Estimation of the curing rate of acrylamide used as a consolidant in heritage sandstone conservation

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Abstract An investigation of the curing (polymerisation) rate of acrylamide was carried out using isothermal and non-isothermal DSC in order to estimate the time for complete conversion of monomer at ambient temperatures. The non-isothermal data were used to model the rate using integral isoconversional and incremental isoconversional kinetic methods. Applying the equations for integral isoconversional methods and extrapolating to ambient temperatures resulted in non-sensical conversion–time curves, where the time estimated decreased for increasing degree of conversion to be reached. This odd behaviour was attributed to the incorrectness of the integration where the kinetic parameters (e.g. the activation energy) are a function of conversion. The problem was addressed by applying incremental methods which provided more reasonable results as the integration is carried out over small conversion increments where the kinetic parameters are assumed to be constant. Estimates of the conversion were compared to isothermal measurements and, although isothermal DSC produced significant variability in the data, extrapolated estimates from non-isothermal kinetic analysis produced, at best, an upper boundary for the estimation of the time to reach a fixed degree of conversion.

Introduction

The objective of this study was to investigate the rate of polymerisation or curing of acrylamide for its application as a consolidant in Sydney sandstone [1, 2]. The kinetics of the solution polymerisation of acrylamide using potassium persulphate as the initiator has been investigated by a number of authors [3–6] resulting in the isothermal kinetic relationship:

$$-\frac{d[M]}{dt} = k[K_2S_2O_8]^{0.5}[M]^{1.25}, \tag{1}$$

where M is the monomer concentration. Equation (1) suggests that the termination is bimolecular and that the mechanism of polymerisation is not simply a chain transfer mechanism. These studies have focussed on the initial rate of polymerisation, and the degrees of conversion modelled are limited to the early stages of conversion. They have also modelled the kinetics from the onset of the polymerisation process and have ignored the presence of the induction period. For the application of acrylamide as a potential consolidant, not only does the induction period need to be incorporated in the kinetic modelling, but also the full range of conversion must also be included.

To address the overall polymerisation kinetics, non-isothermal DSC measurements have been carried out to help determine the ambient temperature rate of the acrylamide polymerisation. Estimation of the curing time does not require an understanding of the mechanistic process. As such model-free single-step approximations may be

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applied to the kinetic analysis for extrapolation to conditions outside the experimental temperature range. In this study two methods of kinetic analysis were applied to the non-isothermal DSC data; the integral isoconversional approach and the incremental isoconversional approach.

Integral isoconversional method

The integral isoconversional approach to kinetic modelling is based on the single-step rate equation:

$$\frac{d\alpha}{dt} = k(T)f(a). \tag{2}$$

If the conversion function, $f(\alpha)$, is independent of temperature and the temperature function, $k(T)$, is independent of the degree of conversion then the integration

$$\int_0^\alpha \frac{d\alpha}{f(a)} = \frac{1}{\beta} \int_0^{T_\alpha} k(T)dT \tag{3}$$

can be carried out for non-isothermal conditions where β is the heating rate. Typically, the Arrhenius equation:

$$k(T) = A \exp\left(-B/T\right) \tag{4}$$

is chosen as the temperature function. Substitution into Eq. (3) yields [7, 8]:

$$\beta = \int_0^{T_\alpha} \frac{1}{A_\alpha \exp\left(B/T\right)} dT. \tag{5}$$

Equation (5) is generally applied to multiple non-isothermal heating rate curves collected at a range of heating rates for a constant degree of conversion making the left-hand side of Eq. (3) a constant which is incorporated in A_α. Equation (5) can be solved numerically for the kinetic parameters A_α and B [7].

Given that the temperature function is simply a mathematical tool and not the rate constant in the single-step approximation, alternative temperature functions can be applied; for example [8]:

$$k(T) = C \exp\left(DT\right) \tag{6}$$

where C and D are constants (kinetic parameters). Equation (6) has been successfully applied to the kinetics of polymerisation of dimethylol urea [9]. Applying the integral isothermal approach using a set of non-isothermal data at constant heating rate yields:

$$T_\alpha = \frac{1}{D} \ln\left(C_\alpha D\beta + 1\right), \tag{7}$$

where C_α accounts for the conversion function constant.

