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A cure kinetics, diffusion controlled and temperature dependent, identification of the Araldite LY556 epoxy

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Received: 15 March 2010 / Accepted: 30 July 2010
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Abstract The curing of the LY556 epoxy system, a DGEBA-type epoxy resin with an anhydride hardener HY917 and a 1-methyl imidazole DY 070 accelerator, mass ratio 100:90:2, was investigated by isothermal and nonisothermal differential scanning calorimetry (DSC). Dynamic measurements were used to evaluate the total, ultimate, heat of the epoxy resin thermosetting reaction and enable experimental conversion determination for isothermal curing. Aiming further finite element modelling of the curing, this article especially focuses on a complete, temperature dependent, cure kinetics parameters identification strategy with the Kamal and Sourour phenomenological model expanded by a diffusion factor. A special attention was given for diffusion description which allows the identification of a fixed order of reaction for the LY556 epoxy resin. Based on isothermal conversion data analysis, the methodology for cure kinetics parameters identification is presented. This led to a temperature dependent identification of all cure kinetics parameters of the LY556 epoxy blend, including diffusion control description and corresponding temperature dependency. Cure kinetics identification quality and importance of diffusion control phenomenon for the curing of the epoxy are then highlighted by computed conversion results that fit almost well the data in the range of temperature used for identification.

Introduction

Epoxyes are widely known for their adhesives, coatings and matrices properties for high performance composites materials. This class of composites has recently emerged in naval and offshore construction since the optimization of the structures became inevitable. Many tools were developed for design efficiency. However, if the strengthening of the composite is mainly driven by the quality of the fibre reinforcement, then it also strongly depends on the quality of the matrix obtained at the end of the curing process. Indeed, the curing of the epoxy is a delicate and complex chemical reaction process that owns a phase change from a liquid state to a solid state. Moreover, the reaction is thermo activated on one hand and is exothermal on the other hand. A coupling between the chemistry and the thermal exists and must be considered for quality control of the curing process of the epoxy. This request is particularly the case for the LY556 epoxy system, usually used for filament winding process, and well known for its high exothermal effects during the curing. Thus, an inappropriate cure schedule can lead to the development of damaging thermal gradients with increasing thickness due to the thermo activated and exothermic behaviour of the thermosetting reaction. An example of damages, like cracks and bubbles, observed after the curing inside of a thick carbon epoxy raiser tube, more and more used for deep water petrol extraction, is presented in Fig. 1.

As a consequence, cure behaviour understanding appears as a necessary study for any improvement of the curing quality of epoxyes and especially for the LY556 system. In this context, accurate cure kinetics identification is a strategic requirement for the solving of the thermal and chemical coupling problem, occurring during the curing of real composites structures, since heat of reaction is related

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Fig. 1 Defects across thickness for thick carbon epoxy raiser tubes (by courtesy of IFREMER: French Research Institute for Sea Exploitation)



to conversion rate, as detailed in the “[Epoxy cure kinetics modelling overview](#)” section. Among existing cure kinetics models, the most used one today is the phenomenological Kamal and Sourour [1] model, extended by Fournier et al. [2] for possible diffusion effects to be taken into account. This modelling approach requires identification of six parameters, including diffusion effects if they exist and will be investigated in this article. Since the curing involves changes in local temperature due to the chemical reaction and the heating schedule, cure kinetics parameters must be temperature dependent. If this is the case for Arrhenius expressions of the phenomenological Kamal and Sourour parameters, then it is not the case for the diffusion part of the cure kinetics. Furthermore, use of constant values for corresponding diffusion parameters led to bad cure kinetics simulation results. This is not satisfying, especially for finite element modelling of the curing of composite parts and, on the other hand, temperature dependency of diffusion factor parameters seems to be not investigated in the literature. A special attention must, therefore, be given to parameters identification technique to set consequently their temperature dependencies.

Therefore, the goals of this article are:

- To provide an easy to use and reliable identification protocol of the six parameters involved in the cure kinetics model.
- To propose consequently a complete temperature dependency of these six parameters, especially for diffusion factor parameters.
- To check if this kind of phenomenological and complete temperature dependent model for the cure kinetics can work properly over a wide range of temperature encountered for cure schedules, to assess its applicability for finite element modelling of the curing.

These questions were examined for the case of the LY556 epoxy for the construction of a temperature coupled, predictive cure kinetics model for the range of temperature used for identification. This appears as a strategic step for the setting of a cure kinetics modelling, as simple as possible, for easy use in further finite element analysis (FEA) of the curing, for local conversion and temperature predictions, hence quality description of the matrix in process.

