

Cure kinetics, glass transition advancement and chemo-rheological modelling of an epoxy vitrimer based on disulphide metathesis

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ABSTRACT

This study develops cure and chemo-rheological models for a vitrimeric system appropriate for use as matrix in continuous fibre composites based on a disulphide-endowed amine/epoxy formulation. The focus is on the processing conditions relevant to liquid composite moulding. Kinetics is investigated using Differential Scanning Calorimetry. An autocatalytic model is developed, simulating the reaction with an average reaction rate error of 5.2 % and degree of cure error of 3 %. The viscosity development is modelled at relatively low degrees of cure, focusing on the liquid moulding infusion window, yielding results with an average relative error of 4.8 %. The glass transition temperature advancement is represented by the Di Benedetto equation, whilst the topological transition temperature of the system is determined using stress relaxation experiments and found to be 149.5 °C. These results set the scene for the development of composites based on the matrix system investigated in this work.

1. Introduction

Vitrimeres are thermosets modified with dynamic covalent bonds so that whilst maintaining their excellent mechanical properties and environmental resistance at service temperatures, they are capable of intra-network associative bond exchange at elevated temperatures. Vitrimeres undergo topology rearrangement without compromising network integrity in terms of the total number and average functionality of crosslinks, even in the presence of solvents. This special behaviour endows vitrimeres with functionalities such as recyclability, self-healing and weldability. The recyclability of vitrimeres can address the question of thermoset end-of-life disposal, whilst their healability is a useful asset for the repair of matrix damage encountered in composites, such as delamination and microcracking. These capabilities make vitrimeres attractive candidates to replace conventional thermosets in composites applications. Since the discovery of vitrimeres [1], research efforts have dealt mainly with the formulation and characterisation of functionality of novel systems based on different thermosetting chemistries such as epoxies [2–5], polybutadienes [6–9], polyurethanes [10,11], polybenzoxazines [12–14], polyimides [15], and polyesters [16–18]. Amongst these developments, chemistries based on the combinations of epoxies with disulphides feature prominently [5,19,20].

As the development of matrix materials with vitrimeric behaviour

matures, the question of producing fibrous composites in industrially relevant ways becomes relevant. This requires the development of understanding of material behaviour of vitrimeres during manufacturing, generation of the corresponding datasets and representation in appropriate material models capturing the cure kinetics and chemorheological behaviour under processing conditions. These can facilitate the optimisation of processing conditions with respect to filling or consolidation effects as well as curing and development of process stress and strain to allow the adaptation of current composites manufacturing strategies for the production of vitrimer matrix fibrous materials. The processing of composites is accompanied by phenomena governed by cure behaviour such as residual stress development, leading to microcracking which ultimately affects the final product quality, or exothermic heat generation, that can cause temperature overshoots and degradation of material quality, whilst generation of defects, such as porosity and dry spots, is governed by the rheological behaviour of the matrix system and its evolution during the process.

Cure kinetics models are, in their great majority, phenomenological or semi-empirical, with mechanistic modelling used in some exceptional cases. Phenomenological modelling makes use of approximate relationships resembling chemical kinetics expressions to represent reaction rate – the time derivative of degree of cure – as a unique function of fractional conversion (α) and temperature (T):

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$$\frac{d\alpha}{dt} = f(\alpha, T) \quad (1)$$

The functional form f in Eq. (1) involves a number of parameters estimated using fitting of experimental data – typically obtained using Differential Scanning Calorimetry (DSC). Popular phenomenological expressions include the n -th order model:

$$\frac{d\alpha}{dt} = K_1(1 - \alpha)^n \quad (2)$$

in which K_1 is the reaction rate constant, which is an Arrhenius function of temperature, and n is the reaction order, applied to bismaleimides [21] and polyfunctional benzoxazines [22], as well as the autocatalytic model:

$$\frac{d\alpha}{dt} = K_1\alpha^m(1 - \alpha)^n \quad (3)$$

in which m is the autocatalytic reaction order, applied to epoxies [23–26], unsaturated polyesters [27–29], and vinyl esters [30,31]. More complex expressions are derived by combining the n -th order and autocatalytic models, such as the Kamal-Sourour model:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (4)$$

involving an additional Arrhenius rate constant (K_2), which has found wide applications in epoxies [32–34] and unsaturated polyesters [28, 35], and the Karkanis model:

$$\frac{d\alpha}{dt} = K_1(1 - \alpha)^{n_1} + K_2\alpha^m(1 - \alpha)^{n_2} \quad (5)$$

which involves two n -th reaction orders (n_1 and n_2) and has been applied to liquid moulding epoxies [26,36].

In addition to chemical effects, diffusion limitations play a role in the curing reaction. At the beginning of the reaction, molecular diffusion is fast due to the high mobility of chemical species, and the effect of diffusion on the rate of polymerisation is negligible. As crosslinking progresses and the polymer approaches its vitrification point, diffusion becomes slower and starts playing a role in kinetics, gradually becoming the controlling step. Incorporation of this effect in cure kinetics modelling can be carried out by considering the serial nature of the diffusion and chemical processes, which leads to the Rabinowitch model [37]:

$$\frac{1}{K_i} = \frac{1}{K_{ci}} + \frac{1}{K_{di}} \quad (6)$$

where K_i is the overall rate constant and K_{ci} and K_{di} the rate constants of the chemical process and of the diffusion, respectively. In this, K_{ci} follows an Arrhenius dependence and K_{di} a WLF-type behaviour [38,39]. An alternative phenomenological approach modifies rate constants directly by multiplying with a factor that vanishes as the degree of cure approaches a temperature-dependent critical degree (α_c) [40]:

$$K_i = K_{ci}e^{-C(\alpha - \alpha_c)} \quad (7)$$

where C is a coefficient controlling the breadth of the transition to diffusion-controlled kinetics. This approach has been improved by combining with Eq. (6) to obtain [41]:

$$K_i = \frac{K_{ci}}{1 + e^{-C(\alpha - \alpha_c)}} \quad (8)$$

which has been used successfully for modelling the kinetics of liquid moulding epoxy aerospace resins [42].

Models expressing the evolution of rheological behaviour during the cure usually rely on a representation of viscosity (η) as a function of degree of cure and temperature. Common expressions include [43]:

$$\eta = \eta_\infty e^{\frac{U}{RT}} e^{k\alpha} \quad (9)$$

and [44]:

$$\eta = \eta_\infty e^{\frac{U}{RT}} \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{A+B\alpha} \quad (10)$$

where η_∞ has the physical meaning of viscosity of the uncured material at infinite temperature, U denotes the flow activation energy, α_g is the degree of cure at the gelation point, R is the universal gas constant and k , A , B are fitting parameters. In liquid composite moulding applications, for which the evolution of viscosity at the earlier stages of the reaction is critical, the utilisation of degree of cure as an underlying variable of the viscosity model becomes problematic in terms of model accuracy. This fact, which was recognised by Fontana [45], has led to the development of models that rely on following the evolution of viscosity at a reference temperature and using a shifting function $g(T - T_r)$ [45,46] to obtain the value at the temperature of interest:

$$\eta = \eta_r e^{g(T - T_r)} \quad (11)$$

where η_r is the instantaneous viscosity at the reference temperature T_r . A similar approach, which uses an inverse temperature exponential dependence of viscosity:

$$\eta = \eta_r e^{D\left(\frac{1}{T} - \frac{1}{T_r}\right)} \quad (12)$$

alongside the following kinetics applied to the logarithm of viscosity:

$$\frac{d \ln \eta_r}{dt} = A e^{-\frac{E}{RT}} \left(\ln \frac{\eta_r}{\gamma} \right)^l \quad (13)$$

where coefficient D governs the temperature sensitivity, A is the pre-exponential factor, E and l are the activation energy and order of the kinetics respectively, and γ is a fitting parameter that has to be lower than the initial value of reference viscosity, has been used successfully to model commercial liquid composite moulding aerospace systems [47].