Incremental isoconversional method

Both the modelling methods of Eqs. (5) and (7) assume that, in particular, the kinetic parameters are independent of the degree of conversion and, hence, the single-step approximation can be applied. Given that the polymerisation of acrylamide has been demonstrated to be a composite of an induction period and the polymerisation process and that kinetic studies have demonstrated that the reaction deviates from first-order kinetics (Eq. (1)) even for small degrees of conversion (<10 %), it is likely that the kinetic parameters are a function of the degree of conversion making the integration of Eq. (2) to yield Eqs. (5) and (7) mathematically incorrect. The error of this transformation may be reduced if the incremental approach is considered [8, 10]:

$$\beta = \int_{T_{\alpha_1}}^{T_{\alpha_2}} \frac{dT}{A_\alpha \exp\left(B/T\right)} \tag{8}$$

and

$$T_{\alpha_2} = \frac{1}{D} \ln\left(C_{\alpha_2} D\beta + \exp(DT_{\alpha_1})\right). \tag{9}$$

In the incremental method, the integration is carried out over small increments of conversion where it is assumed that the kinetic parameters are essentially constant.

Experimental

Acrylamide and potassium persulphate (KPS) were purchased from Sigma-Aldrich and were used as received. 20 mass % solutions of acrylamide in reverse osmosis and deionised water containing 1 mass % KPS of acrylamide were prepared for each experiment. Non-isothermal measurements were carried out on circa 13 ± 1 mg samples which were placed in TZero hermetically sealed pans in a TA Instruments Q2000 DSC. The non-isothermal DSC data were collected at 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2 and 6.4 °C min^{-1} in a nitrogen purge flowing at 30 mL min^{-1} from 30 to 90 °C. Isothermal measurements were carried out by heating rapidly circa 25 mg samples to 30, 40, 50, 60, 70, 80 and 90 °C. Isothermal conditions were typically reached within 90 s of the start of the experiment.

Results

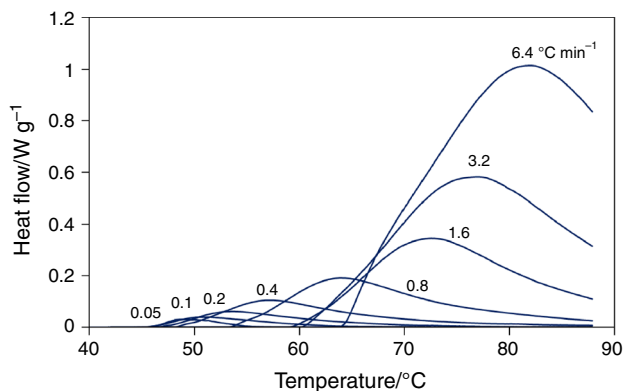The non-isothermal heat flow curves for the polymerisation of acrylamide are shown in Fig. 1. From these heat flow

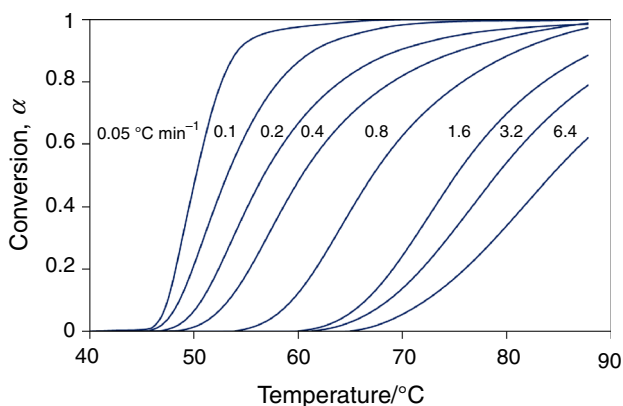**Fig. 1** DSC data for the polymerisation of acrylamide