Consequently, an overview about epoxy cure kinetics modelling is presented in next section, based on differential scanning calorimetry (DSC) analyses. This section highlights cure kinetics modelling for epoxies with the phenomenological Kamal and Sourour [1] model, extended by Fournier et al. [2] for possible diffusion effects to be taken into account. Isothermal and dynamical curing data provided by DSC analyses are then presented for the LY556 epoxy blend. The question of diffusion description is exposed and led to a methodology for cure kinetics order identification. Remaining cure kinetics parameters are presented with a thermal dependent evolution law. The predictive conversion quality of the temperature-coupled cure kinetics model, over the range of temperature used for identification, is assessed in the last part of this article thanks to a solving strategy of the cure kinetics equation, which enables a comparison between computed conversion and experimental conversion data.

Epoxy cure kinetics modelling overview

Cure kinetics of epoxy resins can be studied by different techniques, such as DSC, infrared spectroscopy (IR) and dielectric spectroscopy [3]. In this study, the DSC technique was used to investigate the kinetics of the epoxy resin cured under isothermal and nonisothermal conditions. The different methods to predict the cure reactions and kinetics were reviewed by Barton [4] and Duswalt [5] for different epoxy systems. The proceeding of conversion of the resin and residual heat of curing can be determined from isothermal and subsequent nonisothermal (dynamic) DSC scans [6]. The related data can also be used to draw the conversion rate as function of time and describe it by means of a suitable kinetic model. A large body of works was devoted to assess the cure kinetics of thermosets using isothermal and nonisothermal DSC techniques. Most of the epoxy resins studied in the literature are on base of bisphenol A with amines and anhydrides, as curing agents. Note that the cure kinetics is different for each epoxy system. Keenan [7] pointed out that the exact chemical reaction kinetics is difficult to describe for real resin systems of practical use. However, Keenan also advised that kinetic models can still be useful in providing empirical parameters for modelling and controlling the curing process.

Curing thermosetting materials generally involves the transformation of low molecular weight liquids to amorphous networks with infinite molecular weight by means of exothermic chemical reactions. One of the most widely used methods for cure kinetics determination of thermosetting resin system is the DSC method [3]. Therefore, dynamic and isothermal measurements were done in a conventional DSC apparatus to quantify the released heat during curing and to determine the degree of chemical conversion or degree of cure. The degree of cure is defined as the ratio of the released heat up to the current time by the total (ultimate) heat of reaction. It ranges from 0 for uncured resin to 1 for completely cured resin and denotes the thermo hardening process of an epoxy resin that belongs to a phase change from a liquid state to a solid state.

Dynamic kinetic analysis

One of the interests of this analysis lies in this single heating rate application. A continuous heating of the reactive system will provide enough energy to reach the fully cured state of the system. Thus, the ultimate heat of reaction or total enthalpy (H_U) is the amount of heat generated during dynamic scanning provided by the DSC. H_U is independent of the heating rate and is calculated by following expression (1):

$$H_U = \int_0^{t_f} \left(\frac{dQ}{dt} \right)_f dt \quad (1)$$

where $(dQ/dt)_f$ is the instantaneous rate of heat generated, t_f is the amount of time required to complete the reaction during the dynamic DSC scan.

This data enables degree of conversion determination, during the curing of thermosetting systems, thanks to the fundamental assumption of the DSC technique which considers heat evolution recorded $H(t)$ as being proportional to the degree of conversion. Therefore, the degree of conversion $\alpha(t)$ can be defined as (2):

$$\alpha(t) = \frac{H(t)}{H_U} \quad (2)$$

Moreover, knowledge about heat evolution produced by the thermosetting reaction is strategic data for further chemical and thermal coupling model for the curing of thick composite parts.

Isothermal kinetic analysis

The total isothermal heat of reaction (H_T), which is released at a constant given curing temperature, was calculated by (3):

$$H_T = \int_0^{t_T} \left(\frac{dQ}{dt} \right)_T dt \quad (3)$$

where $(dQ/dt)_T$ is the instantaneous rate of heat generated during isothermal scanning experiments, t_T is the amount of time required to complete the reaction during the isothermal DSC scan. The total released heat H_T at a given plateau is increasing as the curing plateau increases and tends to the ultimate value H_U . H_T depends, therefore, on temperature [8]. The distribution of heat reaction $H(t)$ was determined using the rate of heat generation measured during isothermal scanning experiments [8] and is given by:

$$H(t) = \int_0^t \left(\frac{dQ}{dt} \right)_T dt \quad (4)$$

The actual rate of cure, dz/dt , as function of time, has been calculated through following equation:

$$\frac{dz}{dt} = \frac{1}{H_U} \left(\frac{dQ}{dt} \right)_T \quad (5)$$

Cure kinetics models can be classified into two categories, phenomenological models and mechanistic models. However, mechanistic models are heavy to handle and to identify for thermosetting chemical reaction such as for epoxies. Hence phenomenological or semi-empirical models were considered for the cure kinetics modelling, and moreover these models are usually easy to use from an engineering point of view.

