



Rheological modelling of thermoset composite processing



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ABSTRACT

The rheological properties of epoxy matrices and adhesives during cure are modelled in this work. Three epoxy-amine systems, designed for different applications with distinct curing behaviours, were investigated. Curing times ranged from a few seconds to upwards of 220 min depending on the cure temperature and formulation of the epoxy. The presented time-dependent model adds an exponential fit to Kiuna-Fontana's master curve of dimensionless viscosity, as well as a weighting function for the overall fit, aiming at creating a more accurate model. A major benefit of the approach is that time consuming determination of the cure kinetics using differential scanning calorimetry (DSC) is not required. The developed model was also used to predict the viscosity of a typical, non-isothermal curing cycle for composite manufacturing. It proved to correlate well with both isothermal and non-isothermal processes, demonstrating that it is particularly useful model to describe viscosity for flow modelling or process optimisation.

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1. Introduction

Thermosetting resins undergo crosslinking of monomers during cure, changing the rheological properties of the polymer. The viscosity of the uncured polymer is typically temperature dependent. With increasing network formation, it will undergo non-linear increase in the viscosity, depending on the chemical composition of the epoxy and cure conditions. The numerous resin formulations used in the composite industry have different rheological behaviour during cure and impregnation, depending on the intended application. For example, an injection process like compression resin transfer moulding (CRTM) [1] requires a resin with a very low initial viscosity to fully impregnate the system, followed by a progression in the degree of cure in a matter of a few minutes to achieve an efficient production with short throughput time [2]. The formulation should therefore be highly reactive but include a certain latency in the cure. On the contrary, pre-impregnated composite systems are often B-staged or partially cured [3], where the resin has been exposed to heat during ply or subcomponent production. The higher viscosity ensures that the uncured ply or component is stable enough to assemble, yet will co-cure in

the section stage of the composite production. When modelling flow impregnation in composite materials, selecting a rheological model remains challenging, especially when one imagines integration of fabric binder kinetics [4], multiple material systems [5,6], and/or combined manufacturing [3]. Further challenges in understanding the flow behaviour during cure arise from mass dependence of exothermic heat in reactive systems [2] which is especially relevant for manufacturing of large structures using intricate processing techniques to manage residual stress and warpage [7].

A number of common rheological models depend on the degree of cure, which next to the temperature, is the dominant factor influencing the flow behaviour. The Castro-Macosko model [8] given in eq. (1) is one of the most widely used approaches to predict the viscosity. The viscosity is modelled as a function of the degree of cure, which requires the combination of two models, (i) the cure kinetics model and (ii) the viscosity model, leading to a reduction of accuracy.

$$\eta(\alpha_{cure}, T) = \eta_0 \exp\left(\frac{E}{RT}\right) \left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha_{cure}}\right)^{A+B\alpha_{cure}} \quad (1)$$

Equation (1) requires the adaptation of four modelling parameters η_0 , E , A and B depending on temperature T and degree of cure, α_{cure} , and holds true for when $\alpha_{gel} > \alpha_{cure}$. Additionally the degree of cure at which gelation occurs, α_{gel} , has to be determined either

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experimentally or analytically. Equation (2) presented by Macosko [9] allows the prediction of the degree of cure at gel depending on the functionality of resin, f , and hardener, g , where r is the ratio between resin and hardener.

$$\alpha_{gel} = \frac{1}{\sqrt{r(f-1)(g-1)}} \quad (2)$$

The value for α_{gel} lies between 0.5 and 0.6 for common epoxy-amine systems [10]. The model with parameters in eq. (1) provides a good prediction of resin formulations where the viscosity increases with a simple exponential growth behaviour [11].

A basic empirical approach to model isothermal viscosity as a function of time, instead of the degree of cure, is given in eq. (3). Roller [12] assumed that the initial viscosity and its kinetic analogue follow an Arrhenius behaviour:

$$\ln(\eta(t, T)) = \ln(\eta_0) + \frac{E_\eta}{RT} + tk_k \exp\left(\frac{E_k}{RT}\right) \quad (3)$$

where η_0 is the initial viscosity and E_η is the Arrhenius activation Energy, k_k and E_k are the kinetic analogues of η_0 and E_η , t is the time, and R is the universal gas constant. This simple approach however, only offers very limited accuracy [13,14]. A more recent approach, first proposed by Kiuna [15] and later modified by Fontana et al. [16], was found to have better accuracy compared to the Arrhenius model [17].

This work aims at developing and experimentally validating a novel rheological model for thermosets based solely on the time dependent approach by Kiuna [15]. It is used in an explicit parametric form and requires the separate modelling of three independent mathematical terms with eight modelling parameters in total.

2. Materials

Three very different resin formulations were investigated, covering a broad range of applications and material properties. An overview of the different systems is given in Table 1.

2.1. Prepreg system

To cover the area of prepreg systems a newly designed epoxy-amine formulation was investigated from North Thin Ply Technology, Switzerland. The system is developed for an out-of-autoclave cure at temperatures of less than 80 °C. The formulation exhibits a higher initial viscosity than the laminating or injection systems.