The comparison of a recently developed aerospace-grade epoxy vitrimer based on aromatic disulphide with a commercial resin shows that the thermal and mechanical properties of the epoxy vitrimer are similar to those of the commercial system [20], whilst the efficiency of damage repair in vitrimeric composites has been demonstrated [48,49]. However, the processing characterisation of vitrimers for their optimal application as liquid moulding composite matrices, namely cure kinetics, chemoviscosity and glass transition development models, is currently not addressed. This study addresses this gap for the diglycidyl ether of bisphenol A epoxy/4-aminophenyl disulphide vitrimeric system. Differential Scanning Calorimetry and rheometry are utilised to quantify cure reaction, viscosity evolution and the evolution of the glass transition temperature (T_g) during processing. Cure kinetics, viscosity evolution and T_g models are developed based on the characterisation results. The vitrimeric functionality of the system is also quantified using stress relaxation experiments.

2. Materials and methods

2.1. Materials and resin preparation

Diglycidyl ether of bisphenol A – DGEBA (D.E.R. 332; epoxy equivalent mass of 170.2, molecular weight of 340.4 g·mol⁻¹) – was supplied by Sigma Aldrich/Merck. 4-aminophenyl disulphide (4-APDS), an aromatic diamine with molecular weight of 248.4 g·mol⁻¹ and amine equivalent mass of 62.1 was supplied by Florochem Ltd, UK. The epoxy and amine chemical structures are shown in Fig. 1.

Stoichiometric amounts of the epoxy and diamine (2:1 epoxy/amine mole ratio or 2.74:1 epoxy/amine weight ratio) were used to formulate

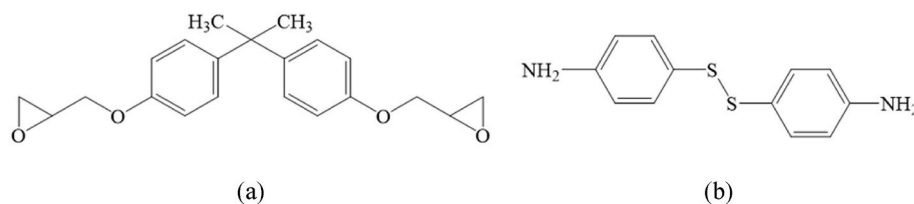


Fig. 1. Chemical structures of (a) DGEBA (D.E.R. 322), (b) 4-aminophenyl disulphide.

the vitrimer. The selection of a stoichiometric formulation is motivated by the target of developing vitrimeric systems with high glass transition temperature and high environmental resistance. To prepare a batch, 10 g DGEBA was measured into a 100 ml beaker and 3.65 g of 4-aminophenyl disulphide was added. The mixture was stirred on a hot plate at 80 °C for 20 min, after which the resin was stored in the freezer at −20 °C for future use.

2.2. Experimental methods and modelling

The cure behaviour of the resin was measured using Differential Scanning Calorimetry (DSC) on a DSC 250 Discovery (TA Instruments) equipped with an RCS cooling system under nitrogen purge at 50 mL/min. Dynamic and isothermal cure experiments were performed to study the cure behaviour of the vitrimer. An amount of resin of 7–10 mg, encapsulated in an aluminium pan, was used. In dynamic runs, the sample was scanned from −50 °C to 250 °C at 1.25 °C/min, 2.5 °C/min, 5 °C/min and 10 °C/min. Isothermal experiments were performed at 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C and 200 °C. The isothermal cure temperature was reached using a 10 °C/min heating ramp from −50 °C and the isothermal conditions were maintained until the DSC heat flow signal reached a plateau, signifying the end of the reaction. This was followed by quenching to −50 °C and reheating up to 250 °C at 10 °C/min to identify any residual cure.

Integration of DSC signals to calculate the evolution of reaction enthalpy was performed using a linear baseline for dynamic and a horizontal baseline for isothermal experiments. The initial reaction enthalpy value was considered in the integration of isothermal experiments, estimated using the results of the dynamic experiment at 10 °C/min. The total enthalpy of the reaction (ΔH) was calculated by averaging the total enthalpy of all experiments for which the residual reaction upon re-heating was negligible. The degree of cure evolution was computed using:

$$\alpha(t) = \frac{H(t)}{\Delta H} \quad (14)$$

where $H(t)$ is the integral of the DSC heat flow signal. The reaction rate evolution was computed by differentiating numerically degree of cure with respect to time.

The modelling methodology implemented in this study involves mapping of reaction rate on temperature and degree of cure as implied by Eq. (1). The validity of Eq. (1) was verified by analysing the effects of various thermal histories representing different conversion pathways on the reaction rate, provided the conversions and the temperatures are identical, irrespective of the differences in thermal history [23]. Dynamic and isothermal calorimetric reaction rates measured at points with the same coordinates on the conversion-temperature space were compared by superimposition.

The kinetics data were used to identify the parameters of the autocatalytic cure kinetics model expressed by Eq. (3) combined with diffusion effects following Eq. (8). The minimisation of model error was carried out using the Generalised Reduced Gradient Nonlinear Optimisation method implemented in the Solver of Microsoft Excel [50]. The error minimised is:

$$\varepsilon = \sum_{i=1}^{ne} \sum_{j=1}^{np_i} \frac{|r_j^i - \hat{r}_j^i|}{np_i r_{max}^i} \quad (15)$$

where r_j^i is the reaction rate of point j of experiment i , r_{max}^i is the maximum reaction rate of experiment i – used to scale the error so that high rate experiments do not dominate the fitting, np_i is the number of data points in experiment i , ne is the number of experiments – 11 in this case, and $\hat{r}_j^i$ is the reaction rate computed by the model for point j . Experimental analysis and cure modelling were carried out assuming an initial degree of cure of 1%. This is commonly done in epoxy systems [51,52] to allow the utilisation of autocatalytic kinetics. This assumption does not affect the results as it is merely a numerical adaptation to allow initiation of the reaction from a finite degree of cure; setting this initial degree of cure to a value within a similar order of magnitude yields the same behaviour with slightly different model parameters. The initial value acts as the initial condition that accompanies the cure kinetics model and its parameters.

The development of glass transition temperature (T_g) during cure was investigated using partially cured samples with 17 different thermal histories comprising material cured dynamically at 1.25 °C/min up to 130 °C, 136 °C, 140 °C, 145 °C, 150 °C, 160 °C, 170 °C, 180 °C and 190 °C, dynamically up to 170 °C at rates of 2.5 °C/min, 5 °C/min and 10 °C/min, isothermally at 150 °C for 10 min, 20 min, 30 min and 40 min as well as a fully cured sample (cured at 150 °C for 100 min) and an uncured sample. The partially cured samples were reheated from −50 °C to 250 °C at 10 °C/min in the DSC and the T_g was identified as the inflection point of the transition step in heat flow curves. The uncured sample was heated from −50 °C to 220 °C at 1.25 °C/min, during which the uncured sample T_g was identified alongside the full cure exotherm. The integrated cure kinetics DSC data were utilised to obtain the degree of cure corresponding to the partially cured samples. The 18 T_g -degree of cure points, corresponding to 17 T_g -degree of cure points of partially cured material and 1 T_g -degree of cure point of uncured materials, were used to identify the parameters of the DiBenedetto equation [53,54] using the same procedure as for the fitting of the cure kinetics model described previously, with the difference that the minimisation function was computed as the sum of absolute error over the 18 data points.