According to Dusi et al. [8], the actual cure rate dz/dt can be related to the isothermal rate of cure $d\beta/dt$. Therefore, Eq. (5) can be rewritten as follows:

$$\frac{dz}{dt} = \frac{H_T}{H_U} \frac{d\beta}{dt} \quad (6)$$

with $\frac{d\beta}{dt} = \frac{1}{H_T} \left(\frac{dQ}{dt} \right)_T$

where $d\beta/dt$ stands for the isothermal reaction rate based on the total isothermal heat of reaction (H_T) at a specific constant temperature instead of the total heat of reaction (H_U) obtained by dynamic differential scanning. Hence, the actual degree of cure $\alpha(t)$ is determined by integrating expression (6) such as:

$$\alpha(t) = \frac{H_T}{H_U} \int_0^t \frac{d\beta}{dt} dt \quad (7)$$

A lot of empirical models, [9–12], have been suggested for degree for cure kinetics. Nevertheless, it appears that the isothermal approach was based on an autocatalytic model which was first found by Horie et al. [13] and extended by Kamal [1, 14]. The phenomenological Kamal and Sourour

model [1] of cure kinetics seems to be the most widely model used in the literature for epoxy systems. This model was, therefore, chosen for the LY556 epoxy system studied in this article and is expressed by Eq. (8). This model accounts for an autocatalytic and non-autocatalytic reaction in which the initial reaction rate is not zero.

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n \quad (8)$$

α is the degree of cure corresponding to the $d\alpha/dt$ rate and denotes the conversion of epoxy groups at a given time t . K_1 describes the rate constant of the reaction of partial order n catalyzed by an accelerator, K_2 is the rate constant of the autocatalytic reaction of partial order m .

However, the solving of the cure kinetics Eq. (8) mathematically tends to 100% of degree of curing. If Eq. (8) is satisfying for the beginning of the degree of conversion evolution, then this is not correct in comparison with final level of degree of curing obtained experimentally since it hardly tends to unity. Indeed, as the curing evolves, the chemical degree of conversion rate is less and less important, and the thermosetting reaction becomes diffusion controlled [2, 15–18]. After gelation, when the flexibility of molecules is less and less important in the glassy state, practically no full conversion state can be reached. A reach of 100% of degree of cure appears therefore utopian, especially for low levels of isothermal curing. Diffusion control usually slows down the reaction and must therefore be taken into account.

At the beginning of the curing, the rate of the thermosetting reaction is dominated by the reactivity of the molecule [15], before being controlled by diffusion phenomena. Fournier et al. [2] proposed a semi-empirical relationship (9) based on free volume consideration to extend the Kamal and Sourour model by a diffusion factor $f_d(\alpha)$ such as:

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n f_d(\alpha) \quad (9)$$

$$\text{with } f_d(\alpha) = \left[\frac{2}{(1 + \exp[(\alpha - \alpha_f)/b])} - 1 \right]$$

α_f is the degree of conversion obtained at the end of a given isothermal curing and hence could be directly obtained as the ratio between H_T and H_U for each isothermal DSC scans. b is an empirical diffusion parameter of the material. The Fournier et al. diffusion factor appears to be the most common relation for diffusion terms to expand the Kamal and Sourour model to enable conversion rate prediction also in the diffusion controlled regime [17].

Thus, as a conclusion of the epoxy cure kinetics identification problem, following parameters have to be identified:

- The total heat of reaction (H_U), for isothermal DSC scans exploitation to carry out corresponding degree of conversion, as defined by Eq. 7.
- The four parameters of the Kamal and Sourour model: m , n , K_1 and K_2 .
- The two parameters of the Fournier et al. diffusion factor model: b and α_f .

Experimental

Epoxy resin

The resin system used in this study is a three-component anhydride-epoxy system from Ciba. The blend consists of a bifunctional DGEBA-type epoxy (Araldite LY556, EEW = 183–192 g/eq, $n = 0.3$), a tetra-functional anhydride hardener (methyl-tetrahydrophthalic anhydride HY917, anhydride equivalent weight = 166 g/eq), and an accelerator (1-methyl imidazole DY 070). The components were mixed in LY556/HY917/DY 070 weight ratio of 100/90/2, resulting in a stoichiometric epoxy-anhydride mixture.