2.2. Fast curing system - XB3585/XB3458

The XB3585 from Huntsman Advanced Materials, Switzerland was mixed with the curing agent XB3458 using a stoichiometric weight ratio of 100:19. This fast-cure epoxy for the automotive industry shows a small latency with a relatively low viscosity for impregnation before the cure behaviour starts and the epoxy gels. This epoxy was already characterised in a previous study [2] and is

used as a comparison to the other tested materials with a slightly changed model in comparison to the previous publication.

2.3. Structural adhesive - Resoltech 3350

“Resoltech 3350”, Resoltech, F, is a rubber toughened epoxy resin mainly used to bond composite structures. It is processed in combination with the amine hardener 3358 at a weight ratio of 100:42. To achieve an easy applicability the resin includes thickening agents, leading to the highest initial viscosity of the three investigated systems.

3. Methods

3.1. Rheological measurements

Rheological measurements of the prepreg and Resoltech 3350 were carried out using an oscillating plate-plate rheometer “PAAR Physica MCR 300”, Anton Paar, Austria. The prepreg system was characterised with a gap thickness of 2.5 mm and the Resoltech 3350 was studied with a gap thickness of 1.5 mm. All of the measurements were conducted with 25 mm diameter steel plates and an angular frequency of 10 s⁻¹ at an amplitude of 1%. The XB3585/XB3458 was studied using a “PAAR Physica MCR 302”, Anton Paar, Austria with disposable aluminium plates with 25 mm diameter and a gap of 1 mm, using the same angular frequency and amplitude as for the other epoxy systems. The epoxy was placed between the preheated plates and the measurement immediately started. Roughly 30–60 s of measurement time was lost due to closing of the plates. The measured data points were time shifted to account for this loss of data with the fast-cure resin.

Depending on the processing parameters proposed by the manufacturers, different isothermal temperatures were chosen for the measurements (Table 1). Further, dynamic measurements and a two-stage cure cycle were measured for the Prepreg system to simulate a representative autoclave cycle.

3.2. Differential scanning calorimetry

The DSC measurements were carried out in a “Q1000 Differential Scanning Calorimeter”, TA instruments, USA, using Nitrogen as a purge gas for the Prepreg and Resoltech 3350 epoxies as described in Table 1 using 2 mg samples. A heating rate of 50 K/min was used to heat up to the isothermal temperature.

A Mettler “DSC 1” was used to measure the XB3585/XB3458 with a sample weight of 5 mg, using nitrogen purge flow to initiate measurements in a pre-heated chamber. Measurements were performed by placing the sample into the pre-heated chamber. Approximately 3–4 s of data were lost while the DSC chamber closed and began recording the heat flow. Nevertheless, accurate measurements were obtained, as demonstrated in Ref. [2].

Table 1

Summary of the matrix systems that were investigated.

Resin	Type	Measurement temperatures (°C)	Gel time
Prepreg system	Prepreg	70, 80, 90	130 min at 80 °C
Fast curing system (XB3585/XB3458)	Injection, automotive	23, 50, 60, 70, 80, 90, 100	1.5 min at 100 °C
Resoltech 3350	Adhesive	30, 40, 50, 60	60 min at 25 °C

4. Results and discussion

4.1. Viscosity

The initial viscosity values vary depending on the application as shown by the isothermal measurements in Fig. 1. Gelation times