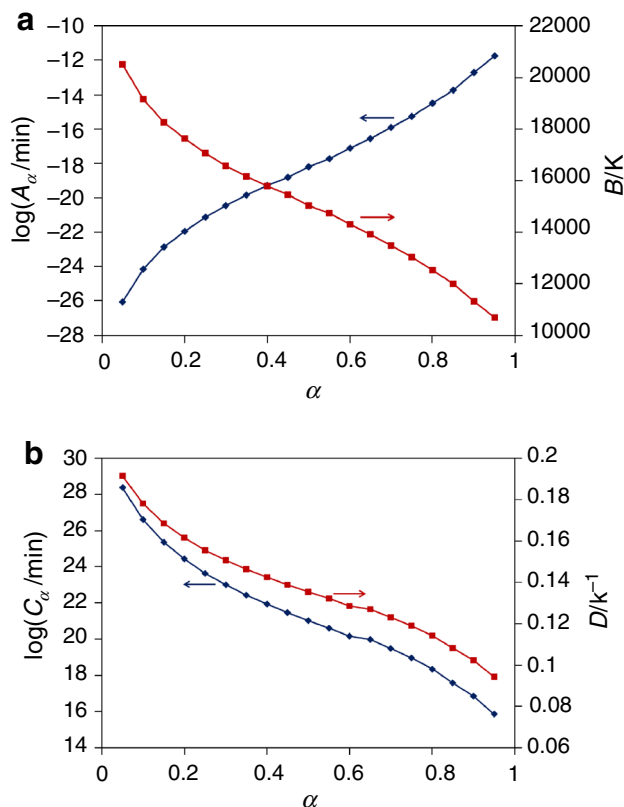**Fig. 2** Conversion data based on Fig. 1

Fig. 3 Calculated values of the kinetic parameters using the integral isoconversional approach for **a** Eq. (5) and **b** Eq. (7) plotted as a function of conversion

curves, the monomer conversion was determined and is plotted in Fig. 2. As complete conversion was only achieved for the 0.05 and 0.1 °C min^{-1} heating curves, conversion for the remaining series was based on the heat evolved using the area for the 0.1 °C min^{-1} curve of 250.2 J g^{-1}. The value of 250 J g^{-1} relates to the 20 % solution and corresponds to a heat of polymerisation for acrylamide of -89 kJ mol^{-1} which is a little higher than the value reported for the thermal polymerisation of solid acrylamide, -75 kJ mol^{-1} [11].

Based on these data, integral and incremental iso-conversional analysis of the reaction kinetics was performed using Eqs. (5), (7), (8) and (9). Parameters A_α and B were determined by means of non-linear least-squares method. The integrals in Eqs. (5) and (8) were evaluated using a continued fraction algorithm adopted from [12]. The sum of squares between the experimental and calculated isoconversional temperatures was minimised using the Nelder–Mead simplex method. The parameters C_α and D in Eqs. (7) and (9) were determined

by the non-linear least-squares minimisation using the programme Origin. The kinetic parameters are plotted as a function of conversion in Fig. 3 for the integral iso-conversional analysis and in Fig. 4 for incremental iso-conversional analysis using an increment, $\Delta\alpha$ ($=\alpha_2 - \alpha_1$), of 0.05. There is a strong dependence of the kinetic parameters for both temperature functions used in the integral isoconversional method [Eqs. (5), (7)] indicating that the temperature function, $k(T)$, is a function of the degree of conversion invalidating Eq. (3). The temperature dependence of the kinetic parameters is significantly reduced, however, by applying the incremental method suggesting improved validity.

The premise of the fitting process was to model the rate of curing at elevated temperature to allow extrapolation to estimate the curing time outside the experimental temperature range. Using the kinetic parameters calculated from Eqs. (5) and (7), it is possible to calculate the estimated reaction time using:

$$t_\alpha = A_\alpha \exp\left(B/T\right) \tag{10}$$

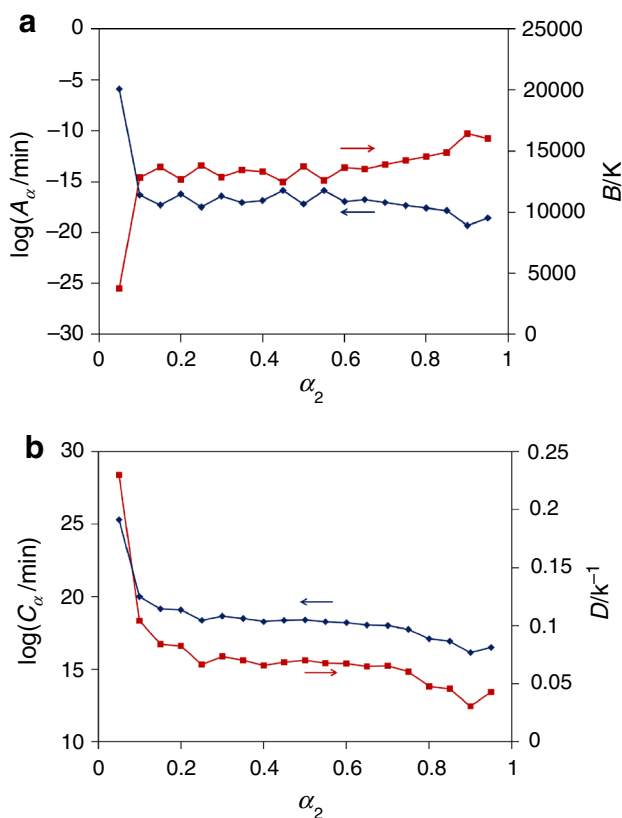for the Arrhenius temperature function, and

a

b

Fig. 4 Calculated values of the kinetic parameters using the incremental isoconversional approach for **a** Eq. (8) and **b** Eq. (9) plotted as a function of conversion using an increment, $\Delta\alpha$ ($=\alpha_2 - \alpha_1$), of 0.05

$$t_\alpha = C_\alpha \exp(-DT) \tag{11}$$

for the exponential temperature function for the integral isoconversional approach. Using the kinetic parameters from Eqs. (8) and (9) it is possible to calculate the estimated reaction time using:

$$t_\alpha = \sum_i \Delta t_i = \sum_i A_{\alpha_i} \exp\left[B_{\alpha_i}/T\right] \tag{12}$$

for the Arrhenius temperature function, and

$$t_\alpha = \sum_i \Delta t_i = \sum_i C_{\alpha_i} \exp[-D_{\alpha_i}T] \tag{13}$$

for the exponential function for the incremental isoconversional approach. The calculated times for 80 % conversion are shown in Fig. 5. In Fig. 5 the values of conversion to 80 % for isothermal measurements (circles) are also plotted. The isothermal measurements show some significant scatter (which has been previously reported for the polymerisation of acrylamide using free radical initiators [6]). The calculated values of the conversion to 80 % appear to be an upper limit and in general the estimated times of the polymerisation are significantly overestimated by the kinetic modelling.
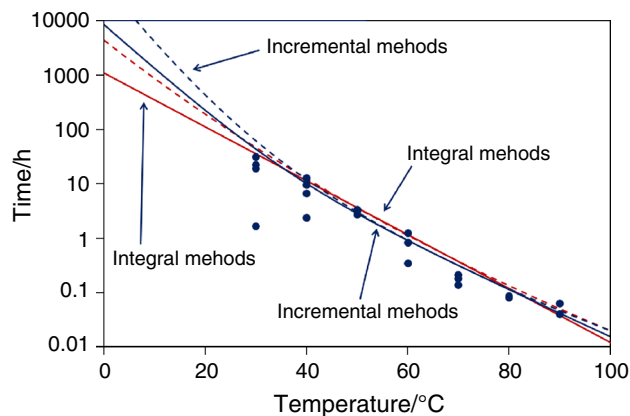

Fig. 5 Plot of the predicted curing times for 80 % conversion based on Eqs. (10), (11), (12) and (13) using the kinetic parameters determined from Eqs. (5), (7), (8) and (9). *Dashed lines* represent data calculated using the Arrhenius temperature function; *solid lines* represent data determined using the exponential temperature function. *Circles* correspond to isothermal measurements for 80 % conversion