The viscosity development of DGEBA/4-APDS was measured using an AR2000ex rheometer (TA Instruments) equipped with a water cooling system. A cone and plate configuration with 2° cone of 40 mm diameter and truncation depth of 54 μm was used. The gap setting in the rheometer was equal to the truncation of the cone. Five isothermal experiments were carried out at 80 °C, 90 °C, 100 °C, 110 °C and 120 °C at a constant shear rate of 300 s^{−1}. The sample was loaded onto the lower plate of the rheometer, which was at ambient temperature, the gap was closed and the temperature was equilibrated for 30 s before shearing. The viscosity was modelled by fitting the experimental data to identify the values of the parameters of the viscosity model in Eqs. (12) and (13) following the procedure described previously for the T_g and kinetics models. The minimisation error was computed as the sum of absolute differences between experimental and model logarithm of viscosity over all data points.

Stress relaxation experiments were carried out on a DMA Q800 (TA Instruments) in tension mode using a single cantilever (2-point bending). Plates of DGEBA/4-APDS epoxy were cast between glass

plates separated by a silicone rubber frame and held together by clamps. Curing was carried out in an oven at 180 °C for 240 min followed by post cure at 200 °C for 60 min. Specimens with dimensions of $35 \pm 0.5 \text{ mm} \times 8 \pm 0.2 \text{ mm} \times 2 \pm 0.05 \text{ mm}$ were cut from the resin plates. The experiments were conducted at five isothermal temperatures of 180 °C, 190 °C, 200 °C, 210 °C, and 220 °C. A strain of 1 % was applied after temperature equilibration and the evolution of relaxation stress and modulus with time was recorded. The relaxation time was estimated using the time at which the relative stress reaches a value of $1/e$ (36.8%). The topology freezing transition temperature (T_v) of the DGEBA/4-APDS epoxy vitrimer was determined using the Arrhenius temperature dependence of inverse relaxation time, the relation between relaxation time, viscosity and modulus, the rubbery modulus and the definition of T_v as the temperature at which viscosity reaches a value of 10^{12} Pa s [1]. The dataset underlying this study is available at the Cranfield online research data repository [55].

3. Results and discussion

3.1. Cure kinetics

The reaction rate curves for the isothermal and dynamic experiments are illustrated in Fig. 2. All dynamic and isothermal DSC experiments,

with the exception of the 140 °C test, resulted in full cure of the material. The total heat of the reaction of the DGEBA/4-APDS system is $454.9 \pm 9.9 \text{ J/g}$. The enthalpy measured corresponds only to the curing epoxy-amine reaction, as any energy exchange due to disulphide bond metathesis has a zero net effect.

In dynamic data, a peak in reaction rate is observed at an intermediate conversion during the cure. This is due to the combined effects of temperature changes and of progression of the reaction. Initially, as the temperature increases, reaction rate increases due to enhanced kinetic energy of reacting groups. As the reaction progresses, reactant concentration declines leading to a reduction of the rate of collisions of reacting groups. Therefore, the reaction rate increases with temperature until it reaches a maximum at an intermediate conversion point at which the decline in reactant concentration dominates the kinetics. The position of the reaction peak shifts to higher temperatures as the heating rate increases, with the reaction peak increasing from 140 °C at 1.25 °C/min to 190 °C at 10 °C/min, due to the shorter exposure to a specific temperature range with increasing heating rate. Similarly, the maximum reaction rate increases with increasing heating rate from $5.9 \cdot 10^{-4} \text{ s}^{-1}$ at 1.25 °C/min to $3.5 \cdot 10^{-3} \text{ s}^{-1}$ at 10 °C/min, due to the occurrence of the maximum at a greater temperature and the Arrhenius dependence of rate constant on temperature.

The reaction rate curves for isothermal experiments reported in

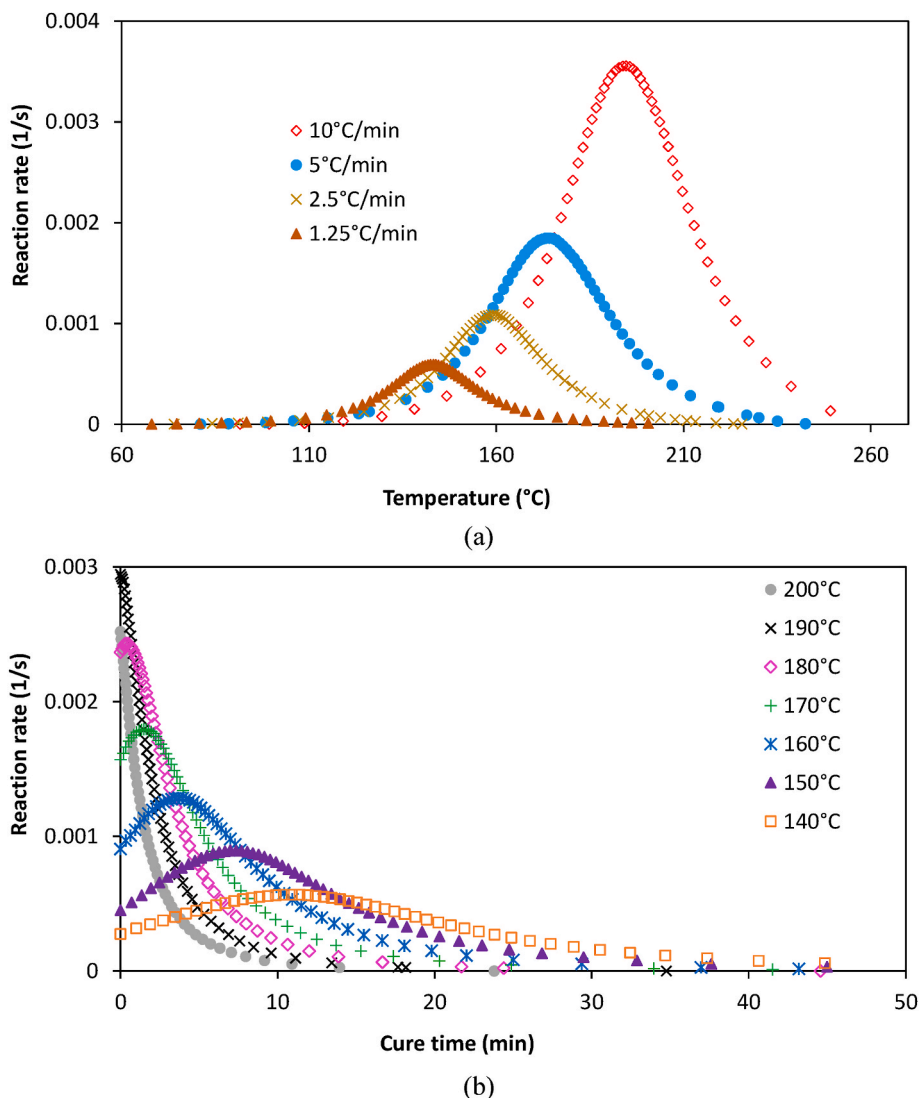


Fig. 2. Experimental cure kinetics of DGEBA/4-APDS system: (a) reaction rate versus temperature in dynamic DSC experiments; (b) reaction rate versus cure time in isothermal DSC experiments.