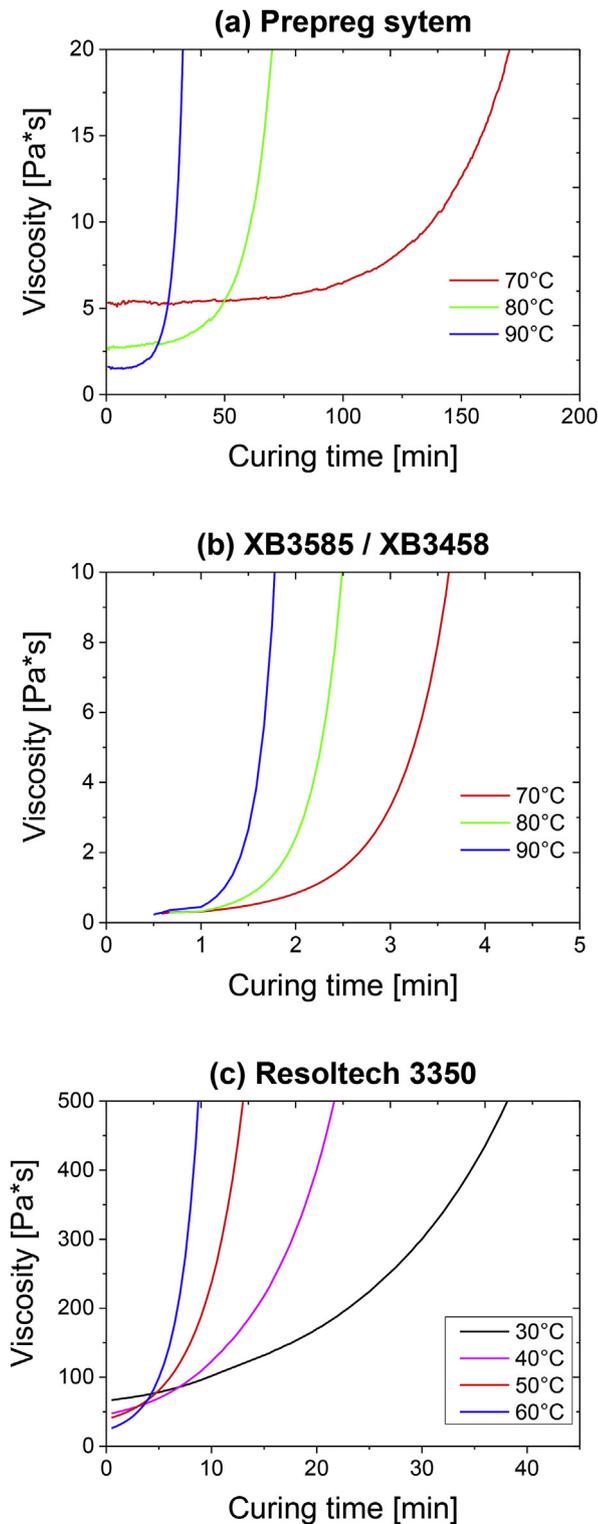


Fig. 1. Isothermal rheological measurements for the investigated resin systems.

ranged from a few seconds to upwards of 220 min depending on the temperature and formulation of the epoxy. Infusion resins have low viscosities to ease dual scale impregnation in fibre reinforced composites, adhesives such as the Resoltech 3350 require higher viscosity values to allow proper filling and adhesion in inhomogeneous bond lines. Despite the differences in composition and reactivity, a characteristic evolution of viscosity behaviour was noted for all the resin formulations. For example, the initial viscosity decrease with higher temperatures increases the processability for infusion resins, such as the XB3585, XB3458 shown in Fig. 1 (b). For such systems, higher temperatures increase the rate of cure and potentially can decrease cycle time when manufacturing a composite part on large scales. For cost effectiveness and energy efficiency, these processes are ideally conducted in isothermal conditions. Therefore, an optimum temperature exists to provide low initial viscosity for composite impregnation followed by a rapid cure. During prepreg manufacturing, plies are consolidated together, with removal of air between layers, without introducing waviness in the precise, pre-defined fibre orientations. Therefore, materials such as the Prepreg system typically require a more complex temperature profile with heating rates and two or more isothermal temperature dwells, as is shown in Fig. 2. The three systems were studied until gel, which was defined from viscosity measurements as the point of crossover between the loss and storage modulus.

4.2. Degree of cure

The degree of cure, α_{cure} , was determined for all three resin systems in order to model the rheological behaviour according to the Castro-Macosko model [8] for comparative purposes. First, dynamic measurements with different heating rates were performed to determine the maximum heat of reaction. Then isothermal measurements were used to calculate the degree of cure. Cure measurements were taken at the same temperature as the rheological measurements to directly implement cure data into the fitting algorithm for the Castro-macosko model.

4.3. Modelling

The proposed model is based on the approach of Kiuna et al. [15] who proposed the following differential equation to describe resin cure for non-isothermal conditions.

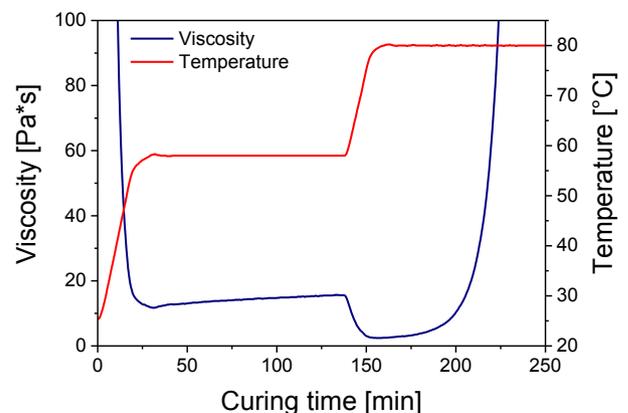


Fig. 2. Viscosity development of the Prepreg system during two stage temperature cycle.

$$\frac{d\alpha_2}{dt} = \frac{k(T)}{g'(\alpha_2)} \quad (4)$$

The dimensionless viscosity, α_2 , is based on experimental data and can be described as,

$$\alpha_2 = \ln\left(\frac{\eta(T, t)}{\eta_0(T)}\right) \quad (5)$$

where $\eta(T, t)$ is the measured viscosity, $\eta_0(T)$ is the viscosity of the uncured material. A dimensionless value τ is also derived from experimental data and represents the elapsed cure time,

$$\tau = k(T) \cdot t \quad (6)$$

with

$$k(T) = \frac{1}{t_1(T)} \quad (7)$$

t_1 is defined as the time when the dimensionless viscosity, α_2 , becomes 1 for a given temperature. This occurs when $\eta(T, t_1) = e \eta_0(T)$, due to the natural logarithm.