Sample preparation

Measurements were carried out by a DSC 20 Mettler Toledo instrument and a 2920CE TA instrument with the MDSCTM option. Heating ramps of 1, 2 and 5 °C/min were performed by the DSC 20 Mettler Toledo instrument for dynamic tests with temperature rising from 25 to 185 °C. In isothermal scanning, the tests were performed with 90, 100, 110, 120, 130 and 140 °C plateaus that are usually applied for cure schedules. For these two kinds of tests, epoxy sample weights were ranging approximately from 8 to 12 mg and were placed in hermetically sealed aluminum pans of the DSC 20 device.

Curing analysis of the LY556 epoxy resin

Nonisothermal curing analysis

To investigate the ultimate heat of the reaction, the heat flow was measured between –50 °C and 250 °C for heating ramps of 1, 2 and 5 °C/min by a differential scanning calorimeter 2920CE TA instrument with the MDSCTM option. An average value of 355 with an uncertainty of ± 25 J/g was found for the LY556 epoxy resin and corresponds to the 2 °C/min nonisothermal DSC scan result. Note that the ultimate heat of reaction H_U is in the right magnitude order in comparison with the literature, especially with the result obtained by Van Assche et al.

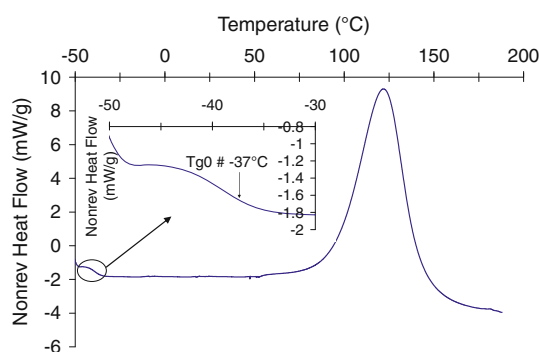


Fig. 2 Heat flow of the LY556 epoxy resin as a function of temperature for nonisothermal curing

[19] for the same LY556 epoxy system, but with two times less DY 070 accelerator, as they found 335 J/g with heating rates ranging from 2.5 to 15 °C/min. On the other hand, accelerator percentage does not impact too much the ultimate heat of the reaction as mentioned by Moon Kwang Um et al. [20]. Thus, value of 355 ± 25 J/g reasonably seems acceptable for the ultimate heat of the reaction of the LY556 epoxy mixture presented in this article.

As displayed in Fig. 2, the glass transition (T_g) of the uncured resin (T_{g0}) is at -37 °C. T_{g0} was read at the inflexion point of the endothermic step of the heat flow. The curing of the epoxy is then started with exothermal peak appearance of the pronounced heat flow and is resolves as it curves. Note that thermal degradation was observed to start in the vicinity of 200 °C.

Isothermal curing analysis

From a convenient and practical point of view, isothermal curing conditions are far more used for curing analysis and process conditions.

In Fig. 3, the conversion of the LY556 epoxy resin system is shown as a function of time for different curing temperatures between 90 °C and 140 °C.

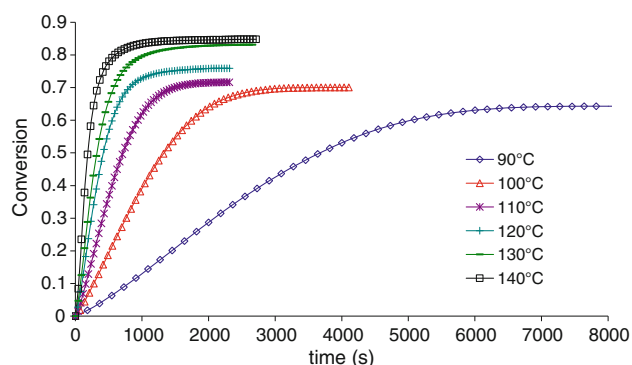


Fig. 3 Experimental conversions as a function of time for the LY556 epoxy system at different isothermal curing temperatures

