

Viscosity: Thermal History Models for Thermosetting Resins

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Abstract

Thermal history dependent viscosity models have been used in various numerical codes to predict variation of the resin viscosity during the resin transfer moulding process (RTM). The models are based on mathematical models which predict the degree of cure of the resin and then uses this to predict the viscosity. The work presented in this paper illustrates some of the difficulties associated with thermal history dependent viscosity modelling for RTM and highlights sources of variation between the behaviour predicted from these models and the real behaviour of the resin. An alternative method is outlined which will circumvent many of the current problems and sources of inaccuracy.

1 Introduction

Resin Transfer Moulding (RTM) is a well established technique for production of automotive components which is now being extended to the production of aerospace components. It involves the injection of a liquid resin into closed moulds which contain the reinforcement in the form of a dry fibre preform, the resin wets out the preform, fills the mould and is then cured in-situ. It is a method which offers good repeatability combined with low costs and the ability to produce complex components which would otherwise be impractical.

Components which are of interest to the aerospace industry are often large with high fibre volume fractions (v_f) and a high degree of fibre alignment. This means that the resistance to flow of the resin through the preform is high so the injection stage of the RTM process will involve high injection pressures, long fill times and/or low resin viscosities. High injection pressures are undesirable as they can lead to problems with mould distortion and fibre movement so resins with low viscosities must be utilised in conjunction with long injection times.

For most uncured thermosetting resins the main way to decrease the viscosity is to increase the injection temperature. Increasing the injection temperature has the undesirable effect of increasing the rate of chemical crosslinking which has the effect of increasing the viscosity; consequently there are two competing

effects and the optimum injection temperature must be determined for the component.

An aspect of RTM which is expensive is the production of quality tooling. To enable the effective design of tools to be carried out with the minimum of redesign to overcome filling problems the process of moulding is being modelled using numerical codes which have been developed by various academic and commercial organisations.

The more advanced numerical modelling codes which are available incorporate viscosity models where the viscosity varies as a function of the temperature and the degree of resin cure, in essence the thermal history of the resin during the processing. This capability enables the code to predict more fully the filling behaviour of the process.

2 Aims

The aims of this paper are to illustrate some of the limitations in the thermal history dependent viscosity models which are currently used in composite process modelling codes and to propose an alternative approach.

3 Modelling Approach

The approach to the modelling of thermal history dependent viscosity which has been used in process modelling codes is to estimate the degree of cure of the resin based on the resin curing kinetics and to relate the viscosity to that degree of cure. In essence, the degree of cure is used as a thermal history parameter.

The model which has been considered in this work is that proposed by Kamal and Sourour which has been incorporated into the *LIMS* code which has been developed by the University of Delaware [1][2]. Other models have been published in the literature which have been used in various numerical process modelling codes, for instance those by Castro and Macosco [3][4][5] and by Lee, Loos and Springer [6][7], which offer different fitting routines to the data, these models use a similar approach to that used in *LIMS* and they have similar limitations and are not considered here in detail.

The degree of cure, α , of the resin is estimated from the curing kinetics of the resin which are determined using differential scanning calorimetry (DSC) and from the thermal history of the resin. The resin curing kinetics in these codes are assumed to follow either n^{th} order or autocatalytic behaviour, these two models can be combined into one model which is written as:

$$\frac{d\alpha}{dt} = \left(\left(A_1 e^{\frac{E_1}{RT}} \right) + \left(A_2 e^{\frac{E_2}{RT}} \right) \alpha^m \right) (1 - \alpha)^n \quad (1)$$

where $\frac{d\alpha}{dt}$ is the rate of curing, A_1, E_1, A_2, E_2, n and m are empirically determined constants which are calculated from a curing exotherm as measured by DSC, T is the absolute temperature and R is the Universal Gas constant. Equation 1 is integrated numerically to give α as a function of α and T .

The determination of the curing kinetic parameters using DSC is carried out by measuring the rate of heat evolved during the cure of the resin. This method of determination requires that the investigation be carried out at temperatures where the curing exotherm is significant. At these temperatures the increase in viscosity of the resin is so rapid that RTM injection is impossible so processing is carried out at temperatures well below the temperature range of determination of the curing kinetic parameters; this is shown in figure 1. The main consequence of this is that the curing kinetic parameters, as determined using DSC, may have no real relationship to the kinetics of crosslinking at injection temperatures, particularly when there is a change in the reaction mechanism.