Combination of the derivative of the dimensionless viscosity (eq. (5)) with the initial model (eq. (4)) leads to the following homogenous differential equation which is equal to the thermal shifting model of Fontana [16].

$$\frac{d\eta}{dt} + \left(-\frac{k(T)}{g'(\alpha_2)} - \frac{d\eta_0}{dt} \frac{1}{\eta_0(T)}\right)\eta = 0 \quad (8)$$

In order to obtain an explicit parametric model for isothermal cure, the differential equation was solved for the viscosity. The model in this form is now solely time and temperature dependent and is easy to adapt to any desired resin system.

$$\eta(t, T) = \exp\left(\frac{k(T)}{g'(\alpha_2)} t\right) \eta_0 \quad (9)$$

It includes three mathematical terms which are fitted separately from experimental data: η_0 , $k(T)$ and $g'(\alpha_2)$. The initial viscosity, η_0 , and the kinetic coefficient, $k(T)$, are modelled according to their known Arrhenius behaviour

$$\eta_0(T) = A_1 \exp\left(\frac{E_1}{RT}\right) \quad (10)$$

$$k(T) = A_2 \exp\left(\frac{E_2}{RT}\right) \quad (11)$$

where A and E are modelling parameters and R is the ideal gas constant.

The parameters were calculated using a least square fit approach of the linearised functions $\ln(\eta_0)$ vs. $1/T$ and $\ln(k)$ vs. $1/T$ as shown in Fig. 3 for the studied resins.

To obtain an expression for the term $g'(\alpha_2)$, an approximation of the function of dimensionless viscosity, α_2 , versus dimensionless time, τ , is required. This relationship is here denoted as the master curve, and its inverse derivative is the function $g'(\alpha_2)$ which results from including eq. (6) in eq. (4).

$$g'(\alpha_2) = \frac{\partial \tau}{\partial \alpha_2} \quad (12)$$

Depending on the functionalities and compositions of resin and hardener in the analysed resin systems, the master curves exhibit different viscosity evolutions with time, as can be seen in Fig. 4 for

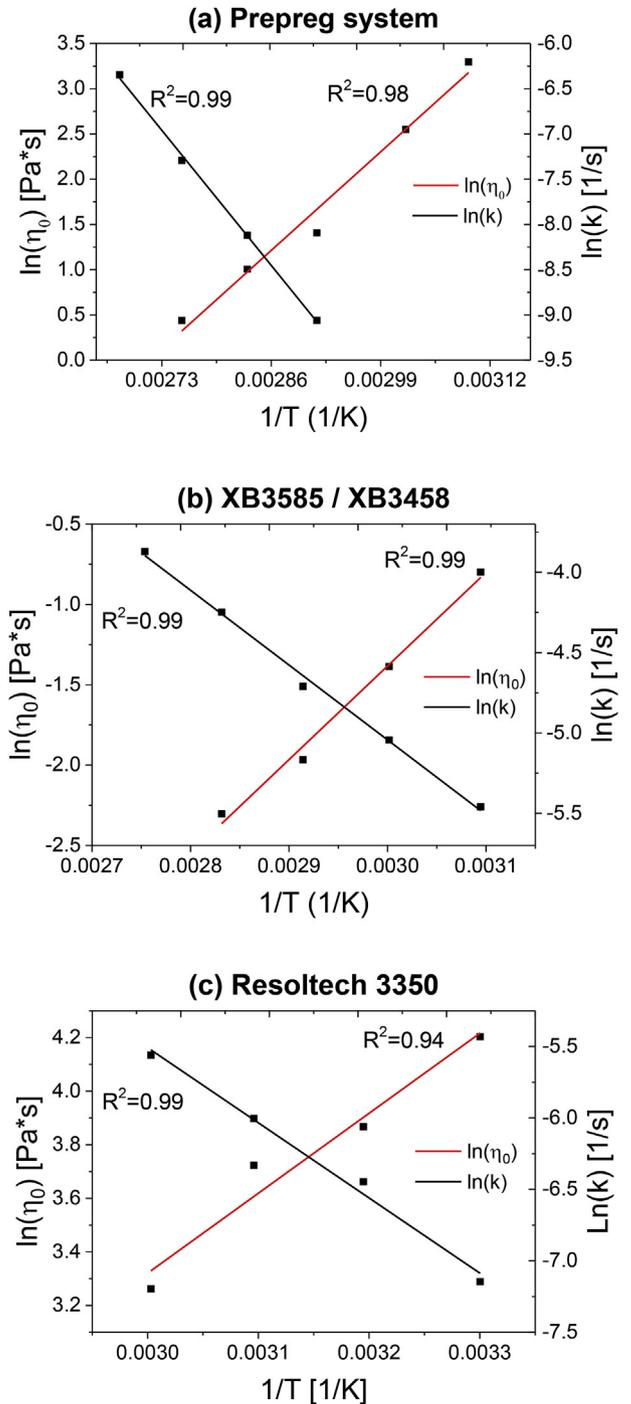


Fig. 3. Arrhenius-fit of (red) initial viscosity η_0 and (black) rate of advance k for (a) the Prepreg system, (b) Fast curing system (XB3585/XB3458) and (c) the Resoltech 3350. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the studied epoxies. The Prepreg system shows an initial latency before a fast rise. Interestingly, the fast-cure resin shows a slower exponential but continual increase in viscosity compared to the Prepreg system. The Resoltech 3350 shows a relative slow, almost linear increase.