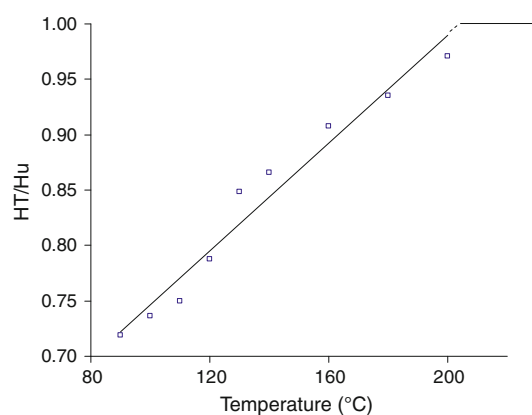


Fig. 4 H_T/H_U versus isothermal temperature

As expected, the total conversion decreases with decreasing temperature and hence could not reach full conversion (i.e. unity). Thus, as a consequence, for Araldite LY556, the ratio H_T/H_U rises with increasing temperature and was approximated by a piece-wise linear function of temperature as shown in Fig. 4 and expressed by Eq. (10):

where

$$\frac{H_T}{H_U} = \begin{cases} 0.00243 T(^{\circ}\text{C}) + 0.50346 & T < 200^{\circ}\text{C} \\ 1 & T > 200^{\circ}\text{C} \end{cases} \quad (10)$$

More precisely, the evolution of H_T/H_U is linear with the temperature until 200 °C and remains constant above 200 °C. H_T is the isothermal heat of reaction and is dependent on the temperature level of the curing plateau. Dusy et al. [8] studies proposed a critical process temperature T_C for the curing plateau to reach a fully cured matrix state. Thus, isothermal curing tests performed with the Araldite LY556 system tend to a critical process temperature of 200 °C for the plateau, since it was experimentally observed that the corresponding heat released H_T did not grow significantly above this temperature for usual curing durations such as 2 h for example. As displayed in Fig. 4, a curing plateau at $T_c = 200$ °C corresponds to #97% of degree of conversion. The remaining 3% could be collected but this requires a very long duration of the plateau at T_c since the curing becomes more and more diffusion controlled. It was then decided to consider T_c value of 200 °C as a reasonable value on one hand and, on the other hand, since thermal degradation start was observed by thermo gravimetric analysis in the vicinity of 200 °C.

Epoxy cure kinetics identification results

Diffusion effect description

As indicated by the phenomenological model of the cure kinetics (Eq. 9) and based on similar analysis done by

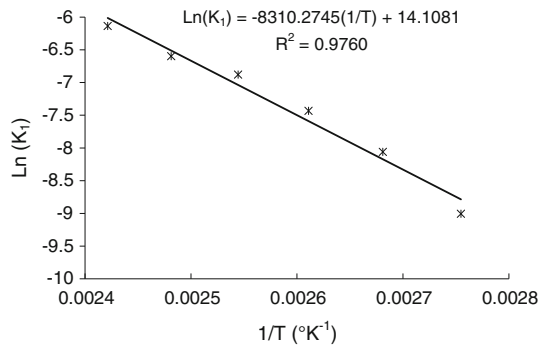


Fig. 7 K_1 Arrhenius evolution versus temperature, from 363°K (90 °C) to 413°K (140 °C)

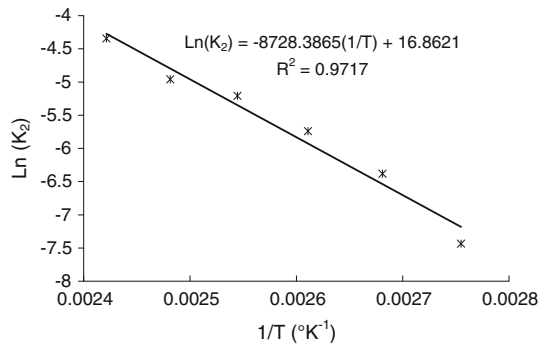


Fig. 8 K_2 Arrhenius evolution versus temperature, from 363°K (90 °C) to 413°K (140 °C)

conversion for each isothermal curing. Thus, according to the cure kinetics Eq. (9), Figs. 5 and 6 plots were fitted with following expression:

$$\left[\frac{\left(\frac{dz}{dt} \right)_{\text{experimental}}}{(1-\alpha)^n} \right] = (K_1 + K_2 \alpha) \cdot f_d(\alpha) \quad (12)$$

with $f_d(\alpha) = \left[\frac{2}{(1 + \exp[(\alpha - \alpha_f)/b])} - 1 \right]$

The Kamal and Sourour K_1 and K_2 data are specific rate constants following an Arrhenius shape versus temperature as expressed by Eq. (13). Temperature dependency observed for K_1 and K_2 , displayed in Figs. 7 and 8, confirms the applicability of the Arrhenius law.

$$K_1 = A_1 \exp\left(\frac{-E_1}{RT}\right) \text{ and } K_2 = A_2 \exp\left(\frac{-E_2}{RT}\right) \quad (13)$$

Kamal and Sourour cure kinetics parameters obtained by the one shot identification method are listed in Table 1.

