gel viscosity. On the other hand, various resins might comply with a set demould time provided that their elastic modulus G' is higher than the required value to demould after $t_{demould}$. Due to the changing viscoelastic behaviour of a curing epoxy resin, these two approaches require two different testing frequencies. One low, to capture the viscous resin behavior for the initial viscosity measurements, and the other high, to capture the elastic resin behaviour approaching $t_{demould}$.

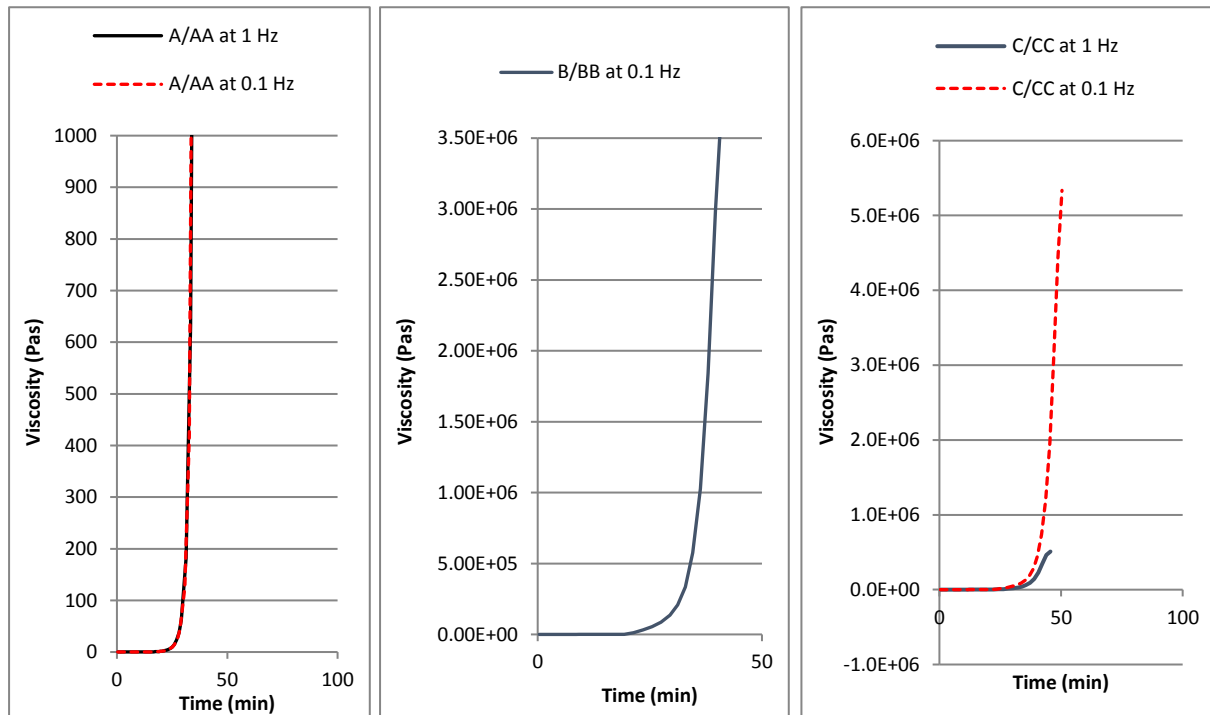


Figure 3. Rheology data for the three epoxy systems curing at 85 °C

Figure 3 presents viscosity data for the three epoxy resin systems curing isothermally at 85 °C. Data has been plotted for two rheometrics test frequencies, 0.1 and 1 Hz. It looks that the 0.1 Hz frequency captures the early viscosity rise at gel point and is in fact closer to the state of slow flow conditions present at RTM. The three systems all have a low starting viscosity but differ in terms of the start of gel time. Depending on the maximum filling time requirement, one may choose all or narrow the selection to complete filling during RTM before resin gel occurs.

Figure 4 presents the data of the shear storage modulus, G' , versus time for the three epoxy resin systems curing isothermally at 85 °C. A high test frequency of 100 Hz was employed to capture best the elastic behaviour of the material. Epoxy systems A/AA and B/BB exhibit a fast rise of the storage modulus after the gel point, followed by some reduction of G' after 4 MPa which we suspect is due to the detachment of the solid specimen from the rotating disc plates used for the rheological tests. System C/CC demonstrates a steady rise of G' with available data values above 10 MPa.

A dynamic mechanical analysis (DMA) test of a curing system provides data for the storage and viscous shear modulus, G' and G'' , respectively, so G' is related to the demould time according to Figure 2(b) and G'' is used to determine the viscosity μ according to the relation: $\mu = G''/\omega$ where ω is the angular frequency. Performing DMA on a curing system is also used to determine the gel point (Figure 5(a)). However, given that the gel time may vary by up to 1 second for different test frequencies, a method was developed to determine the gel point as is illustrated in Figure 5(b) where testing at different frequencies is used to determine the gel time from the intercept of the curves of $\tan\delta$ obtained at the chosen frequencies versus curing time, where $\tan\delta = G''/G'$.