The simplest approximation of $\alpha_2 = \tau$ for eq. (12) leads to $g'(\alpha_2) = 1$. Combination with eq. (9) results in the dual Arrhenius

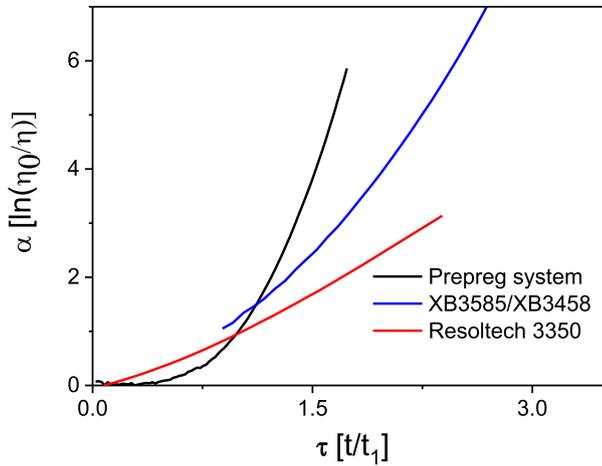


Fig. 4. Master curves of all three resins showing normalised viscosity versus normalised time.

model (eq. (3)). Using an exponential function (eq. (13)) to model the dimensionless viscosity $\alpha_2 = f(\tau)$ proved to be an accurate, yet relatively simple approximation for all the different growth behaviours of the used epoxy systems.

$$\alpha_2 = y_0 + A_3 \exp\left(\frac{\tau}{E_3}\right) \quad (13)$$

The exponential function includes three modelling parameters, y_0 , A_3 and E_3 . Introducing these parameters allows for a better description of the relationship $\alpha_2 = f(\tau)$ which is shown in Fig. 4 to change for different resins, and which is considered as $\alpha_2 = \tau$ in existing modelling approaches [15]. For some epoxy systems the value of y_0 was not necessary, and therefore set as zero. Taking the first derivative of the inverse function of the modelled dimensionless viscosity (eq. (12) and (13)) leads to the term $g'(\alpha_2)$.

$$g'(\alpha_2) = \frac{E_3}{\alpha_2} = \frac{E_3}{y_0 + A_3 \exp\left(A_2 \exp\left(\frac{E_2}{RT}\right) \frac{t}{E_3}\right)} \quad (14)$$

The rheology of the resin systems is highly sensitive to different curing temperatures. A slightly varying heating rate or end temperature causes a shift in the gel time. To easily adjust this offset in the time axis, parameters A_4 and E_4 were added to the time dependent terms of the model. The following equation shows the expanded model for isothermal cure, including all the modelling parameters A_1 to E_4 .

$$\eta(t, T) = A_1 \exp\left(\frac{E_1}{RT}\right) \exp\left[\frac{A_2 \exp\left(\frac{E_2}{RT}\right) t (A_4 T + E_4) \left[y_0 + A_3 \exp\left(A_2 \exp\left(\frac{E_2}{RT}\right) \frac{t (A_4 T + E_4)}{E_3}\right)\right]}{E_3}\right] \quad (15)$$

An overview of all the values for the modelling parameters is given in Table 2.

Up to now, the derivation has been based on isothermal conditions. Fast-cure cycles, i.e. with the XB3585/XB3458, typically use isothermal mould temperatures in order to not increase the cycle

time with heating and cooling. However, isothermal conditions are not always the most convenient. To optimise the cure in terms of time and material properties, like achievable degree of cure, void content and fracture toughness, industrial applications often require a non-isothermal curing process. An example are injection processes, where the temperature is kept low in the flow phase to achieve a reduced rate of cure. With the part being fully impregnated, the temperature is raised, which results in a faster cross-linking and higher degree of cure. The numerical integration of the time dependent mathematical terms proved to be a precise method to obtain a model for any user defined, non-isothermal curing cycle

$$\eta(t, T) = \sum_{t_i, \Delta t_i=1}^n A_1 \exp\left(\frac{E_1}{RT(t_i)}\right) \exp\left[A_2 \exp\left(\frac{E_2}{RT(t_i)}\right) \Delta t_i (A_4 T(t_i) + E_4)\right] \cdot \frac{1}{E_3} \left[y_0 + A_3 \exp\left(A_2 \exp\left(\frac{E_2}{RT(t_i)}\right) \frac{\Delta t_i (A_4 T(t_i) + E_4)}{E_3}\right)\right] \quad (16)$$

The term Δt_i is the chosen time discretisation duration and $T(t_i)$ is the temperature during this period. The terms A_1 , E_1 describe the Arrhenius dependence of zero-cure viscosity on temperature as shown in Fig. 3. The terms A_2 , E_2 describe the acceleration of the curing reaction depending on temperature, which is used to define the dimensionless viscosity α_2 and dimensionless time τ . The function $\alpha_2 = f(\tau)$ is defined by y_0 , A_3 , E_3 . The terms A_4 , E_4 provide straightforward temperature-dependent adjustments for linear offsets in the time axis.