E_1 and E_2 values appear to be in a good magnitude order with the literature for epoxies as for instance compared with Harsch et al. [15] that found 65.1 kJ/mol and 68.2 kJ/mol for E_1 and E_2 , respectively, but for a different epoxy system (Araldite CY179). Note that A_1 and A_2 values, respectively $1339879.17 \text{ s}^{-1}$ and $21042820.69 \text{ s}^{-1}$, are deduced from the y-intercept in the $\text{Log}(K_1)$ and $\text{Log}(K_2)$ plots versus $1/T$,

Table 1 Cure kinetics coefficients of the LY556 epoxy resin system for the Kamal and Sourour model

| $A_1 \text{ (s}^{-1}\text{)}$ | $A_2 \text{ (s}^{-1}\text{)}$ | $E_1 \text{ (kJ/mol)}$ | $E_2 \text{ (kJ/mol)}$ |
|-------------------------------|-------------------------------|------------------------|------------------------|
| 1339879.17 | 21042820.69 | 69.14 | 72.62 |
| $m = 1; n = 2$ | | | |

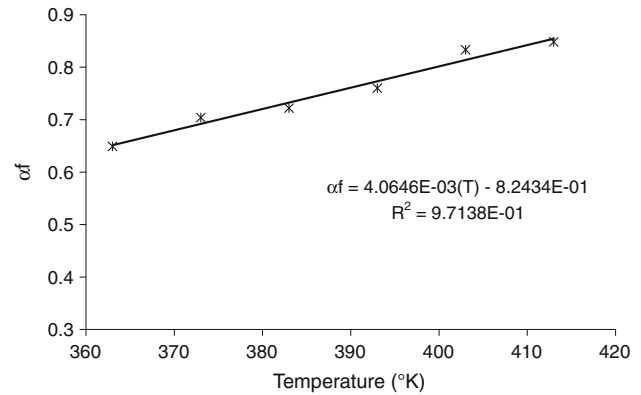


Fig. 9 Final conversion α_f evolution versus isothermal temperature, from 363°K (90 °C) to 413°K (140 °C)

and consequently are strongly depending on the slope of the linear shape of the Arrhenius law for K_1 and K_2 as shown in Figs. 7 and 8, hence on E_1 and E_2 values that were observed to be acceptable. It seems therefore reasonable to consider values of Kamal and Sourour model, as listed in Table 1, as being acceptable for the LY556 epoxy resin system.

To what concerns diffusion factor parameters b and α_f their evolution were found to be coherent with the physics. Indeed, since final level of degree of conversion reachable obviously increases with curing plateau level, its identification was logically found as a growing function of temperature and could be fitted by a linear function as displayed in Fig. 9. On the other hand, diffusion effects are more and more pronounced with plateau level as shown in Fig. 6, hence diffusion parameter b was logically found as a growing function of temperature and could also be fitted by a linear function as displayed in Fig. 10. Temperature dependency obtained for diffusion factor parameters b and α_f are exposed in Table 2.

Discussion

A methodology for cure kinetics parameters identification was exposed. No fitting difficulties were encountered by the one shot identification of the parameters. Note that diffusion factor parameters b and α_f evolve linearly with isothermal curing temperature in the range of temperature used for identification. However, from a physical point of view, evolution of α_f cannot exceed 100% of conversion

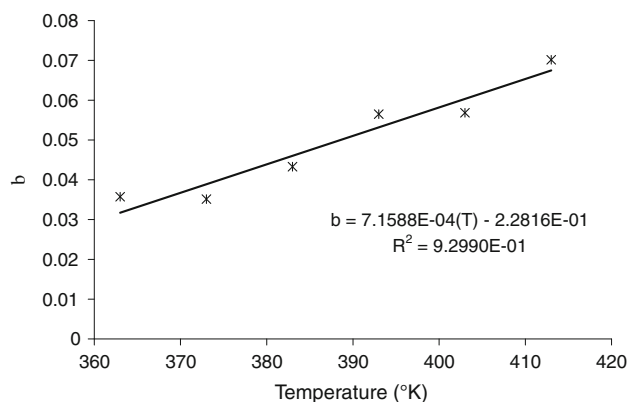


Fig. 10 Diffusion parameter b evolution versus temperature, from 363°K (90 °C) to 413°K (140 °C)

Table 2 Temperature dependency of diffusion parameter b and final degree of conversion α_f for the LY556 epoxy resin system

| b | α_f |
|---|--|
| $b = 7.1588 \text{ E-}4 \text{ T (°K)}$ $- 2.2816 \text{ E-}1$ | $\alpha_f = 4.0646 \text{ E-}3 \text{ T (°K)}$ $- 8.2434 \text{ E-}1$ |

and must therefore be limited to unity for the modelling, if necessary.