The Kamal and Sourour viscosity model utilises the degree of cure of the resin as described above to predict the viscosity of the resin. This model may be written as [1]:

$$\eta = a_0 e^{\frac{a}{RT}} e^{\left(\alpha \left(\frac{b}{RT} - b_0 \right) \right)} \quad (2)$$

Parameters which must be determined are a, a_0, b and b_0 , these are calculated from viscosity isotherm experiments.

4 Experimental

Three generically different thermosetting resins were investigated in this work: a one part untoughened epoxy resin; a modified cyanate ester resin and a bismaleimide resin.

The curing kinetic parameters which were used in equation 1 were fits to n^{th} order models as determined using a Mettler-Toledo DSC820 with a TA8000 controller using the standard kinetic fitting software.

The parameters for the viscosity model were determined from a set of isothermal viscosity experiments which were carried out on the resins, starting with fresh resin for each isotherm. The instrument used was a Carri-Med CSR 500 controlled stress rheometer fitted with an extended temperature module. The experiments were carried out in flow mode with a constant stress being applied. Removable aluminium platens were used, the thermal effects being accounted for by calibration of the temperature with a calibrated thermocouple.

5 Discussion of Results

The initial processing of the data involved using the thermal history of the resin and the resin curing kinetics to convert the viscosity versus time curves into viscosity versus degree of cure curves via numerical integration of equation 1.

Processing of the subsequent viscosity versus degree of cure plots to yield the Kamal and Sourour viscosity model parameters was carried out using three fits of regression lines to the data, each of which had an inaccuracy associated with it.

The first fit was for a plot of $\ln(\eta)$ versus α for each temperature. The slope of the least squares fit line gave $\left(\frac{b}{RT} - b_0\right)$ while the intercept gave $\left(\frac{a}{RT} + \ln(a_0)\right)$: these fits assumed a linear relationship which was not always the case (see figure 2).

From the first curve fit, plotting the intercept, i.e. $\left(\frac{a}{RT} + \ln(a_0)\right)$, versus $\frac{1}{T}$, the gradient of the least squares fit line gave the value of $\frac{a}{R}$ while the intercept gave $\ln(a_0)$.

As for the determination of a and a_0 , plotting the slope of the first curve fit, i.e. $\left(\frac{b}{RT} - b_0\right)$, versus $\frac{1}{T}$, the gradient gave the value of $\frac{b}{R}$ while the intercept gave $-b_0$.

For the Kamal and Sourour viscosity model there is an upper temperature limit defined by $\frac{b}{b_0}$ above which the model is mathematically invalid, this limit was noted in the original paper [1]. Above this temperature the viscosity will decrease with increasing degree of cure which does not happen in practice. In addition, as $T \rightarrow \frac{b}{b_0}$ the accuracy of the fits to the real situation will become worse leading to a lack in confidence in the predictions of the model. For the resins investigated the values of b/b_0 determined were as given in table 1 along with the intended resin injection temperatures.

Resin	b/b_0 °C	Injection Temp. °C
Epoxy	142	140
Cyanate Ester	115	110
Bismaleimide	115	90

Table 1: Limiting temperatures for the Kamal and Sourour model for the resins investigated in this work with the desired injection temperatures.

The values of b/b_0 which are given in table 1 are close to the processing ranges of the resins so the Kamal and Sourour model is of doubtful use for these resins.