To model the evolution of viscosity during a heating ramp for the Prepreg system, the evolution of temperature was discretised in time steps of $\Delta t = 30$ s. This discretisation showed a sufficiently accurate prediction of the rheological behaviour, as shown in Fig. 5, which displays the capabilities of the isothermal (a) and non-isothermal (b) model for the Prepreg system.

4.4. Modelling results

The independent adjustment of initial viscosity and the non-dimensional viscosity in the time dependent model led to a highly accurate prediction of the overall start and curvature of rheological data under isothermal cure conditions, as shown in Fig. 5. Modelling the viscosity progression of the two stage Prepreg system cure cycle with an isothermal hold at 60 and 80 °C (Fig. 6) is more complex but also more important than pure isothermal cure cycles. Accurate prediction by the proposed non-isothermal model (eq. (16)), as shown in Fig. 6, allows to predict the viscosity for the whole cycle and aids in process optimisation. The presented model

seems to accurately determine changes in viscosity and the duration of the processing zones which are critical for designing an optimised impregnation strategy.

In order to obtain a comparison between the time dependent model and a more common approach, the Castro-Macosko model (eq. (1)) was adapted to the viscosity data of all three resin systems.

Table 2
Modelling parameters for the time dependent model that were used.

Resin	A ₁ (Pa*s)	E ₁ (J/(mol*K))	A ₂ (-)	E ₂ (J/(mol*K))	A ₃ (-)	E ₃ (-)	A ₄ (1/K)	E ₄ (-)	Y ₀ (-)
Prepreg system	1.31E-10	69668	1.03E-10	-91600	0.878	0.895	0	0.81	-1.2
Fast curing system (XB3585/XB3458)	1.32E-08	52931	7518	-38710	2.7	2.2	0.0029	-0.2361	0
Resoltech 3350	0.0034	24800	28940	-43734	3.47	3.5	00031	-0.1262	0

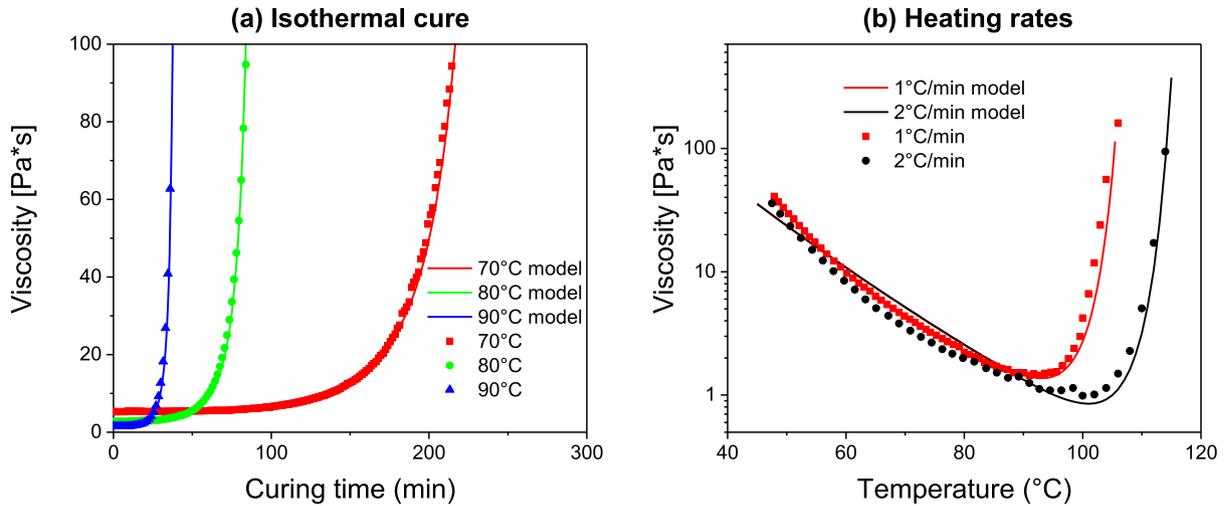


Fig. 5. Modelled and measured viscosities for (a) isothermal cure and (b) cure under different heating rates for the Prepreg system.

The four modelling parameters were obtained using a non-linear least square fit. The values for the different resin systems are given in Table 3.

