

MODELING OF RESIN CURE KINETICS FOR MOLDING CYCLE OPTIMIZATION

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ABSTRACT

During the last years, the numerical simulation of Liquid Composites Molding (LCM) turned out to be a useful tool to assist in process design and optimization. To appropriately simulate LCM manufacturing, accurate material characterizations must be carried out. In a more competitive industrial environment, fast and reliable characterization techniques are required to implement effective numerical simulations. Resin cure kinetics modeling software called **PolyKinetic** has been developed to assist in material characterization and process simulation. In this work, recent advances on resin cure kinetics modeling are presented and compared. Different kinetic models for an epoxy resin are discussed. Modeling of the percentage of catalyst is also included, together with rheological analyses and a model of gel time to estimate the allowable injection time from calorimetric data. **PolyKinetic** software turns out to be a very useful tool to characterize the cure kinetics of thermosetting resins in a fast and reliable way. **PolyKinetic** is a freeware package available to all the scientific and industrial community through the *Chaire sur les Composites à Haute Performance (CCHP)* of École Polytechnique de Montréal.

INTRODUCTION

Polymer composite materials have been increasingly used in several industrial applications for the last few years. As the composite industry grows, thick parts and pieces of complex shape have become more common. Thermoset composites have also gained much interest in the automotive industry and many applications have successfully demonstrated their effectiveness. High specific mechanical properties, corrosion resistance and low fatigue effects are main factors for the selection of such materials over traditional metallic solutions. Liquid Composite Molding (LCM) and other manufacturing techniques such as Sheet Molding Compound (SMC), Resin Transfer Molding (RTM) or Compression RTM have gained attention due to their capability to produce composite parts in medium to large production volumes. Resin cure kinetics and the evolution of viscosity play a key role to ensure proper fiber impregnation and reduce cycle time. From the thermal point of view, the molding cycle is closely related to the chemical and

rheological behavior of the resin. Therefore, to optimize the molding cycle in LCM manufacturing, the chemical and rheological behaviors of thermosetting polymers must be well known. Based on the material behavior during resin cure, a computational analysis of the process cycle can be carried out. Process simulation allows a proper selection of processing parameters such as the injection pressure and the mold and resin temperatures [1, 2]. In a more competitive industrial environment, fast and reliable characterization techniques are required to implement numerical simulations for engineering design and process planning.

In this work, recent advances on resin cure kinetics modeling are presented and compared. Different kinetic models for an epoxy resin are discussed. Modeling of the percentage of catalyst is also included, together with rheological analyses and a model of resin gel time to estimate the allowable injection time from calorimetric data. Resin cure kinetics modeling software called ***PolyKinetic*** has been developed to assist in material characterization for process simulation and optimization.

MODELING OF RESIN CURE KINETICS

Modulated Differential Scanning Calorimetry (M-DSC) is a well known technique to measure the curing reaction of thermosetting resins. Assuming that the non-reversible heat flow measured is entirely related to the exothermic reaction of the polymer, M-DSC data can be used to determine the reaction rate $d\alpha/dt$ and the degree of conversion α in the following form:

$$\dot{H} = \frac{dH}{dt} = \frac{d\alpha}{dt} \cdot H_T \quad (1)$$

$$\alpha = \int_0^t \frac{d\alpha}{dt} \cdot dt \quad (2)$$

where \dot{H} is the instantaneous heat generated by the cross-linking polymerization of the resin, and H_T is the total heat of reaction during cure. A large number of studies have been conducted on the cure kinetics of thermosetting polymers, and various kinetic models have been proposed in the literature [3-6]. Generally, researchers have studied the connection of the chemical reaction with the other independent variables, such as time and temperature. In general, kinetic models can be of phenomenological or mechanistic origin. A phenomenological model captures the main features of reaction kinetics, but ignores the details of how individual species react with one another. On the other hand, mechanistic models are obtained from the balance of chemical species involved in the reaction. Hence, they provide better prediction and interpretation. However, because thermosetting reactions are rather complex, mechanistic models usually require more kinetic parameters than phenomenological models. Therefore phenomenological models are more popular for thermosetting polymers. Although several simultaneous reactions occur during the curing process, simple models have been developed based on the assumption that only one chemical reaction can represent the whole cure process. Kamal and Sourour [3] have shown that the following model describes adequately the cure kinetics of epoxy resins:

$$\frac{d\alpha}{dt} = (K_1 + K_2 \cdot \alpha^m) \cdot (1 - \alpha)^n \quad (3)$$

$$K_{1,2} = k_{1,2} \exp(-E_{1,2}/T)$$

where K_1 and K_2 are rate constants with an Arrhenius type of dependence with temperature, and m and n are catalytic constants. Ruiz and Trochu [4] have also proposed a kinetic model based on Bailleul's model [5] considering the effects of glass transition temperature on the reaction rate. In this approach, the rate of conversion $d\alpha/dt$ is defined by the following set of equations:

$$\frac{d\alpha}{dt} = K_1(T) \cdot K_2(\alpha) \cdot K_3(T, \alpha) \cdot K_4(I_d) \quad (4a)$$

$$K_1(T) = k_{ref} \cdot \exp[-A \cdot (T_{ref} / T - 1)] \quad (4b)$$

$$K_2(\alpha) = \sum_{i=0}^s a_i \cdot \alpha^i \quad (4c)$$

$$K_3(T, \alpha) = (\alpha_{max} - \alpha)^n; \quad n = f(T) \quad (4d)$$

Recently, Riccardi et al. [6] have proposed a novel kinetic model to describe the cure of epoxy resins following a chemical mechanism. The following kinetic equations result from the proposed model:

$$\begin{aligned} \frac{d\beta}{dt} &= k_1 - (k_1 + k_2)\beta \\ \frac{d\alpha}{dt} &= k_3(1 - \alpha) i_0 \beta \end{aligned} \quad (5)$$

where i_0 is the initial concentration of initiator, and β the ratio between the initiator concentration in the active and inactive forms. Parameters k_1 and k_2 are Arrhenius functions of temperature. When the curing temperature reaches the glass transition temperature of the resin, a strong increase of the resin viscosity is observed. The reaction rate is not controlled anymore by the speed of the chemical reaction, but more by the speed of the diffusion of the reactants [7]. The mobility of the reactants is then restricted and limited by the reduction of the free volume. To consider the diffusion effect, Poehlein and al. [7] introduced a diffusion factor $f(\alpha)$ to correct the kinetic model predictions:

$$\left(\frac{d\alpha}{dt}\right)^{corrected} = \frac{d\alpha}{dt} \cdot f(\alpha); \quad f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (6)$$

where C is a constant, and α_c the critical conversion. For $\alpha \ll \alpha_c$, $f(\alpha)$ is equal to unity and the effect of diffusion is negligible. The selection of a proper catalyst percentage is a key factor here, because it allows reducing cycle time and thus increases productivity. Han and al. [8] proposed a standard kinetic model to consider the effect of the concentration of catalyst on the cure reaction. According to this model, the rate of conversion of the resin is directly proportional to the concentration of catalyst. Consequently, the Kamal-Sourour model of equation 3 can be expressed in the following way:

$$\frac{d\alpha}{dt} = [B](k'_1 + k'_2 \alpha^m) \cdot (1 - \alpha)^n \quad (7)$$

$$\text{with } \frac{k_1}{[B]} = k_1' \text{ and } \frac{k_2}{[B]} = k_2'$$

where $[B]$ is the concentration of catalyst, and k_1' and k_2' are normalized Arrhenius functions.

PolyKinetic is a freeware initially developed at the *Chaire sur les Composites à Hautes Performance (CCHP)* of *École Polytechnique de Montréal*. This software allows the modeling of resin cure kinetics from experimental results of differential scanning calorimetry. As illustrated in Fig. 1, the software is composed of three main modules: (1) processing of DSC data; (2) modeling of cure kinetics; and (3) prediction of resin cure under various experimental conditions. All the above kinetic models were included in **PolyKinetic** to provide an easy and robust solution and compare their respective performance to predict resin cure. **PolyKinetic** uses a least-square Levenberg-Marquardt non linear regression algorithm to calculate the unknown parameters of the kinetic models.

EXPERIMENTAL CURE ANALYSES

M-DSC data of an epoxy anhydride-based resin were collected for various heating rates (from 1 to 5°C/min) and different percentages of catalyst (from 1 to 2,5 parts per weight). These experimental data were entered into **PolyKinetic** and used to construct various kinetic models. Initially, a Kamal-Sourour model was created to fit DSC data. As can be seen in Fig. 2, reaction rates and degrees of conversions are well described by this phenomenological model with a minimum error at the end of the chemical reaction. Similar results were also obtained with Ruiz model with a slight improvement at the end of cure. The mechanistic model of Riccardi was then calculated to fit experimental data. As shown in Fig. 3 (a), an appropriate prediction of the degree of conversion is obtained with this approach, although an important error is observed at the end of the chemical reaction. To improve the predictions at the end of cure, the model of Riccardi was combined with the diffusion control equation (6) as depicted in Fig. 3 (b). Even if the use of a diffusion control equation improves the model predictions at the end of cure, it seems that the mechanistic model is not as well suited as Kamal-Sourour one to fit these experimental data.