The inaccuracy of the modelling is a combination of experimental factors, such as the unpredictable variation in the length of the induction period and the mathematical incorrectness of the integration of Eq. (3) [13]. This incorrectness can be easily seen by plotting conversion as a function of time for the integral isoconversional method (Fig. 6a, b). Figure 6a shows the expected increase in the length of time taken to reach higher degrees of conversion at 50 °C. Indeed, both the Arrhenius and exponential temperature functions provide similar results (Fig. 6a) as might be expected as 50 °C is within the experimental temperature range. The conversion–time plot for 25 °C using the integral method is shown in Fig. 6b. In this case non-sensical curve shapes are observed for both temperature functions (Eqs. (4) and (6)). The calculated time taken to reach higher degrees of conversion is initially reduced! This impossible situation must arise from the integration of Eq. (3) making any kinetic analysis at best an empirical curve-fitting exercise. For the integral isoconversional methods, the incorrectness of the integration of Eq. (3) applies to any temperature function used and although not shown here, similar results to those observed in Fig. 6 are also observed when alternate temperature functions are used [13].

The problem of the nonsensical conversion–time curves produced from extrapolation to temperatures outside the experimental measurement region is overcome by applying the incremental isoconversional method where, over a short range of conversion, the kinetic parameters are assumed to be essentially constant. This is confirmed in the data plotted in Fig. 7 where there is an increase in the degree of conversion with time. Again there is good correlation
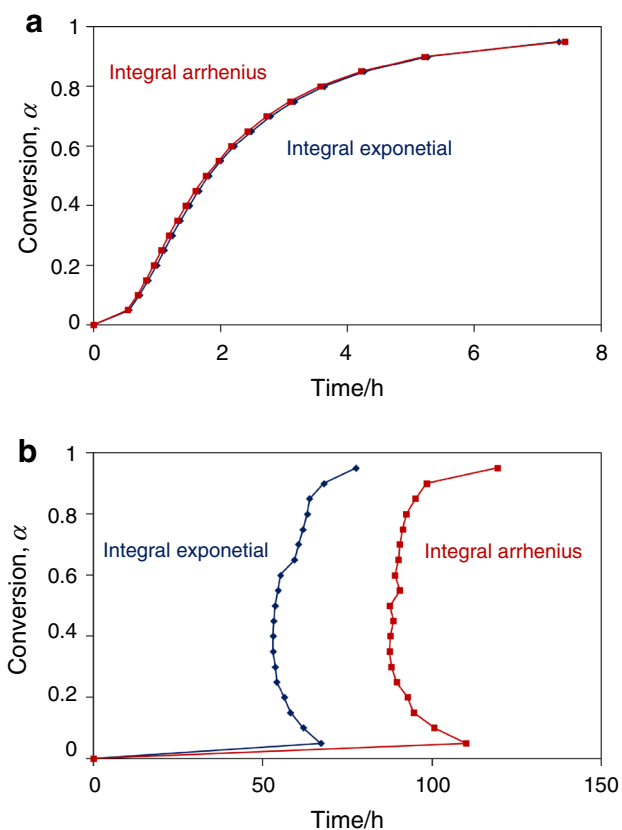
Fig. 6 Conversion plotted as a function of time calculated using Eqs. (10) (*squares*) and (11) (*diamonds*) for **a** 50 °C and **b** 25 °C. The kinetic parameters were calculated by fitting Eqs. (5) and (7) to the non-isothermal data plotted in Fig. 2

Fig. 7 Conversion plotted as a function of time calculated using Eqs. (12) and (13) for **a** 50 °C and **b** 25 °C. The kinetic parameters were calculated by fitting Eqs. (8) and (9) to the non-isothermal data plotted in Fig. 2 using an increment, $\Delta\alpha$ (=$\alpha_2 - \alpha_1$), of 0.05

between the calculated data for 50 °C between the Arrhenius and exponential temperature function models [Eqs. (12), (13)] which is expected as 50 °C is within the experimental temperature range. Significant deviation between estimates is, however, observed at lower temperatures.