In Fig. 7 the two models are compared to the experimentally obtained viscosity of the three resins. Both models show a relatively good correlation, but deviate from the experimental results. For the

4-parameter Castro-Macosko the curvature was underestimated. To minimise the sum of squares in the least square fit this divergence is compensated by lowering the initial viscosity, which leads to a two point crossover of model and experimental data. This results in an acceptable overall accuracy but neither the initial viscosity, nor the high degrees of cure will be modelled perfectly – which are crucial if B-stage processing schemes are being utilised [3].

To characterise the quality of the models, a weighted coefficient of determination, R², was calculated.

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - f_i)^2 g_i}{\sum_{i=1}^n (y_i - \bar{y})^2 g_i} \quad (17)$$

where y_i refers to values of the measured viscosity, f_i is the corresponding modelled value, \bar{y} the mean of the measured data and g the weighting factor. It was determined that the most significant properties of the model should be its ability to predict the viscosity during the impregnation and flow phase. The use of a non-weighted coefficient of determination is highly influenced by the larger residuals at high degrees of cure, where even the smallest offset causes a great error because of the high viscosity values. To reduce this effect, the early stages in the curing process were given a higher weighting factor, g. The weighting factor significantly changes the predicted quality and leads to higher values for R² in the flow regime.

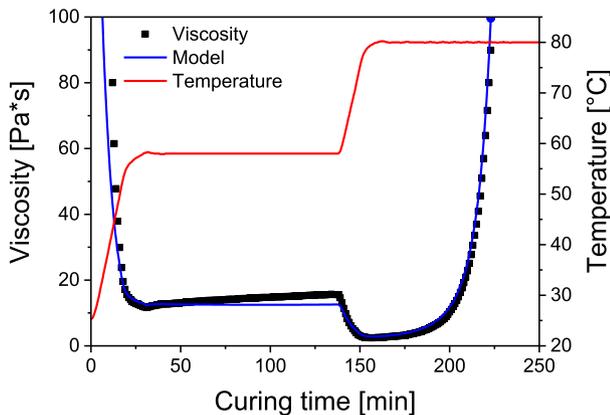


Fig. 6. Comparison of modelled and experimental measured viscosity for a two stage temperature cycle of the Prepreg system.

Table 3
Modelling parameters for the Castro-Macosko models that were implemented.

Resin	η ₀ (Pa*s)	E (J/(mol*K))	A (-)	B (α ⁻¹)	α _{gel}
Prepreg system	3.0611e-11	73277.62	3.3464	-0.4910	0.3583
Fast curing system (XB3585/XB3458)	1.7625E-23	136129.78	11.9993	-15.9584	0.5758
Resoltech 3350	1e-3	27711.56	4.6791	-8.9664	0.4329