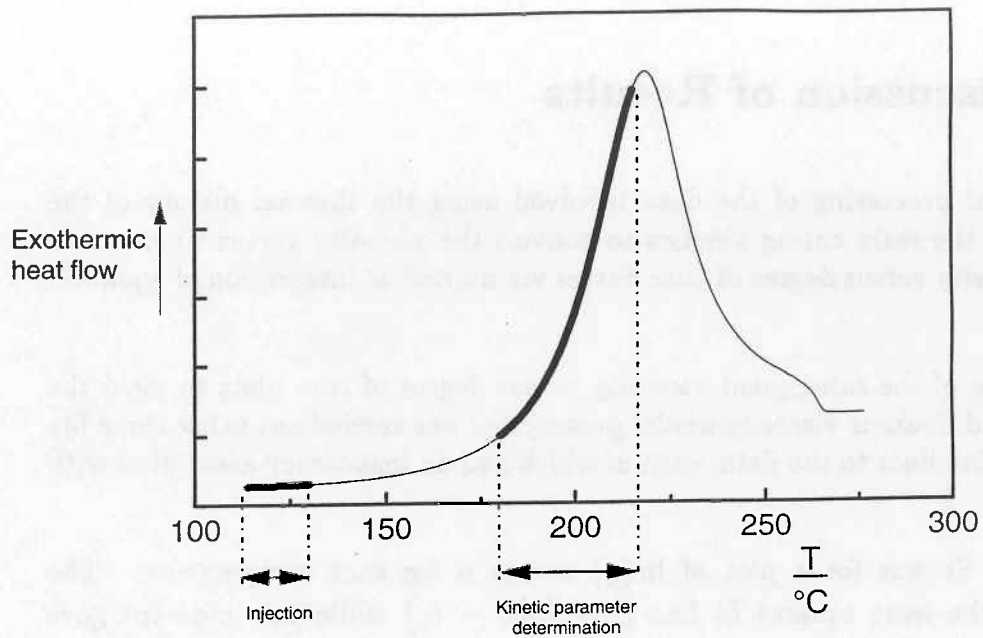


Figure 1: DSC curve from a thermosetting resin showing the range of temperatures for curing kinetic parameter determination and that for injection of the resin during RTM.

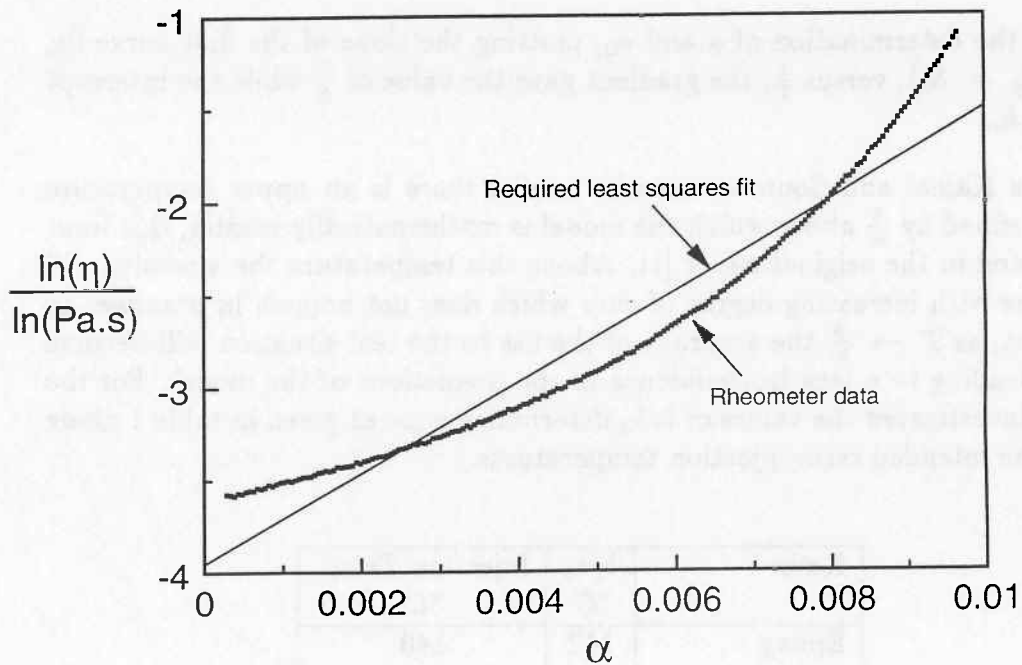


Figure 2: Viscosity, η , on a log scale as a function of the degree of cure, α , for a resin showing the difference between the rheometer data and the assumed straight line fit.

The other main limitation to the use of the approach outlined above is that a great deal of curve-fitting has to be carried out which makes the assumption that the actual behaviour follows the model behaviour. This has been found to be not the case for the resins investigated in this study where the fit of the mathematical curve to the viscosity versus degree of cure plots was found to be poor as can be seen, for instance, in figure 2.

6 Alternative Approach

The work presented in this paper has shown that there are some serious limitations in the approach that is currently used to model the temperature and thermal history dependencies of the viscosity of a thermosetting resin during the very early stages of cure. An alternative approach must be sought in order to circumvent these problems.

Two main areas of inaccuracy in the current approach have been highlighted, these are in the determination of the resin curing kinetics using DSC and in the fitting of mathematical curves to the viscosity data.