Nevertheless, fitting accuracy and corresponding cure kinetics parameters identification quality must be assessed. This was performed by comparisons between computed conversion and conversion data provided by DSC analyses, as presented in next chapter.

Cure kinetics modelling quality

Quality of cure kinetics parameters identification for the LY556 epoxy blend was checked by comparison of conversion provided by the cure kinetics model and DSC data. However, it is important to point out that the comparison with the data is a necessary step to check the reliability and the efficiency of the linear temperature dependency presented for diffusion factor parameters b and α_f . A solving technique for the cure kinetics Eq. (9) is therefore required and is presented in next sub section. Hence, comparison results are presented and discussed.

The solving technique of the cure kinetics model

From a technical point of view, an Euler explicit method was used to solve the cure kinetics Eq. (9). This solving technique was chosen for its convenience to be set in further FEA analysis model of the curing. The Euler explicit solving method for cure kinetics Eq. (9) was validated by comparison with reference methods such as the

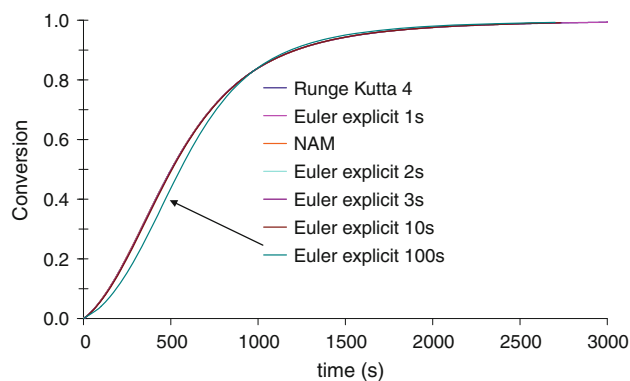


Fig. 11 Validation of the Euler explicit solving for cure kinetics, isothermal case

Runge–Kutta fourth order method, with adaptive steps for error control, and the Numerical Asymptotic Method (NAM) [25], with series convergence control for error minimization, as shown in Fig. 11 for isothermal case. In Fig. 11, the maximum increment of time applicable for the Euler explicit method is around 10 s, but for the convenience of the conversion prediction 1 s time increment was used for the solving.

Comparison results

Once cure kinetics parameters identified, comparisons between conversion computed by the cure kinetics model and DSC data for 100, 110, 120, 130 and 140 °C isothermal curing conditions are presented in Figs. 12, 13, 14, 15, 16 and 17. Isothermal temperature evolution versus time is the temperature input for the Euler explicit solving method of the cure kinetics model defined by Eq. (9).

Discussion

Comparison with conversion data led to satisfying results. Conversion prediction fits well conversion data for isothermal curing, but in a lesser extent for the 90 °C