Fig. 2b show peak values at intermediate conversions, which is indicative of an autocatalytic mechanism. The isothermal reaction peak shifts to shorter times for higher temperatures, whilst the initial reaction rate has a finite and increasing value with increasing temperature. Maximum rates under isothermal conditions range from $5.7 \cdot 10^{-4} \text{ s}^{-1}$ at 140°C to $2.9 \cdot 10^{-3} \text{ s}^{-1}$ at 190°C . This behaviour is attributed to the Arrhenius dependence of rate constants on temperature. The increasing part of isothermal curves, from the beginning of isothermal cure to the peak, diminishes with increasing temperature to the extent that for higher temperatures, such as 190°C and 200°C , the peak disappears completely, and maximum reaction rate occurs at the start of the isothermal cure. This is attributed to the fact that the material cures during the heating ramp to reach the isothermal temperatures. Knowledge of the evolution of the cure from the corresponding dynamic test at $10^\circ\text{C}/\text{min}$ allows the calculation of the initial degree of cure for the isothermal tests, which is reported in Table 1. The isothermal cure at high temperatures starts from degrees of cure exceeding 40%, which explains why the autocatalytic character is not manifested as maximisation of reaction speed at intermediate times as it is the case at lower temperatures. Furthermore, at the highest temperature of 200°C the reaction starts at 65%, which is well past the location of the reaction rate peak. Therefore, the rate at the beginning of the 200°C isothermal segment is lower than the corresponding reaction rate for the 190°C , which occurs at an initial degree of cure of 46%, which is closer to the point of the reaction rate peak.

As previously stated, the basis for using an expression of the type given in Eq. (1) for modelling cure kinetics is the assumption that reaction rate is a unique function of degree of cure and temperature. This means that reaction rate shows no path dependence when mapped onto the degree of cure – temperature space, i.e., once a point in this space is reached, the reaction rate is the same irrespective of thermal history. Testing the validity of this assumption involves superimposing the results obtained for identical degree of cure – temperature points reached under isothermal and dynamic conditions [23]. This involves interpolating results of $1.25^\circ\text{C}/\text{min}$, $2.5^\circ\text{C}/\text{min}$, $5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$ dynamic experiments at the isothermal temperatures of 140°C , 150°C , 160°C , 170°C , 180°C , 190°C and 200°C and overlaying reaction rate – degree of cure points reached dynamically with the isothermal curves as depicted in Fig. 3. The dynamic results at the corresponding temperatures are in close agreement with the isothermal curves over the whole range. The average absolute difference between dynamic and isothermal rate data is $3.4 \cdot 10^{-5} \text{ s}^{-1}$, whilst the average relative difference is 5.9%. This result confirms the validity of the assumption implied by Eq. (1) and allows application of a phenomenological model to represent the kinetics of DGEBA/4-APDS cure by expressing reaction rate as a function of degree of cure and temperature only. This result also validates the assumption that the enthalpy measured by DSC provides a quantitative metric of the degree of conversion that is uniquely mapped to the state variables of the reaction.

Based on these observations, a combination of Eqs. (3) and (8) expressing autocatalytic behaviour with diffusion limitations in the way proposed in Ref. [40] was selected for modelling the cure of the DGEBA/4-APDS system as follows:

$$\frac{d\alpha}{dt} = \frac{A_1 e^{-E_1/RT} \alpha^m (1 - \alpha)^n}{1 + e^{C[\alpha - (\alpha_{cT}T + \alpha_{co})]}} \quad (16)$$

Table 1

Initial degree of cure of isothermal experiments reported in Fig. 2; isothermal temperature reached at a rate of $10^\circ\text{C}/\text{min}$.

Isothermal temperature ($^\circ\text{C}$)	140	150	160	170	180	190	200
Degree of cure at time zero of the isothermal segment (–)	0.03	0.04	0.08	0.15	0.28	0.46	0.65

where E is the activation energy, A the pre-exponential factor and α_{cT} and α_{co} are coefficients controlling the critical degree for diffusion as a function of temperature and R is the universal gas constant. The role of the denominator in Eq. (16) is to incorporate mobility and diffusion limitations as the polymer approaches the glass transition during crosslinking. The fitting involving the seven parameters of Eq. (16) was carried out using the procedure described in Section 2.2 to minimise the error expressed by Eq. (15).

The cure kinetics parameters identified are reported in Table 2. Fig. 4 provides a comparison of experimental and model data for dynamic and isothermal experiments. Both dynamic and isothermal data are reproduced successfully by the cure kinetics model. The model underestimates slightly the reaction rate at the later stages of the $10^\circ\text{C}/\text{min}$ experiment, which corresponds to temperatures over 200°C , whilst it overestimates slightly the rates in the 190°C and 200°C isothermal experiments, which coincide with the later stages of cure at these temperatures. This is consistent with the superposition data presented in Fig. 3, in which isothermal reaction rates at the highest temperatures tend to be lower than the corresponding data points. The model fitting finds a compromise between these two, which results in slight overestimation of isothermal rates and slight underestimation of dynamic rates in this region of the temperature-degree of cure space. The rest of the experimental data are followed very closely by the model, including the partial completion of cure, at about 0.88, in the lowest isothermal cure at 140°C . Table 3 summarises the average absolute and relative error in reaction rate for each experimental condition. The absolute error ranges from $1.8 \cdot 10^{-5} \text{ s}^{-1}$ to $12.4 \cdot 10^{-5} \text{ s}^{-1}$, which in terms of relative error translate to 2.3 %–9.3 %. The average absolute error over all conditions is $5.0 \cdot 10^{-5} \text{ s}^{-1}$ and the relative error 5.2 %. A comparison with the superposition average absolute and relative differences of $4.2 \cdot 10^{-5} \text{ s}^{-1}$ and 7.2 % respectively shows the optimal performance of the model as it represents the experimental results with an accuracy similar to the inherent consistency of the dataset, without overfitting or significant model deviations.

The validity of the cure kinetics model can be tested further by using it to predict the evolution of degree of cure under isothermal and dynamic cure conditions. This involves integrating the reaction rate computed using Eq. (16) for the thermal profile of the corresponding experiment and comparing model to experiment degree of cure. Fig. 5 illustrates the comparison with experiments for dynamic and isothermal conditions. The model reproduces the evolution of degree of cure in DSC experiments very closely. Given the fitting of the kinetics model expressed by Eq. (16) was carried out on the reaction rate data, this reinforces the model validity.

Some small deviations are observed in the initial stages of low-rate dynamic experiments and the final stages of low temperature isothermal tests. This relates to the fact that the data is denser in the areas where most of the cure reaction occurs, making the regions of low temperature-intermediate degree of cure and low temperature-high degree of cure to have a weaker contribution to the determination of the kinetics parameters. Lower prioritisation of these regions is also consistent with practicalities of cure, in which under a typical ramp-dwell profile the material is expected to attain intermediate and high degrees of cure at higher temperature than those corresponding to these regions.