The curing kinetics determination is carried out at temperatures significantly above the range of injection temperatures for those resins for RTM so it is desirable to circumvent this stage. The approach which is proposed here is based on the observation that the material property which is most sensitive to the degree of crosslinking in the resin at the levels of interest here is the viscosity itself so a method based solely on viscosity measurements is desirable.

Look-up tables have been suggested as a potential method of determining the time dependency of the viscosity in a modelling code. While this method is very accurate for isothermal conditions it is not able to deal with a shift of temperatures for a curing thermosetting resin owing to the changes in the rate of crosslinking with temperature. The method proposed here is a simple extension to that method with the utilisation of the superposition principle to enable navigation between temperatures.

The approach divides the variation in viscosity into the temperature dependency, which can be described by normal Arrhenius behaviour, and the time dependency at a series of isothermal temperatures. Thus the behaviour at temperature T_j at a time t_i can be described by an equation of the form:

$$\eta_{ij} = A e^{\frac{\Delta H}{RT_j}} + \mathcal{F}_{ij}(t_i(T_j)) \quad (3)$$

The first term on the right hand side of equation 3 $\left(A e^{\frac{\Delta H}{RT_j}} \right)$ is the Arrhenius temperature dependency which can be used as a shifting factor for the isothermal curves. This term is the viscosity of the resin before any crosslinking, that

is at $t = 0$. The second term on the right hand side of equation 3 ($\mathcal{F}_{ij}(t_i(T_j))$) is simply the set of experimental isothermal viscosity curves at temperatures T_j over the time range in each case of 0 to t_i which have been shifted by the Arrhenius factor.

The shifting of the viscosity curves is simply carried out by determining the viscosity at $t = 0$ and subtracting this from the viscosity in the input curve.

6.1 Utilisation of the Approach in a Modelling Code

The above approach to normalisation of the viscosity data allows the raw data to be used in a modelling code to predict the viscosity of the resin for a complicated thermal history.

Navigation between equivalent levels of crosslinking at different temperatures can be performed on the basis that at one temperature the degree of crosslinking will be the only factor determining the viscosity of the resin. Consequently a change in temperature can be dealt with by a transition to the point on the shifted time-temperature-viscosity surface at the new temperature where the viscosity is the same as at the previous temperature, i.e.:

$$\eta_1 = \eta_2 = A e^{\left(\frac{\Delta H}{RT_1}\right)} + \mathcal{F}_1(t_{\eta_1}, T_1) = A e^{\left(\frac{\Delta H}{RT_2}\right)} + \mathcal{F}_2(t_{\eta_2}, T_2) \quad (4)$$

where η_j is the viscosity at temperature T_j which corresponds to the time t_{η_j} . This shift is illustrated in figure 3.

Figure 3 shows a plot of the data from a series of isotherms for epoxy resin plotted as shifted viscosity (on a log scale) against time into the isotherm on the rheometer; in this example $T_3 > T_2 > T_1$. If, for example, the curve for T_3 is considered, if the resin is held at this temperature for, say 750 s the viscosity will follow the T_3 curve for that time. If after 750 s the temperature is reduced to T_1 then the curve for that temperature must be used for increases in the viscosity owing to crosslinking. The translation from the T_3 curve to the relevant point on the T_1 curve is carried out by a horizontal translation so the shifted viscosity remains the same: the equivalent time to 750 s on the T_3 curve on the T_1 curve is about 1 400 s.

After processing at the new temperature a further temperature change to T_2 can be accommodated similarly by a horizontal transition as illustrated in figure 3, followed by a hold at T_2 and return to T_3 for the rest of the processing.

The actual viscosity at any time can be calculated from the shifted viscosity using the Arrhenius shift parameters outlined above.

6.2 Limitations

The approach described above has many advantages over the currently employed method but there are some limitations which must be considered; these relate to the assumptions made, the data range, curve fitting for the initial viscosity and consideration of high levels of cure.

6.2.1 Temperature Superposition Assumptions

The assumption has been made that the temperature dependency is unaffected by the degree of crosslinking. This situation is improbable so the approach is, at best, an approximation but it is a better approximation than the currently used approach.

The use of a simple equation (equation 3) to describe the temperature dependent viscosity shift may not be valid for all resins over a large range of temperatures and times so refinement of the method with a more advanced algorithm may be required. This is outside the scope of this work.

