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An exponential chemorheological model for viscosity dependence on degree-of-cure of a polyfurfuryl alcohol resin during the post-gel curing stage

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Abstract. In the present study, the chemorheological behavior of a bio-based polyfurfuryl alcohol (PFA) resin has been determined by rheological isothermal tests at different curing temperatures for the post-gel curing stage of the resin, using three different amounts of catalyst (2, 4 and 6 wt %). Instead of modeling the evolution of the complex viscosity using a widely used chemorheological model such as the Arrhenius model for each tested temperature, the change of the complex viscosity as a function of the degree-of-cure was predicted using a new exponential type model. In this model, the logarithm of the normalized degree-of-cure is used to predict the behavior of the logarithm of the normalized complex viscosity. The model shows good quality of fitting with the experimental data for 4 and 6 wt % amounts of catalyst. For the 2 wt % amount of catalyst, scattered data leads to a slightly lower quality of fitting. Altogether, it is demonstrated that the new exponential model is a good alternative to conventional chemorheological models due to its simplicity and suitability.

1. Introduction

For composite materials, to achieve both optimization of the manufacturing process and tailor-making of the final composite properties, fundamental knowledge of the properties of the constituent materials phases is required. Thus, the study of polymers and fibers employed as matrix and reinforcements of composites is of great importance. In the case of a thermosetting polymer resin, the analysis of its kinetics of curing, and its evolution of properties during crosslinking, including the gelling and vitrification transitions that may occur, are crucial.

The gel point of a thermosetting polymer resin is defined as the point at which the behavior of the resin is more similar to a solid than to a liquid; the point at which the insoluble, infinite-molar-mass network is formed (note that the matrix may still contain unreacted soluble intermediates) [1]. After this point, in the post-gel stage, the kinetics of the curing reactions are commonly changed compared with the pre-gel stage, e.g. the curing rate is typically reduced. The chemorheology of the curing process of a bio-based polyfurfuryl alcohol (PFA) resin during its pre- and post-gel stages has been investigated in previous studies [2,3] employing conventional and widely used chemorheological models, such as the Arrhenius model [1]. The basis of the present study is to use a new exponential



model to predict the chemorheological behavior of a PFA resin during the post-gel stage. The degree-of-cure evolution is estimated from rheological variables, such as the complex modulus, which have been determined in a previous study [2]. The new exponential model is shown to be a simple and reliable model.

2. Theory

2.1. Chemorheology

The term used to define the viscoelastic behavior of chemically reacting systems is *chemorheology* [4]. A chemorheological study of a thermosetting polymer resin is typically addressing variations in viscosity due to chemical reactions and process conditions, together with characterization of the molecular network growth and transitions such as gelation and vitrification [5]. Monitoring the variation of rheological properties of a resin during curing allows modelling of the process. The models commonly employed in the literature use viscosity as the selected rheological property, either the steady viscosity (η), or the complex viscosity (η^*), where the latter one is used in the case of oscillatory tests. The steady viscosity is only useful for obtaining chemorheological parameters during the pre-gel stage, since when the resin approaches its gel point, the steady viscosity will be approaching infinity. On the other hand, the complex viscosity is a more suitable parameter to study the curing process of a resin since it can be used for both the pre-gel and the post-gel stages.

2.2. Chemorheological models

The complex viscosity of a thermosetting polymer resin is affected by a number of variables. It can be expressed as a function of temperature (T), pressure (P), shear rate ($\dot{\gamma}$), time (t) and filler properties (F) [5]:

$$\eta^* = f(T, P, \dot{\gamma}, t, F) \quad (1)$$

The relevant effects on the chemorheological behavior can be separated as: cure effects ($\eta_c^* = f(T, t)$), shear rate effects ($\eta_s^* = f(T, \dot{\gamma})$), and filler effects ($\eta_f^* = f(F, T, t)$). The effect of pressure is commonly very low, and it is typically not taken into account unless for certain manufacturing processes such as high pressure injection molding and resin transfer molding [5]. When studying curing processes of resins, the shear rate is usually fixed to simplify the analysis. Thus, in cases where fillers are not present in the resin, it can be considered that only cure effects are relevant, i.e. $\eta^* = \eta_c^*(T, t)$.

Among a number of models in the literature, the Castro-Macosko model is a frequently employed model to describe the variation of the steady dynamic viscosity of a polymer resin during the pre-gel stage as a function of the degree-of-cure [6]. The Castro-Macosko model is shown in Eq. (2):

$$\frac{\eta}{\eta_0} = \left(\frac{\alpha_{\text{gel}}}{\alpha_{\text{gel}} - \alpha} \right)^{A+B\alpha} \quad (2)$$

where η is the steady dynamic viscosity of the resin at a given degree-of-cure (α), η_0 is the initial viscosity (viscosity of the resin before curing), α_{gel} is the degree-of-cure at the gel point, and A and B are empirical model constants.