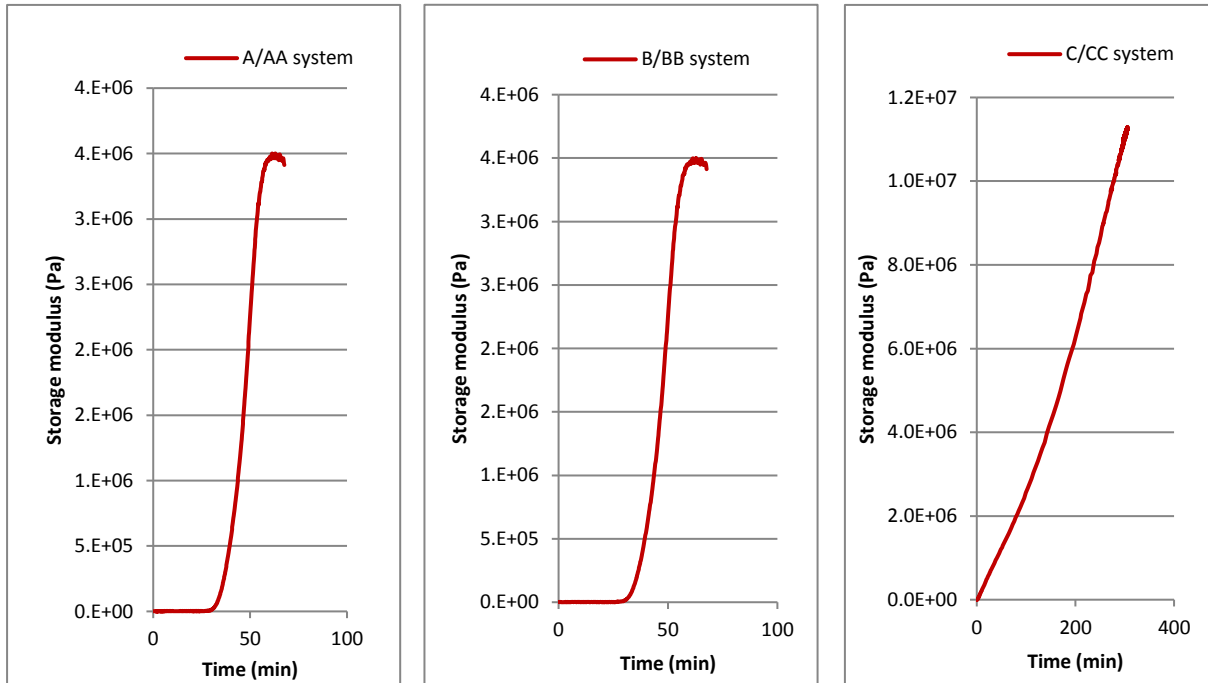


Figure 4: Shear storage modulus data from rheological tests of the three epoxy systems curing at 85 °C; test frequency is 100 Hz.

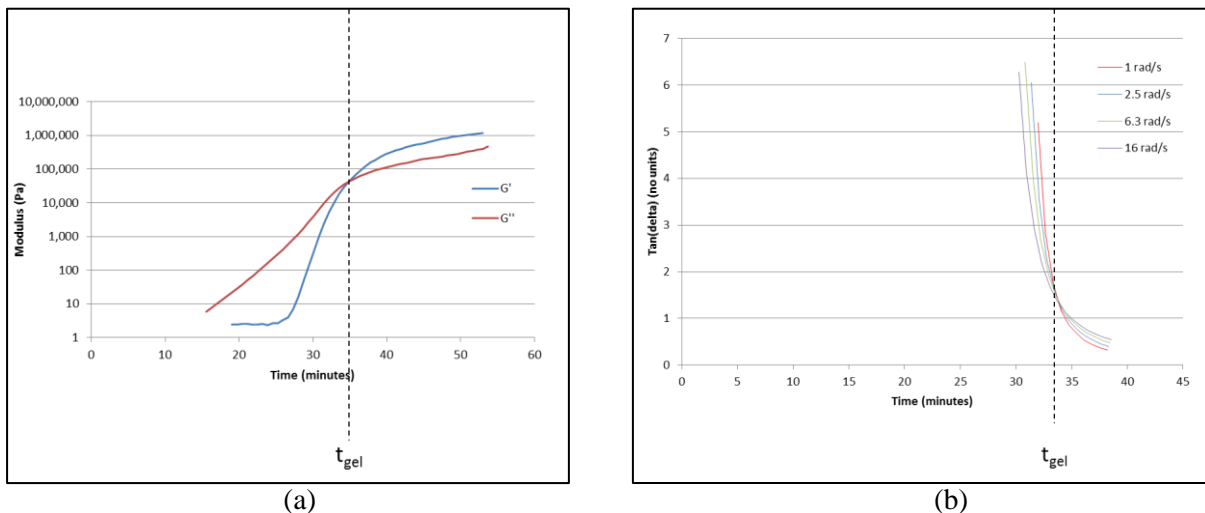


Figure 5. Diagram demonstrating two methods to determine the gel time of a curing resin system, using DMA