6.2.2 Data Range

For the case where the resin has been held at a high temperature and then is cooled there will often not be any data available at the lower temperature for a corresponding shifted viscosity. This situation will require determination of viscosities over long times, this will be considerably more accurate than the extrapolation technique required in the current methods.

6.2.3 Curve Fitting

There is still some curve fitting in this approach. However, the curve fitting is only carried out to determine the viscosity at $t = 0$ for each temperature, curve fitting which is less prone to variation than the curve fitting which has to be carried out on the viscosity as a function of degree of cure curves and the use of curve fitting to establish the resin curing kinetics.

6.2.4 Higher Levels of Cure

The approach outlined here is for low levels of cure where the viscous flow is significant. It is not a technique which can consider the higher levels of cure with any degree of confidence owing to the assumption that the superposition is independent of the degree of cure. It also cannot deal with any heating from a curing exotherm. For RTM this is not likely to be a problem but this area will need to be addressed for reaction injection moulding techniques.

6.3 Summary of Approach

The approach described above has significant advantages over the currently used method: the advantages may be summarised as follows:

1. the amount of curve fitting is significantly reduced and is limited to extrapolation of the viscosity curve to $t = 0$;
2. curve fitting is not required for the viscosity as a function of time or degree of cure;
3. viscosity data are used directly to determine the variations in viscosity behaviour;
4. the determination of resin curing kinetics does not have to be carried out.

7 Conclusions

The work presented here has shown that:

1. the Kamal and Sourour model can only be used at temperatures below the limiting value given by b/b_0 which is often in the range of temperatures for injection for RTM;
2. the determination of the resin curing kinetics for the currently used method model must be carried out at temperatures significantly above the injection temperatures meaning that the real kinetics of the crosslinking of the resin during injection may be very different to those modelled;
3. the alternative approach which has been proposed will afford a more accurate method of determining the viscosity from the resin thermal history.

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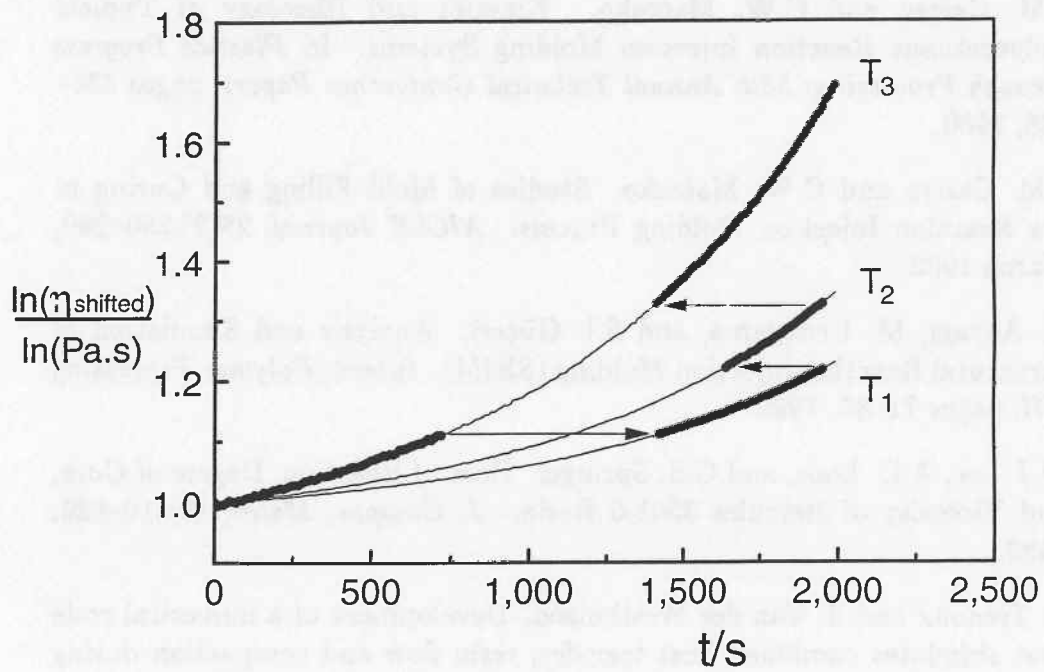


Figure 3: Temperature shifted viscosity as a function of the isotherm time for a series of isotherms over a range of temperatures of interest for the epoxy resin showing the horizontal shift relating to a change in temperature.