A simple and reliable model that could predict the change of viscosity during the post-gel stage – in the same way that the Castro-Macosko model does for the pre-gel stage – would be of great interest. The widely used Arrhenius model turns into a complicated model when viscosity is expressed as a function of the degree-of-cure, instead of as a function of time. Taking the Castro-Macosko model as inspiration, the model for the post-gel stage should propose a function that can predict the ratio between the complex viscosity at a certain time after gelation, and the complex viscosity at the gel

point, i.e. η^*/η_{gel}^* . Due to the high viscosity values of the resin in the post-gel stage, the natural logarithm of the ratio ($\ln(\eta^*/\eta_{gel}^*)$) is more appropriate to use. In analogy to the Castro-Macosko model, the proposed relationship should relate to the maximum degree-of-cure ($\alpha = 1$) since the model should predict the change of the complex viscosity for the range $\alpha_{gel} \leq \alpha < 1$. Altogether, the proposed new functional relationship for the post-gel stage is described by Eq. (3):

$$\ln\left(\frac{\eta^*}{\eta_{gel}^*}\right) = f\left(\ln\left(\frac{1-\alpha_{gel}}{1-\alpha}\right)\right) \quad (3)$$

In the literature, a phenomenological sigmoidal model has been successfully applied to predict the chemorheological behavior of resins, such as polyurethane resins [7,8]. However, to the best of the author's knowledge, an exponential empirical model that can forecast the behavior for the post-gel stage has not been used. In the present study, based on the experimental behavior observed for a PFA resin at different curing temperatures, a Box-Lucas like exponential equation will be used for the functional relationship proposed in Eq. (3). Moreover, to properly model the post-gel curing stage of the PFA resin, the parameters of the model will be proposed in a way so that they have a physical meaning.

3. Experimental procedure

3.1. Materials

A bio-based polyfurfuryl alcohol (PFA) resin under development, FuroLite 050915A, and an "S type + D" acid catalyst based on p-toluenesulfonic acid dissolved in water (45 % aqueous solution), were supplied by Transfurans Chemicals BVBA (Belgium). According to the supplier's datasheet, the specifications of the PFA resin are: water content 5.40 % and monofurfuryl alcohol content below 1 %.

3.2. Instrumentation

Rheological runs were performed using an AR Rheometer 2000 (TA Instruments[®]) with a 25 mm diameter upper plate and a Peltier lower plate. Normal force was zeroed and fixed during the tests to prevent contact loss between the sample and plates. Five isothermal curing runs of the PFA resin in the temperature ranges 65 – 85 °C, 55 – 75 °C and 50 – 70 °C (using a 5 °C increment) for 2, 4 and 6 wt % amounts of catalyst, respectively, were carried out for 60 min. Six frequencies equally separated on a logarithm scale were employed in the range from 1 to 10 Hz, and the applied strain was fixed at 0.1 % for all the amounts of catalyst tested. A 20 °C min⁻¹ heating ramp was programmed in order to reach the various curing temperatures from a starting temperature of 20 °C. All samples were first stabilized at the starting temperature for 2 min before the heating ramp was applied. All rheological measurements were performed within the linear viscosity region of the PFA resin (strain sweep tests were performed to ensure the applied strain was within the linear viscosity region). Three replicates were used for each experimental setting.

4. Results and discussion

By plotting $\ln(\eta^*/\eta_{gel}^*)$ vs. $\ln((1-\alpha_{gel})/(1-\alpha))$ in Figure 1, it is clear that the change of the logarithm of the normalized complex viscosity can be described by an exponential function. Moreover, by plotting the results in this way, no effect of the changed applied isothermal curing temperatures can be seen. Some scattering is found between the applied curing temperatures, especially for the 2 wt % amount of catalyst, however, the scattering is decreased when the amount of catalyst is increased. This can be explained, as was also done previously for the Arrhenius model [2], by the existence of small gradients of catalyst in the resin (heterogeneity), and the larger impact of these gradients on the behavior of the complex viscosity during the post-gel stage.