The level of accuracy of the model in reproducing the evolution of degree of cure is confirmed by the average absolute and relative errors reported in Table 3. The absolute error in degree of cure ranges from 0.0035 to 0.025 with the corresponding relative error in the 0.4 %–8.7 % range. The overall average absolute error in degree of cure across all experiments is 0.01, corresponding to an overall relative error of 3%. This accurate model can form the basis of process development for the DGEBA/4-APDS system based on the stoichiometric formulation utilised here. Modification of the formulation by altering the epoxy-to-amine ratio would lead to similar kinetics qualitatively with changes in the

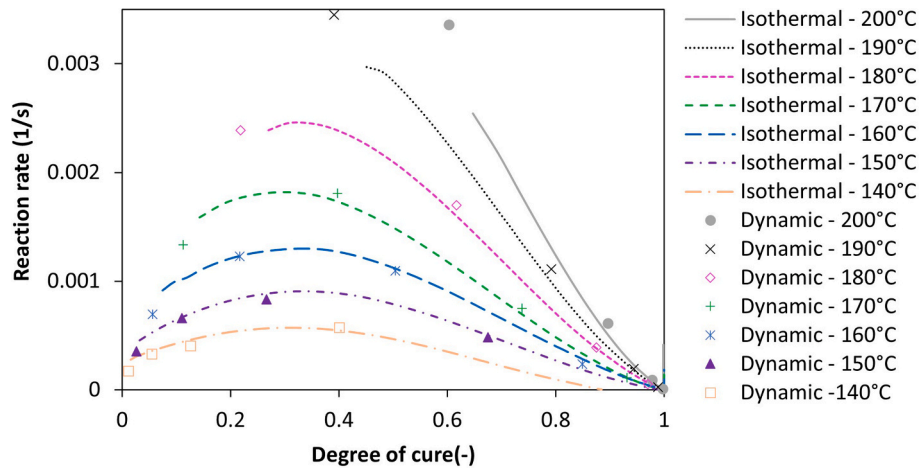


Fig. 3. Superposition of dynamic and isothermal reaction rate versus degree of cure data for DGEBA/4-APDS vitrimer.

Table 2

DGEBA/4-APDS kinetics parameters values for the model represented by Eq. (16); α_0 is the initial degree of cure used in the analysis.

α_0 (-)	A_1 (s ⁻¹)	E_1 (J mol ⁻¹)	m (-)	n (-)	C (-)	α_{CT} (K ⁻¹)	α_{co} (-)
0.01	27,190	55,810	0.697	1.53	29.5	0.0095	-3.07

values of the cure kinetics model parameters. Similarly, the model is specific to the dynamic bonds involved in the formulation and captures their overall effect, in terms of both occurrence of exchange reaction and effects on the crosslinking polymer structure.

3.2. Glass transition temperature development

The experimental measurements of T_g for different states of cure of the DGEBA/4-APDS vitrimer are illustrated in Fig. 6. The points correspond to a variety of thermal histories for reaching the partial cure state isothermally or dynamically, with the values of T_g following a single curve supporting the conclusion that material state can be captured by the degree of cure reached in the study of cure kinetics. The T_g varies over a wide temperature range from -18 °C in the uncured state to 162.6 °C in the fully cured state. The low value of -18 °C for the uncured material T_g points to a desirably low viscosity at typical infusion temperatures, whilst the high value of 162.6 °C at full cure is characteristic of aromatic ring of amine curing agents. The evolution of the glass transition temperature is modelled using the DiBenedetto equation as follows:

$$T_g = T_{g0} + \frac{\lambda \alpha (T_{g\infty} - T_{g0})}{1 - \alpha(1 - \lambda)} \quad (17)$$

where $T_{g\infty}$ and T_{g0} are the values of the glass transition temperature of the fully cured and uncured system respectively and λ is a parameter controlling the convexity of the evolution curve. Table 4 reports the values of the three model parameters obtained by fitting, whilst the DiBenedetto curve is also shown in Fig. 6. The average error of the fitting of the model is 3.5 °C. The model follows very closely experimental values at high degrees of cure with the experimental $T_{g\infty}$ being identical to the model value obtained. Greater deviations are observed at low degrees of cure with the experimental T_{g0} at -18 °C being lower than the model value.

3.3. Rheological modelling

The development of viscosity of the DGEBA/4-APDS system in the temperature range of infusion processing is illustrated in Fig. 7. The

results window is selected up to viscosities of 1 Pa·s, which is significantly greater than the levels required for liquid moulding, usually in the range of 10–200 mPa·s [56,57]. The initial viscosity decreases with increasing temperature as a result of enhanced molecular mobility, with an initial viscosity of 12 mPa·s at 120 °C and of 53 mPa·s at 80 °C. The increase of viscosity with time is exponential, whilst the realistic infusion times, before the viscosity increases beyond values that would make reinforcement impregnation challenging, are in the range of around 20 min at 120 °C to around 100 min at 80 °C. The time spent at low viscosity is a decreasing function of temperature as a result of the acceleration of cross-linking with increasing temperature. This causes a trade-off as, at high temperatures, infusion can be fast due to the low initial viscosity; however, the processing time over which infusion becomes challenging due to the increasing viscosity is shorter. At low infusion temperatures the situation is reversed, with an inherently slower process due to the greater initial viscosity, but a significantly greater time window over which the process can be completed without issues.

The rheological behaviour of the system is simulated by combining Eqs. (12) and (13) in a single differential equation to facilitate integration:

$$\frac{d\eta}{dt} = A e^{-\frac{E}{RT}} \eta \left[\ln \eta + D \left(\frac{1}{T_r} - \frac{1}{T} \right) - \ln \gamma \right] - \frac{D\eta}{T^2} \frac{dT}{dt} \quad (18)$$

Here all temperatures are in K and the initial condition of the integration is:

$$\eta_{t=0} = \eta_r^0 e^{D \left(\frac{1}{T_r} - \frac{1}{T} \right)} \quad (19)$$

where η_r^0 is the initial viscosity at the reference temperature (T_r). The results of the fitting are illustrated in Fig. 8, whilst the parameters of the model are summarised in Table 5. The fitting is very close to the experimental data for all curves, with deviations observed only for the 100 °C experiment, for which the model underestimates viscosity at the later stages of the process. The error of the model is summarised in Table 6 for the different experiments. The average absolute error is in the 1–17 mPa·s range, whilst the relative error is 1.0–10.1 %. The average absolute error over all tests is 6.5 mPa·s and the average relative error 4.8 %. The highly accurate representation of effects in the low viscosity range demonstrates the advantages of the model utilised here, which allows effects of early cure represented very closely to experimental behaviour for the window of temperature-material state most relevant to liquid composite moulding.