Finally, taking into account the reaction kinetics (equation (2)), its constants for the three resin systems determined from the fitting of the DSC data and presented in Table 1, and the viscosity evolution data presented in Figure 3 (as shown in the example of combined graph in Figure 6(a) for system A/AA), the experimental viscosity data was plotted against the reaction term to investigate the fitting of the chemico-rheological relations (4) or (5) for each of the three epoxy resin systems investigated in this study. The results of this fitting exercise are presented in Table 2. System A/AA fits only equation (4) (fit demonstrated in Figure 6(b)), whereas systems B/BB and C/CC can fit either equation (4) or equation (5), with similar values for μ_{0T} derived from the best fits using either of these two equations.

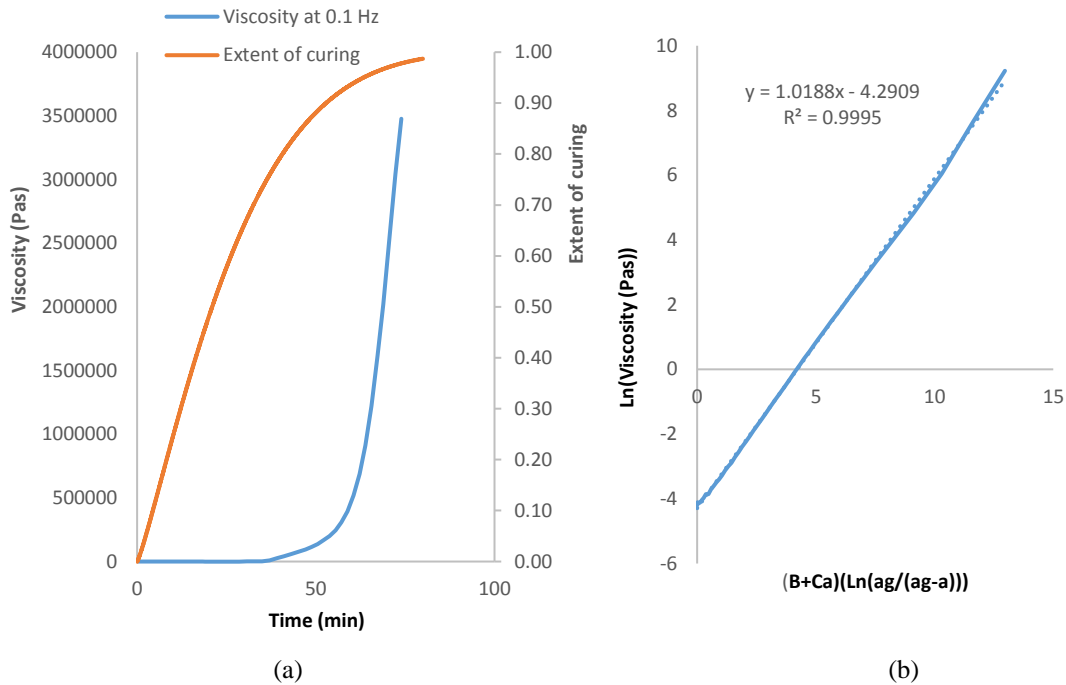


Figure 6. Chemico-rheology for system A/AA at 85 °C: (a) Viscosity and predicted reaction kinetics time profiles; (b) best fit according to equation (4)

Epoxy system	Model equation	μ_{0T} (Pas)	B	C	α_g
A/AA	(4)	0.014	5	3	0.9
B/BB	(4)	0.027	60	0	0.8
	(5)	0.025	84.7		
C/CC	(4)	0.016	86	0	0.95
	(5)	0.0155	94.85		

Table 2. Chemico-rheological model constants derived from the DCS analysis and the rheological tests (at 0.1 Hz) of the three epoxy/curing agent systems of this study

5 CONCLUSIONS

On the basis of the above methodology and framework, the three tested resin systems were compared in terms of reaction kinetics and rheology as a function of curing time, including viscosity data from dynamic rheometry at a frequency of 0.1 Hz and storage shear modulus at a frequency of 100 Hz. The data plots were then related to different RTM process requirements in terms of temperature, filling time and demould time limits.

The data obtained and kinetic models used indicate the ability to gain a greater understanding of the resin systems used in an industrial process while using standard test equipment. Improved data handling will enable the resin systems to be implemented to greater effect and efficiency.

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