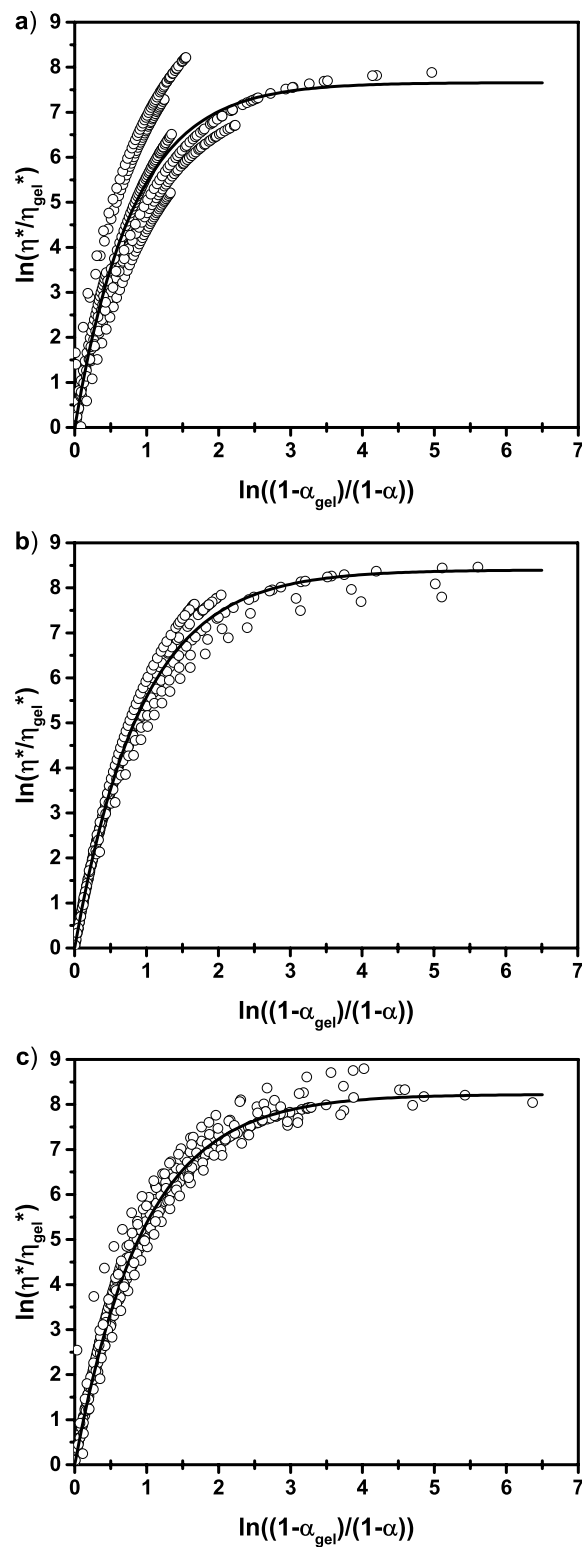


Figure 1. Natural logarithm of the experimental normalized complex viscosity (symbols) and the predicted normalized complex viscosity (lines) vs. natural logarithm of the normalized degree-of-cure

for a PFA resin with a) 2 wt % of catalyst; b) 4 wt % of catalyst; c) 6 wt % of catalyst. For each amount of catalyst, results are shown for a range of applied isothermal curing temperatures.

The Box-Lucas type equation ($y = b \cdot [1 - \exp(-a \cdot x)]$) was chosen to describe the exponential behavior of the PFA resin. Based on this equation, and by giving physical meaningful values to its constants (a and b), an exponential empirical model is proposed to predict the chemorheological behavior of the PFA resin in the post-gel stage. The model is described by Eq. (4):

$$\ln\left(\frac{\eta^*}{\eta_{gel}^*}\right) = \ln\left(\frac{\eta_{\alpha=1}^*}{\eta_{gel}^*}\right) \cdot \left[1 - \exp\left(-a \cdot \ln\left(\frac{1 - \alpha_{gel}}{1 - \alpha}\right)\right)\right] \quad (4)$$

where $\eta_{\alpha=1}^*$ is the complex viscosity of the fully cured resin, and a is a model parameter that describes the complex viscosity rate with respect to the degree-of-cure. The model parameter $\ln(\eta_{\alpha=1}^*/\eta_{gel}^*)$ represents the logarithm of the maximum reachable ratio between the complex viscosity at any time during the post-gel stage, and the complex viscosity at the gel point. This parameter can either be measured directly, or it can be determined by fitting the model to experimental data. The equation shown in Eq. (4) can be simplified to Eq. (5):

$$\ln\left(\frac{\eta^*}{\eta_{gel}^*}\right) = \ln\left(\frac{\eta_{\alpha=1}^*}{\eta_{gel}^*}\right) \cdot \left[1 - \left(\frac{\alpha - 1}{\alpha_{gel} - 1}\right)^{-a}\right] \quad (5)$$

The proposed new model is a two-parameter model. The applicability of the model is valid for the range of degree-of-cure from the gel point to the fully cured resin.