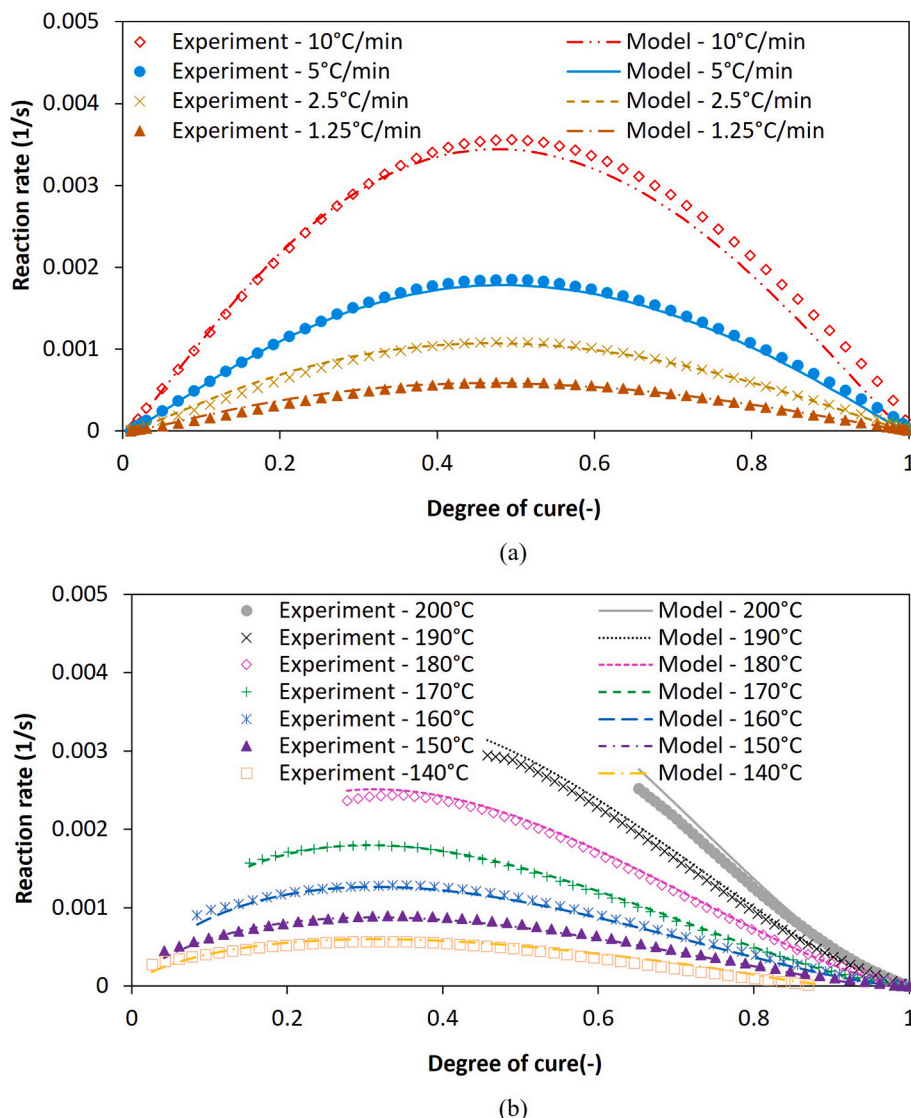


Fig. 4. Cure kinetics modelling of DGEBA/4-APDS: Comparison of model and experiment reaction rate in dynamic (a) and isothermal (b) conditions.

Table 3

Average absolute error and average relative error in reaction rate and degree of cure of the cure kinetics model of DGEBA/4-APDS. Relative error computed over experimental points exceeding reaction rate of $2.5 \cdot 10^{-4}$.

Experiment	Reaction rate		Degree of cure	
	Absolute error	Relative error	Absolute error	Relative error
1.25 °C/min	$1.8 \cdot 10^{-5} \text{ s}^{-1}$	4.5 %	$12.5 \cdot 10^{-3}$	5.4 %
2.5 °C/min	$2.5 \cdot 10^{-5} \text{ s}^{-1}$	4.2 %	$13.1 \cdot 10^{-3}$	7.0 %
5 °C/min	$4.4 \cdot 10^{-5} \text{ s}^{-1}$	4.4 %	$8.2 \cdot 10^{-3}$	3.9 %
10 °C/min	$12.4 \cdot 10^{-5} \text{ s}^{-1}$	7.9 %	$8.5 \cdot 10^{-3}$	8.7 %
140 °C	$4.1 \cdot 10^{-5} \text{ s}^{-1}$	9.3 %	$24.9 \cdot 10^{-3}$	4.0 %
150 °C	$2.4 \cdot 10^{-5} \text{ s}^{-1}$	4.1 %	$14.6 \cdot 10^{-3}$	1.7 %
160 °C	$3.3 \cdot 10^{-5} \text{ s}^{-1}$	4.3 %	$14.0 \cdot 10^{-3}$	1.6 %
170 °C	$3.1 \cdot 10^{-5} \text{ s}^{-1}$	3.7 %	$3.5 \cdot 10^{-3}$	0.4 %
180 °C	$4.2 \cdot 10^{-5} \text{ s}^{-1}$	2.3 %	$6.7 \cdot 10^{-3}$	0.7 %
190 °C	$7.1 \cdot 10^{-5} \text{ s}^{-1}$	4.7 %	$5.5 \cdot 10^{-3}$	0.5 %
200 °C	$9.8 \cdot 10^{-5} \text{ s}^{-1}$	7.5 %	$5.5 \cdot 10^{-3}$	0.5 %

3.4. Topological transition temperature

Fig. 9a reports the isothermal stress relaxation curves of the DGEBA/4-APDS system, whilst Fig. 9b presents the normalised stress relaxation curves. The relaxation modulus follows a behaviour close to an exponential decay as indicated by the step drop in a logarithmic time scale. The plateau relaxation modulus depicted in Fig. 9a increases marginally with increasing temperature from 180 °C up to 200 °C, due to the entropic contribution in the elastic behaviour of the rubbery material, which is indicative of a retention of the thermosetting character of the system. Beyond 200 °C, this trend reverses as the thermosetting character of the vitrimer becomes weaker. The relaxation times estimated using the time required to reach a reduction in modulus by $1/e$ are reported in Fig. 10, alongside the fitting of an Arrhenius dependence of the inverse of relaxation time on temperature. The coefficient of determination of the fitting is 0.99, and the activation energy is 196.8 kJ/mol. To determine the topological transition temperature (T_v), the rubbery modulus of the material was approximated by averaging the initial

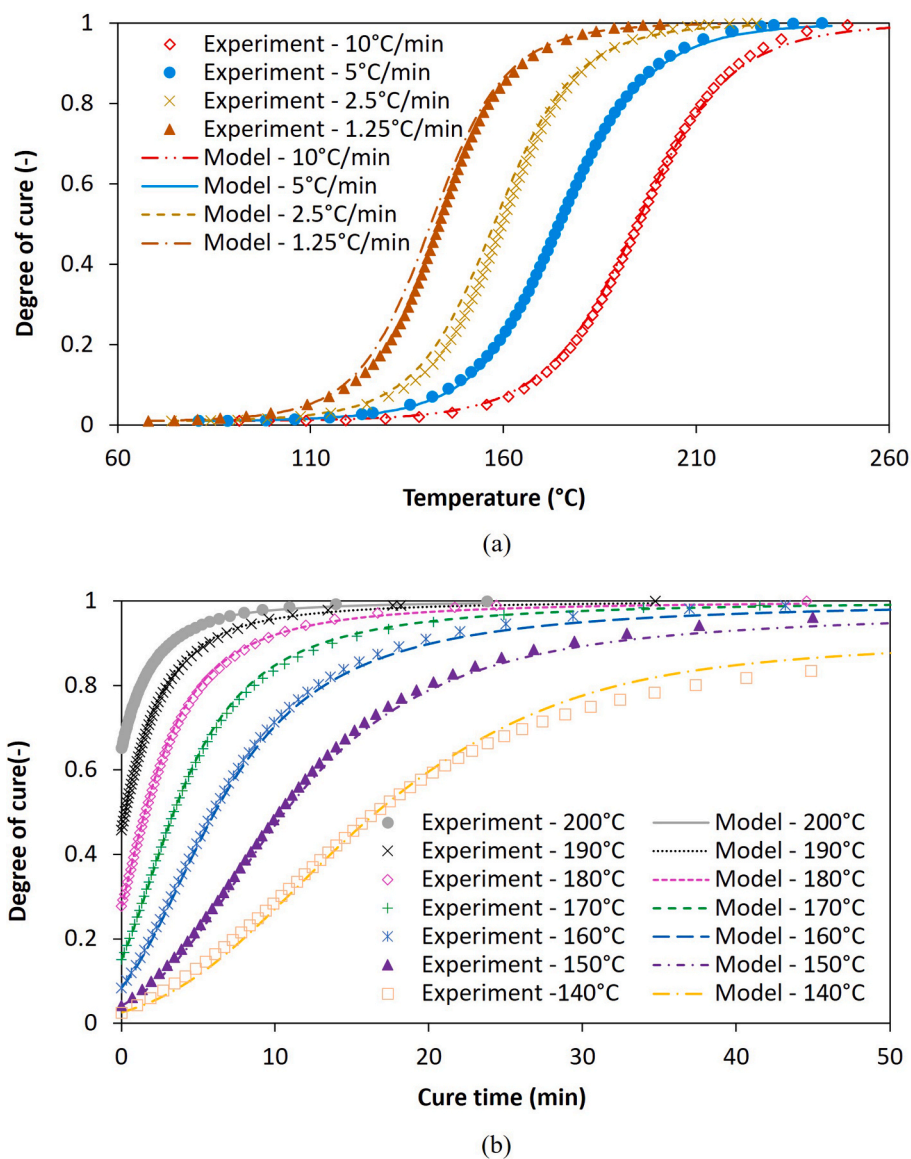


Fig. 5. Cure kinetics modelling of DGEBA/4-APDS: Comparison of model and experiment degree of cure evolution in dynamic (a) and isothermal (b) conditions.