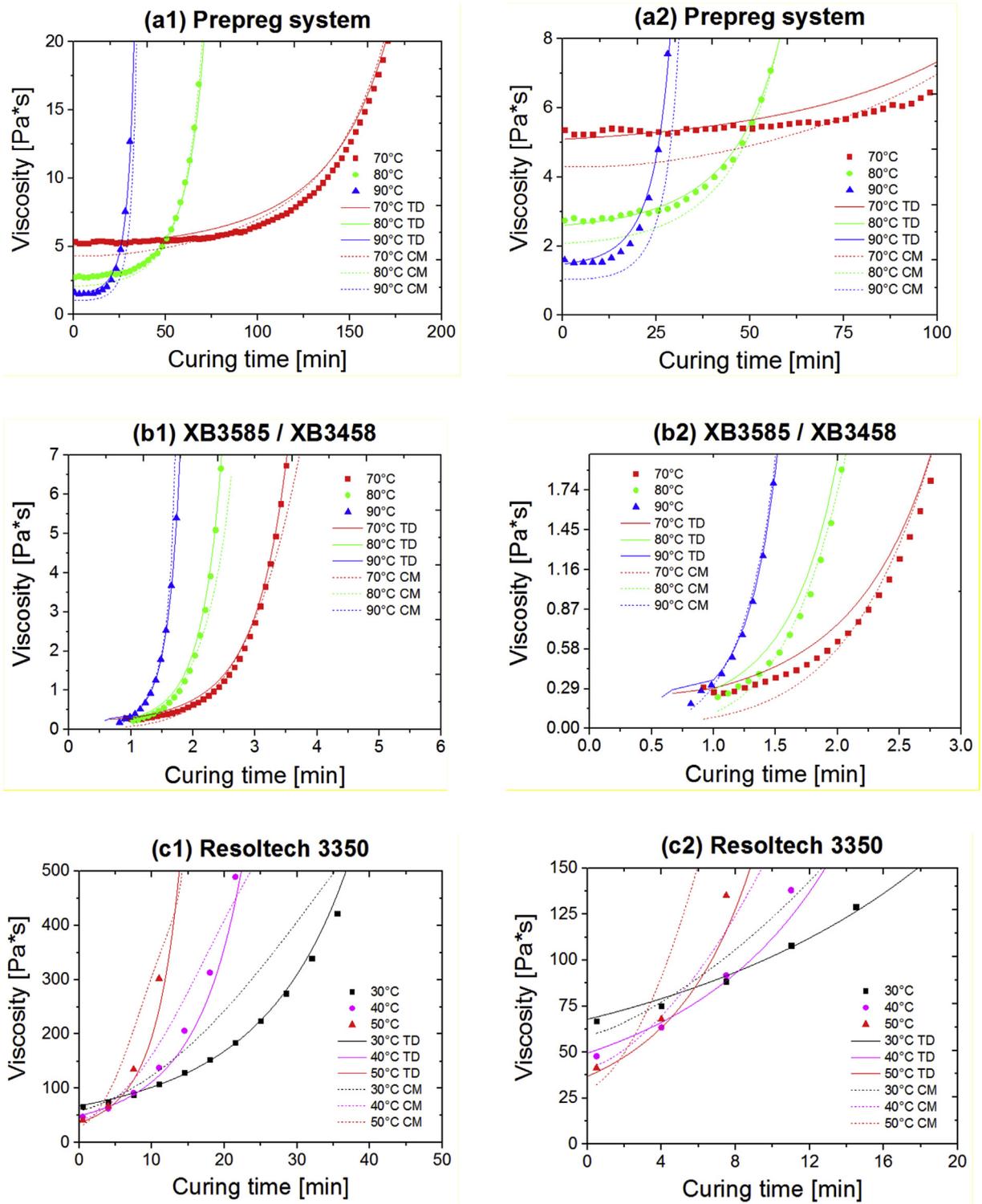


Fig. 7. Comparison of measured viscosity with time dependent model (TD) and Castro-Macosko model (CM) for (a) the Prepreg system (b) for the fast curing system (XB3585/ XB3458) and (c) for the Resoltec 3350. The right images are a zoom at low viscosity for each respective system.

The weighting factor was decreased gradually based on a sigmoidal function (eq. (18)). The function was adapted to the measured viscosities to start at the time 0 with a weighting factor of 0.95 and decrease to a factor of 0.05 at the point in time when a viscosity of $20 \cdot \eta_0$ is reached (Fig. 8).

$$g(x) = 1 + \frac{1}{1 + \exp(-x)} \tag{18}$$

As evidenced in the overview of the coefficients of determination (Table 4), the used time dependent model provides a very

Table 4
Values for weighted R^2 comparing the models to experimental results.

Resin	Weighted coefficient of determination	
	R^2 Time dependent [%]	R^2 Castro-Macosko [%]
Prepreg system	99.48	99.90
Fast curing system (XB3585/XB3458)	99.69	99.44
Resoltech 3350	98.76	85.03

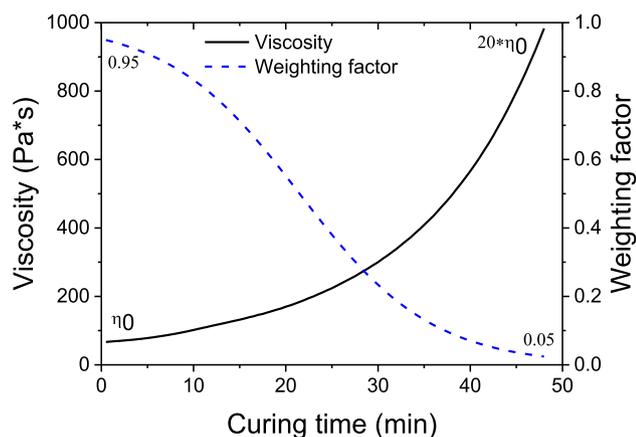


Fig. 8. Illustration of decreasing weighting factor for calculation of coefficients of determination. The weighting factor is applied according to each resin's initial viscosity.

accurate method to model the isothermal rheological behaviour of a broad range of matrix systems. Especially systems showing a high curvature of the dimensionless viscosity can be modelled very accurately with the more flexible time dependent model.

5. Conclusions

The time-dependent rheology model developed in this work is able to predict isothermal and non-isothermal viscosity evolutions without the need for an underlying calculation of the degree of cure, achieving nevertheless remarkable accuracy. The model may be fit without a cure model, using only isothermal rheology measurements taken in the range of non-dimensional time τ from 0 to 1. As shown by the R-squared values, the presented time-dependent model matches or exceeds the predicting ability of the known Castro-Macosko rheological model in the three epoxy systems that were studied. A simple analysis of these measurements provides non-dimensional parameters which, although different for each resin, capture the monotonic increase in viscosity which is a behaviour shown by all epoxies. Even on epoxies showing initial viscosities and curing times that are different by orders of magnitude, this time-dependent model offers remarkable modelling flexibility for accurate predictions of both isothermal and non-isothermal rheology. The capacity to accurately model this behaviour without experimental cure kinetics parameters provides a clear advantage for reliably and efficiently defining processing cycles and flow simulation, which are critical for the quality of epoxy-based composite materials with increasing complexity and

combined manufacturing approaches.

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