In Figure 1, the resulting model predictions for the post-gel curing stage of the PFA resin are shown. The established model parameters are exhibited in Table 1. As can be seen from the mean square error values, the quality of the fittings is good for the 4 and 6 wt % amounts of catalyst. For the 2 wt % amount of catalyst, the fitting is however less good due to the more scattered data, as already indicated above, and explained by the gradients of catalyst in the resin. This problem was not observed for the larger amounts of catalyst since the gradients are getting smaller as the amount of catalyst is increased.

Table 1. Established model parameters of the exponential chemorheological model for the post-gel curing stage of a PFA resin.

Amount of catalyst (wt %)	$\ln\left(\frac{\eta_{\alpha=1}^*}{\eta_{gel}^*}\right)$	a	Mean square error
2	7.7	1.2	0.6
4	8.4	1.1	0.1
6	8.2	1.1	0.1

Next, the suitability of the model is evaluated:

- The model consists of a simple equation that relates the complex viscosity (a ratio) with the degree-of-cure for the post-gel curing stage; therefore, simplicity is a clear benefit of the model. For Arrhenius models, a relatively complicated equation is required when the model

is used to predict the change of η^* with respect to the degree-of-cure; in some cases, a six-parameter Arrhenius model is required to obtain reliable predictions.

- For a known complex viscosity, the model can be used to determine the degree-of-cure of a resin in its post-gel stage; in this way, rheology is a fast and easy alternative to other well-known possibilities such as DSC, TMA, and FTIR.
- The results show similar ratios for the parameter $\ln(\eta_{\alpha=1}^*/\eta_{gel}^*)$ independently of the curing temperature under isothermal tests – notice the ratio is between both complex viscosities at the same temperature –. The overall values of the ratio in Table 1 are similar to the ones that can be determined for each of the applied different temperatures, e.g. for the 6 wt % amount of catalyst, the overall value is 8.2, and it is 8.0 at 65 °C, and 8.3 at 70 °C. Therefore, only a few isothermal tests could be used to determine the parameters of the model – in principle, a single temperature could be enough; however, more than one temperature is recommended –.
- The estimated $\ln(\eta_{\alpha=1}^*/\eta_{gel}^*)$, obtained by fitting the model to the experimental data, could also be a good indicator of the effect of the amount of catalyst on the cross-linking density of the fully cured resin. Therefore, this parameter could be employed to compare the importance of the amount of catalyst added to the system beside the curing rate. In this work, similar values were found for this parameter, 8.40 and 8.23 for 4 and 6 wt % amounts of catalyst, respectively, and this seems to indicate that the same cross-linking density was reached by both amounts of catalyst – 2 wt % amount of catalyst was not considered due to the high scattering found, as mentioned before –; however, this result should be checked in further works. Moreover, this parameter can be easily measured at different curing temperatures and compared with the obtained by the model either to check the validity of the model or to avoid a compensation effect between both parameters of the model.
- In principle, the a parameter of the model can be used as an indicator of how the curing rate is changed by the amount of catalyst. A higher curing rate is expected when the catalyst amount is increased, and the same behavior is expected for the a parameter, i.e. the higher amount of catalyst, the higher value of a . In the present study, the a parameter is determined in the range from 1.1 to 1.2, considering only 4 and 6 wt % amounts of catalyst; however, with no clear effect of the amount of catalyst. Further studies are needed to reveal the real utility of this parameter in the model, which probably will depend on the resin system under study.
- The complex viscosity of the fully cured resin can be predicted at any temperature if the complex viscosity is known at the gel point. Likewise, the complex viscosity of the resin at its gel point can be predicted at any temperature if the complex viscosity is known for the fully cured resin. Further improvements of the model should be focused at finding a simple equation that can predict the change of the complex viscosity at the gel point as a function of temperature, and deploy this equation into the model.

5. Conclusions

A new empirical chemorheological model was proposed based on the experimental behavior found for a bio-based polyfurfuryl alcohol resin cured using three amounts of catalyst under isothermal conditions. Then new chemorheological model was an exponential type equation. It is indicated that the model employed is a suitable chemorheological model for the post-gel curing stage due to the good agreement found with the experimental results when a 4 or 6 wt % amount of catalyst was employed. However, the modeling of the curing process when a 2 wt % catalyst was used could not be conducted satisfactorily; the main reason for the unsuccessful application of the model and the scattering found

for the data could be the heterogeneity of the samples due to a insufficient amount of catalyst was employed to keep a constant concentration of it in the whole sample. Further work on the validation of the model under different conditions and for other resins and the development of the model to be employed under non-isothermal conditions is still required.

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