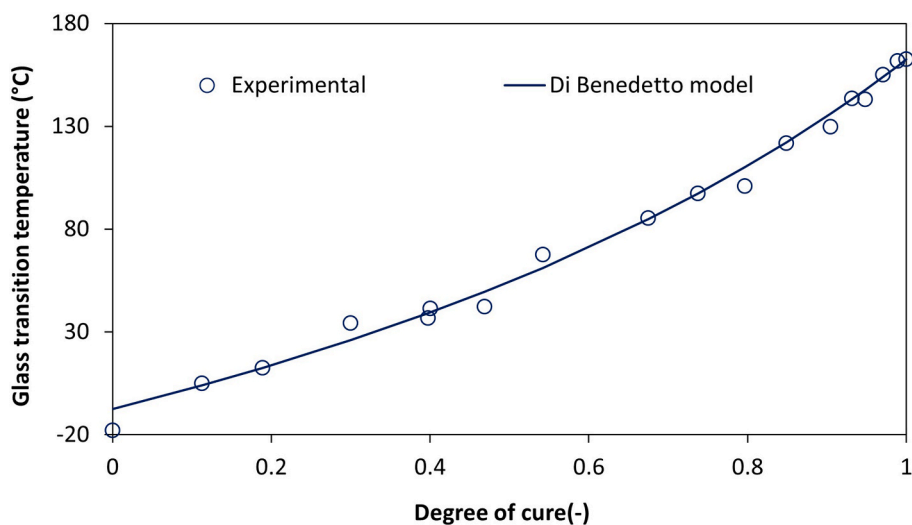


Fig. 6. Development of the glass transition temperature of the DGEBA/4-APDS vitrimer as a function of the degree of cure.

Table 4DGEBA/4-APDS DiBenedetto T_g development model parameters and error.

$T_{g\infty}$ (°C)	T_{g0} (°C)	λ (–)	Average absolute error (°C)
162.6	–7.5	0.572	3.5

relaxation modulus over the five experiments. The value found is 24 MPa, which for the assumed viscosity of 10^{12} Pa·s at transition, corresponds to a relaxation time of 41700 s. T_v is determined as the temperature at which the Arrhenius dependence reported in Fig. 10 reaches this value and is equal to 149.5 °C. It should be noted that the topological transition temperature found here is higher than that reported in the literature for a similar epoxy-aminophenyl disulphide system [58]. This can be attributed to differences in the epoxy prepolymer and relative fraction of 4-APDS.

The topological transition temperature of 149.5 °C for the DGEBA/4-APDS epoxy vitrimer system is lower than its glass transition temperature determined by calorimetry. This means that effective reprocessing and healing of the system can be carried out at temperatures over the T_g , a behaviour that is desirable as the matrix system maintains its functionality derived from its thermosetting nature up to its maximum functional temperature at the glass transition, whilst over this it attains its functionality as a vitrimer. Although bond metathesis is possible at

temperatures above T_v and below the T_g , lack of molecular mobility makes it very slow; once T_g is reached, rate and mobility limitations are lifted, and bond exchanges occur at high rates, allowing healing and reprocessing.

Table 5

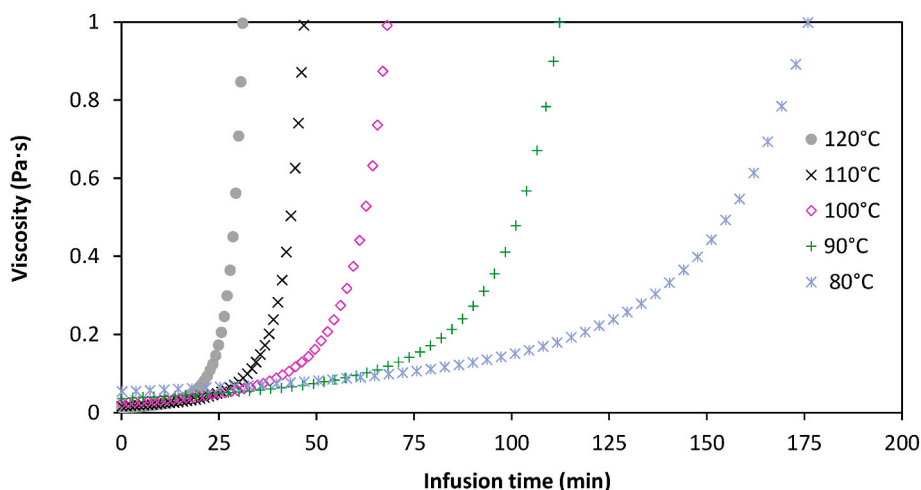
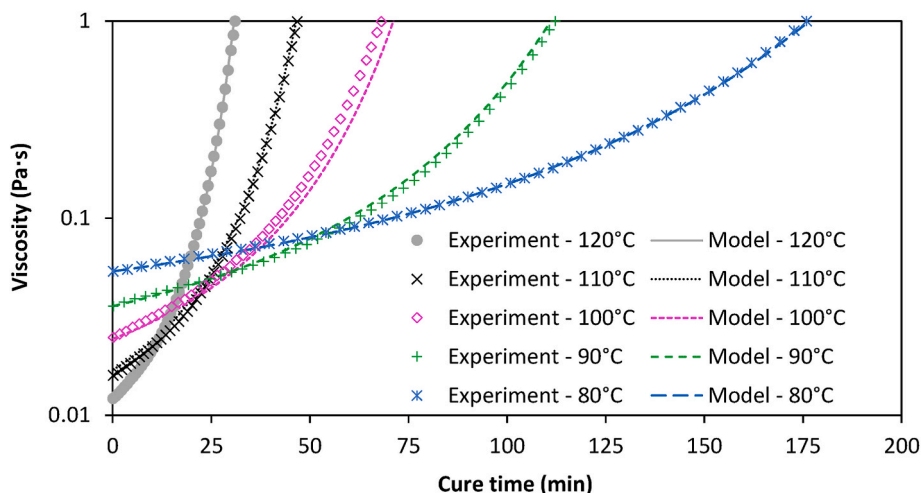
DGEBA/4-APDS viscosity development parameters values for the model represented by Eq. (18). Fitting performed for viscosity levels up to 500 mPa s.

T_r (K)	η_r^0 (mPa·s)	A (s ^{–1})	E (J mol ^{–1})	l (–)	γ (mPa·s)	D (K ^{–1})
353.15	53.6	14,300	55,410	1.4	17.3	5180

Table 6

Average absolute error and average relative error of the viscosity model of DGEBA/4-APDS.