The polymerisation of acrylamide in solution is demonstrably a minimum of two processes: an induction period (the period prior to observation of measurable change) and the conversion process itself [which is also likely to be multiple processes as indicated by Eq. (1)]. The modelling of these multiple-step processes with a single-step approximation results in poor extrapolated estimates of the conversion time (Fig. 5) and non-sensical conversion–time curves when using the integral isoconversional approach. In the incremental approach, the induction period is addressed as the first step of the kinetic analysis, i.e. in the time taken to reach a degree of conversion of 0.05, and, essentially, subsequent incremental steps should account for any change in the mechanism. Extrapolation using the incremental model, however, significantly over-estimates the conversion time when compared to conversion times determined from isothermal measurements. The
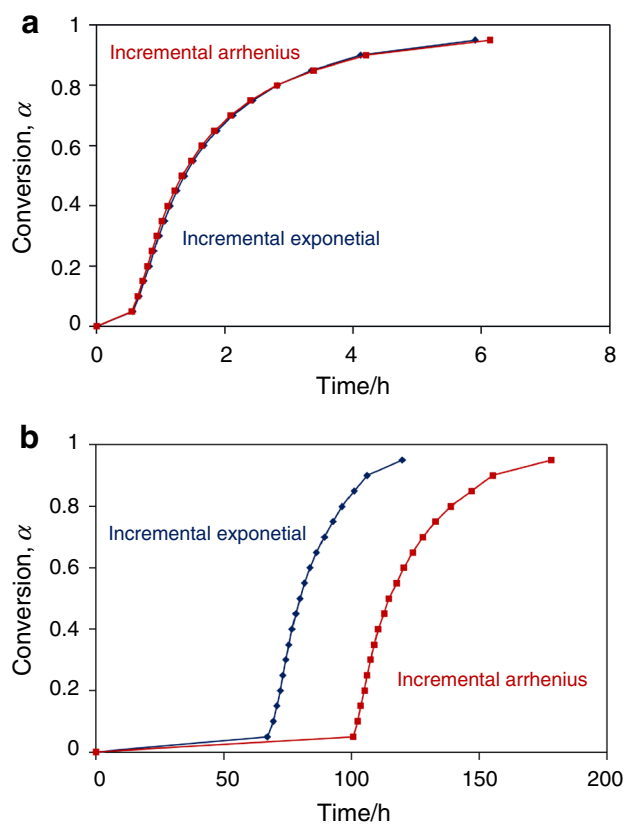
best agreement with the isothermal measurements is actually reached when employing the integral method using the exponential temperature function, Eq. (6), despite the nonsensical conversion–time curves. Even in this case, the estimates calculated using Eq. (11) appear to be an upper limit of the time taken to reach a fixed degree of conversion as measured using isothermal DSC.

It is also notable that the use of the Arrhenius equation as the temperature function for both the integral and the incremental methods produces longer estimates of the conversion time. As the modelling is conversion function free and no mechanism is implied by the single-step approximation, this exaggerated deviation suggests that it is more appropriate to use non-Arrhenius functions for the temperature function such as Eq. (6).

Conclusions

The modelling of the polymerisation of acrylamide using non-isothermal isoconversional methods has been carried out in this study. Non-isothermal methods of data

acquisition are generally preferred as data acquired are much more reproducible. The application of integral and incremental isoconversional methods in the modelling of the data does, however, pose some significant problems. Integration of the general rate equation demands that the kinetic parameters in the temperature function are independent of the degree of conversion. For the polymerisation of acrylamide, this is demonstrably not the case. The polymerisation consists of a minimum of two steps and, given the nature of polymerisation processes, there are likely to be many more than two steps involved in the complete conversion of acrylamide making the application of Eqs. (5) and (7), in particular, inappropriate. The issue of the problem of integrating the rate equation has widespread implications as non-isothermal integral methods are commonly used to model kinetic data. Despite this problem, the best estimates of the conversion time are provided by the integral isoconversional method [Eq. (11)] based on the non-Arrhenius temperature function given by Eq. (6).

Investigation of the isothermal polymerisation of acrylamide resulted in some significant variability in the conversion process. However, within broad experimental bounds, this study has found that, based on the polymerisation time of up to 30 h at 30 °C, acrylamide has the potential to be used as a practical consolidant in sandstone. This is a reasonable curing time for application under ambient conditions especially where time for diffusion of the consolidant into the sandstone is required prior to polymerisation and consolidation. Given the promising polymerisation rate of acrylamide at ambient temperature, further studies will be carried out to determine the rate of polymerisation in situ in sandstone.

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