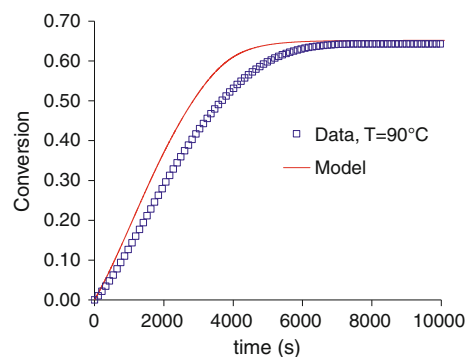


Fig. 12 Computed conversion versus data for the 90 °C isothermal curing

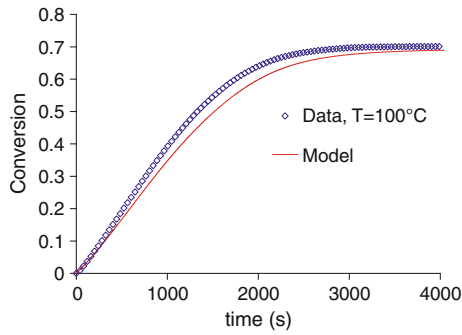


Fig. 13 Computed conversion versus data for the 100 °C isothermal curing

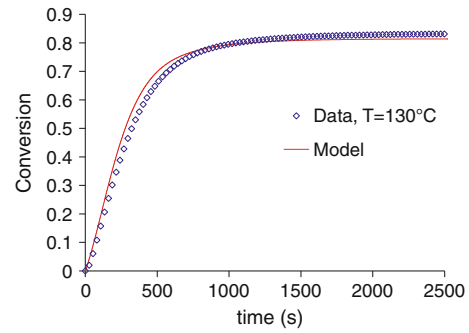


Fig. 16 Computed conversion versus data for the 130 °C isothermal curing

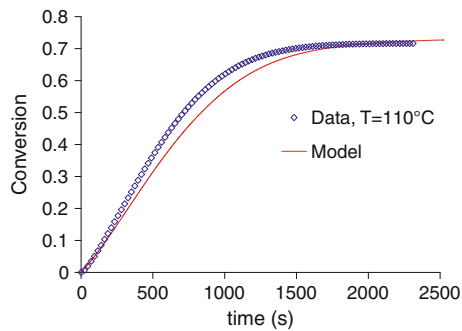


Fig. 14 Computed conversion versus data for the 110 °C isothermal curing

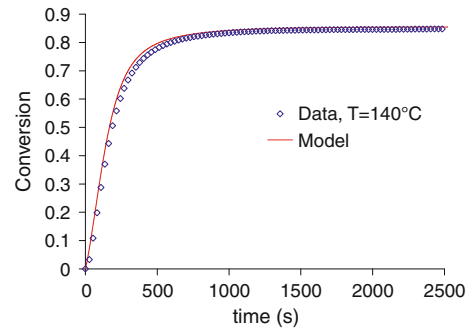


Fig. 17 Computed conversion versus data for the 140 °C isothermal curing

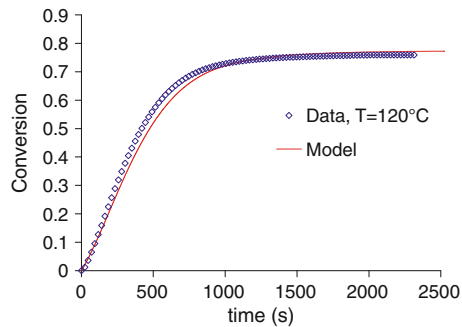


Fig. 15 Computed conversion versus data for the 120 °C isothermal curing

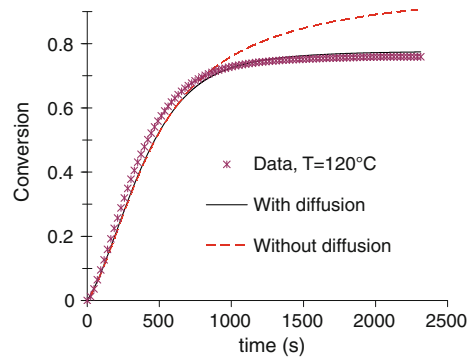


Fig. 18 Impact of diffusion factor on cure kinetics simulation results compared with DSC data of a 120 °C isothermal curing

isothermal curing. In this case, a maximum gap of around 15% was observed between conversion computed and DSC data, in the vicinity of the gelation area. This is clearly related to K_1 and K_2 Arrhenius evolution identification, as displayed in Figs. 7 and 8, that does not match the 90 °C data in the same way as for other isothermal curing data. If necessary, this can be easily improved by increasing DSC data or by spacing isothermal curing as far as possible for linear fit accuracy.

On the other hand, the final level of conversion predicted is very satisfying and stays within 5%. Anyway, as demonstrated in Fig. 18 for a 120 °C isothermal curing, the

Kamal and Sourour model needs to be extended by a diffusion factor for the curing of the LY556 epoxy blend presented in this article.

Conclusion

A methodology for cure kinetics parameters identification of the LY556-HY917-DY 070 epoxy blend, widely used for filament winding process, was presented. The phenomenological Kamal and Sourour cure kinetics model

was completed by a diffusion model developed by Fournier et al. A special attention was given for the description of diffusion effects on one hand, and a temperature dependency for diffusion factor parameters was presented on the other hand and this is new. Diffusion factor parameters b and α_f can be described by a linear dependency to the temperature, within the range of curing temperature investigated, between 90 °C and 140 °C for the LY556 epoxy. The parameter identification protocol led to a complete temperature dependent cure kinetics model and corresponding computed conversion results fit almost well the data in the usual range of curing temperatures, with a simple Euler explicit solving technique. The complete temperature dependent cure kinetics, diffusion controlled, model presented in this article enables further application, within industrial FEA software, for the cure process modelling of real 3D thermosetting fibre reinforced parts. Indeed, computer FEA solutions for the cure kinetics governing equation take advantage of such analytical models instead of tabular data, and are currently developed by the authors for the thermal and chemical coupling problem occurring during the curing of real 3D thermosetting composite parts.

Acknowledgements This study was funded by the Brest Metropole Oceanne council of the city of Brest in Brittany and the Social European Funding (FSE). The material support of the ENSIETA graduate school of engineering and of the IFREMER Institute in Brittany is gratefully acknowledged.

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