Experiment	Absolute error	Relative error
80 °C	1.2 mPa·s	1.0 %
90 °C	8.0 mPa·s	4.7 %
100 °C	18 mPa·s	10.8 %
110 °C	4.1 mPa·s	6.7 %
120 °C	1.0 mPa·s	1.1 %

**Fig. 7.** Viscosity evolution of the DGEBA/4-APDS vitrimer as a function of time at different isothermal infusion temperatures.**Fig. 8.** Viscosity development model of the DGEBA/4-APDS system: Comparison of model and experimental results.

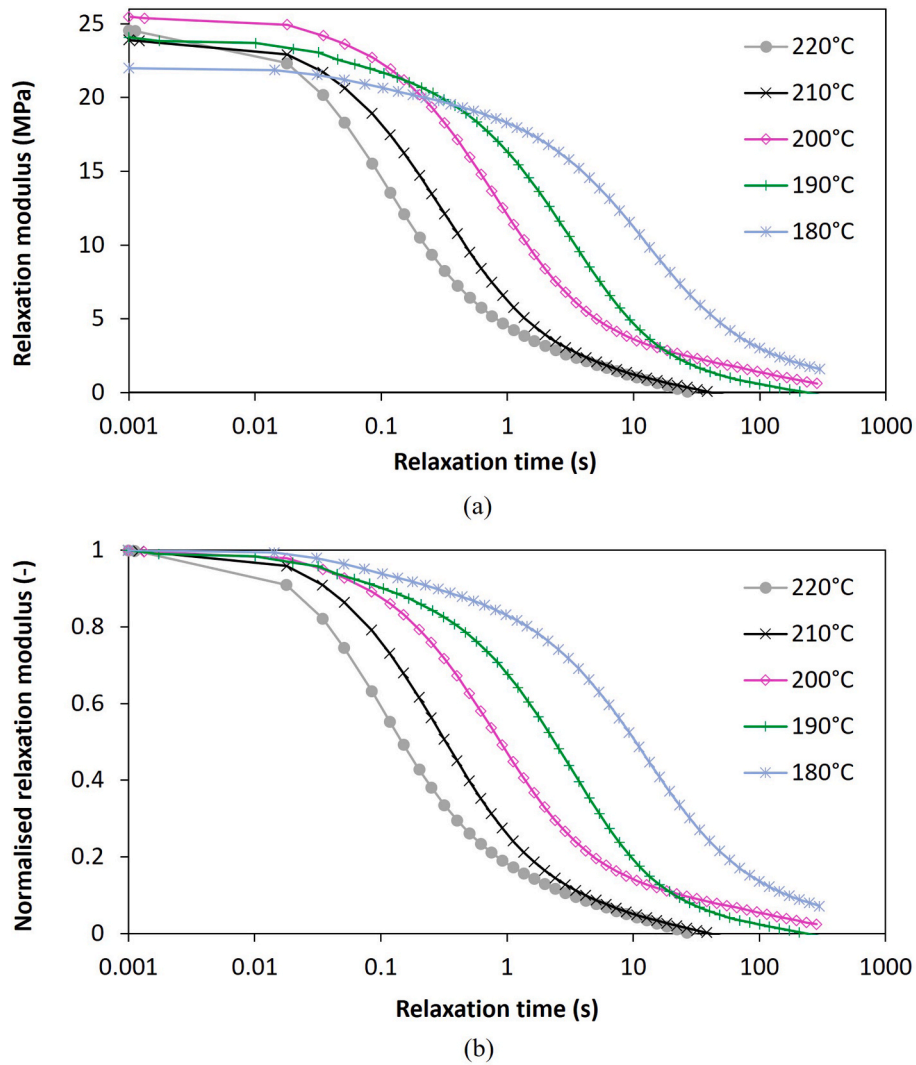


Fig. 9. (a) Stress relaxation curves of DGEBA/4-APDS system; (b) Normalised stress relaxation curves.

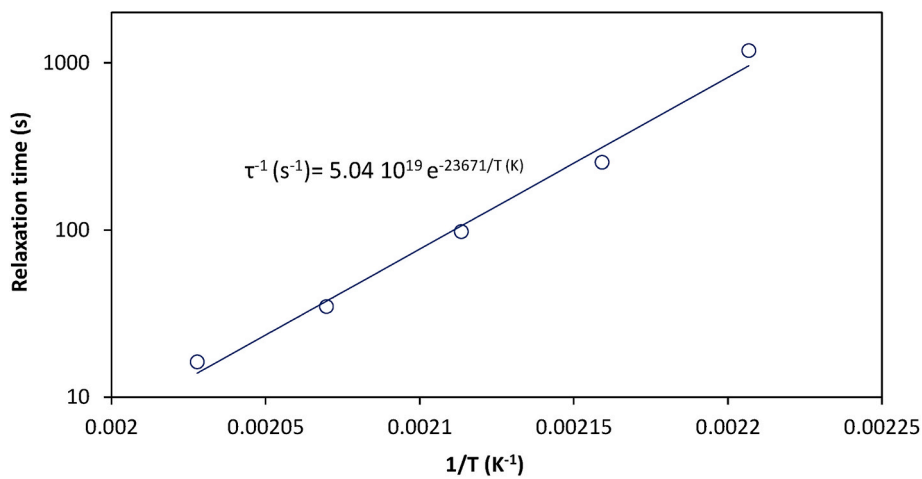


Fig. 10. Relaxation time as a function of temperature.

4. Conclusions

A phenomenological cure kinetics model was developed in this study for the DGEBA/4-APDS epoxy vitrimer. Also, the dependence of the

glass transition temperature on the degree of cure and the viscosity evolution during liquid composite moulding were modelled, focusing on the infusion window of liquid composite moulding, for which the degree of cure is relatively low. An autocatalytic model successfully reproduces

the cure behaviour of the system, with reaction rate average absolute error of $5.0 \cdot 10^{-5} \text{ s}^{-1}$ and a relative error of 5.2 % over all experimental conditions. The degree of cure absolute error is 0.01, corresponding to an overall relative error of 3% over all experimental conditions. The glass transition advancement in the DGEBA/4-APDS epoxy vitrimer from a value of -18°C for the uncured material to 162.6°C for the fully cured polymer is represented by the DiBenedetto equation with an average error of 3.5°C , whilst the T_v of the vitrimer is 149.5°C , with dynamic bond exchange reaction activation energy of 196.8 kJ/mol . The chemoviscosity model developed in this study represents accurately the rheological behaviour of the resin in the low viscosity range, with an average absolute error of $6.5 \text{ mPa}\cdot\text{s}$ and average relative error of 4.8 % over all tests. These models, which also capture the effect of dynamic bond exchange, where this plays a role in the polymerisation reaction, are characteristic of the specific combination of disulphide bonds and epoxy/amine crosslinking system.

The cure kinetics, glass transition advancement and chemoviscosity model models reported in this study represent the polymerisation of stoichiometric combination of diglycidyl ether of bisphenol A and 4-aminophenyl disulphide. This set of results provides the necessary material information to guide the application of DGEBA/4-APDS system as a liquid moulding epoxy vitrimer, setting the scene for development in the area of processing of composites based on a vitrimeric epoxy matrix.

CRedit authorship contribution statement

Festus Ifeanyi Anagwu: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Alexandros A. Skordos:** Conceptualization, Data curation, Formal analysis, Methodology, Software, Supervision, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The dataset underlying this research is available at Cranfield Online Research Data Repository at <https://doi.org/10.17862/cranfield.rd.22890563>.

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