The interest of having an accurate kinetic model lies in its capability to predict higher degrees of conversion for a given temperature cycle. To compare the predictions of different kinetics model, a new technique called *IsoConversion Map* [9] was proposed. This technique is based on the isoconversion methodology [10] that permits to compare dynamic and isothermal DSC data. As shown in Fig. 4, the *IsoConversion Map* consists of two sets of curves, one for constant heating rates and one for constant temperatures. To estimate the degree of conversion for a given temperature cycle consisting of heating rates and isothermal cures, the two set of curves are sequentially used (see example in Fig. 4). In this way, the resulting evolution of the degree of conversion is extracted directly from DSC data (i.e., without kinetic modeling). In this work, the *IsoConversion Map* methodology was applied to evaluate the experimental DSC data for a temperature cycle consisting of two heating rates followed by two isothermal cures at 80°C and 150°C respectively. Fig. 5 depicts a comparison of experimental cures obtained through the *IsoConversion Map* with Kamal-Sourour and Riccardi mechanistic models. It can be clearly observed that the prediction of Kamal-Sourour model is far from the experimental data, while the mechanistic model gives an accurate prediction. This shows that Riccardi's mechanistic model is

more appropriate to calculate the degree of conversion than other more standard phenomenological models.

RHEOLOGICAL STUDIES

To optimize the molding cycle in LCM manufacturing, the evolution of resin viscosity during the injection stage must be known with accuracy. Characterization and modeling of the viscosity of a non-reactive resin as a function of temperature follows a well known and relatively simple experimental procedure. In the case of reactive resins, rheological analyses are complex and less accurate. In this work, isothermal rheological analyses were carried out to characterize the complex viscosity evolution of an epoxy resin for various percentages of catalysts. The determination of the gelation point for thermoset resins is critical to evaluate the rate of polymerization and it is a key factor in process cycle optimization. The gel point is usually defined as the time at which the storage modulus exceeds the loss modulus (i.e., $\tan \delta = 1$), but this point corresponds to a high resin viscosity. In LCM process analysis, a processing gel time may be defined as the point at which the resin viscosity curve has a slope of 10% (see Fig. 6 (a)). This criterion results in a viscosity increment between 2 to 5 times from the initial value. At this point the resin will not flow under normal injection pressures. Fig. 6 (b) shows the extracted gel times from rheological data while applying the 10% slope criterion. The gel time can also be estimated from DSC data if a given degree of conversion is related to the resin gelation point. In this work, for the epoxy resin tested, a degree of conversion of 20% was considered at the gel point. For each dynamic DSC curve, the time at which the resin reaches 20% of conversion has been extracted and plotted in Fig. 7. As observed in the kinetic models presented before, at the beginning of the reaction the resin cure kinetics follows an Arrhenius type of temperature dependence. Therefore, the gel time can be evaluated by a time integral Arrhenius function as follows:

$$Gel\ time(T, t) = t_{ref} - \int_0^t \exp(-B \cdot (T_{ref} / T - 1)) \cdot dt \quad (8)$$

$$t_{ref} = C \cdot \exp(-D \cdot CatPhr) \quad (9)$$

where T_{ref} is a reference temperature, B , C and D are constants and t_{ref} a reference time function of the percentage of catalyst $CatPhr$ in the resin formulation. The parameters of the proposed gel time model were obtained from the experimental values extracted from dynamic DSC data (see Fig. 7). The gel time model fitted to dynamic DSC data was then used to predict the gel times during isothermal cures. The predictions of the proposed model were then compared to the experimental gel times extracted from rheological tests. As shown in Fig. 8, a good agreement is observed between the experimental rheological data and the model predictions. Therefore one may conclude that the proposed model is appropriate to predict processing gel times.

CONCLUDING REMARKS

In order to understand the impact of epoxy cure kinetics modeled by a mechanistic approach, a comparative study was conducted between the phenomenological and mechanistic models. Through the use of the *IsoConversion Map* technique, it has been observed that a mechanistic model is more accurate than phenomenological ones. A gel time model is also proposed to

calculate the allowable injection time directly from dynamic DSC data. The results of this model were compared to rheological data, and a good agreement could be observed between the two. All the above kinetic models were included in *PolyKinetic* freeware for easy and robust identification of resin kinetic parameters.

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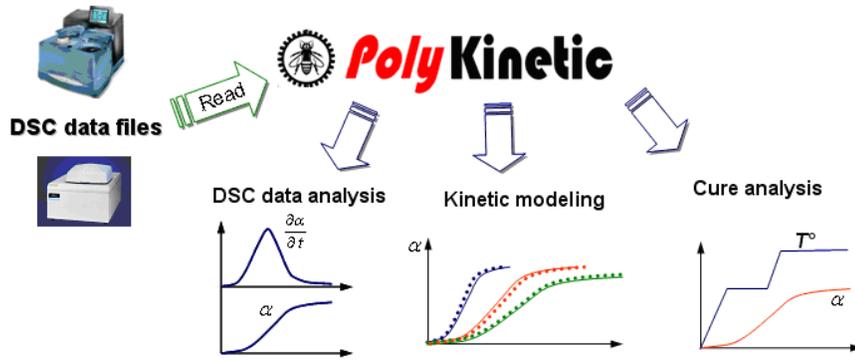


Figure 1. Schematic representation of *PolyKinetic* software modules

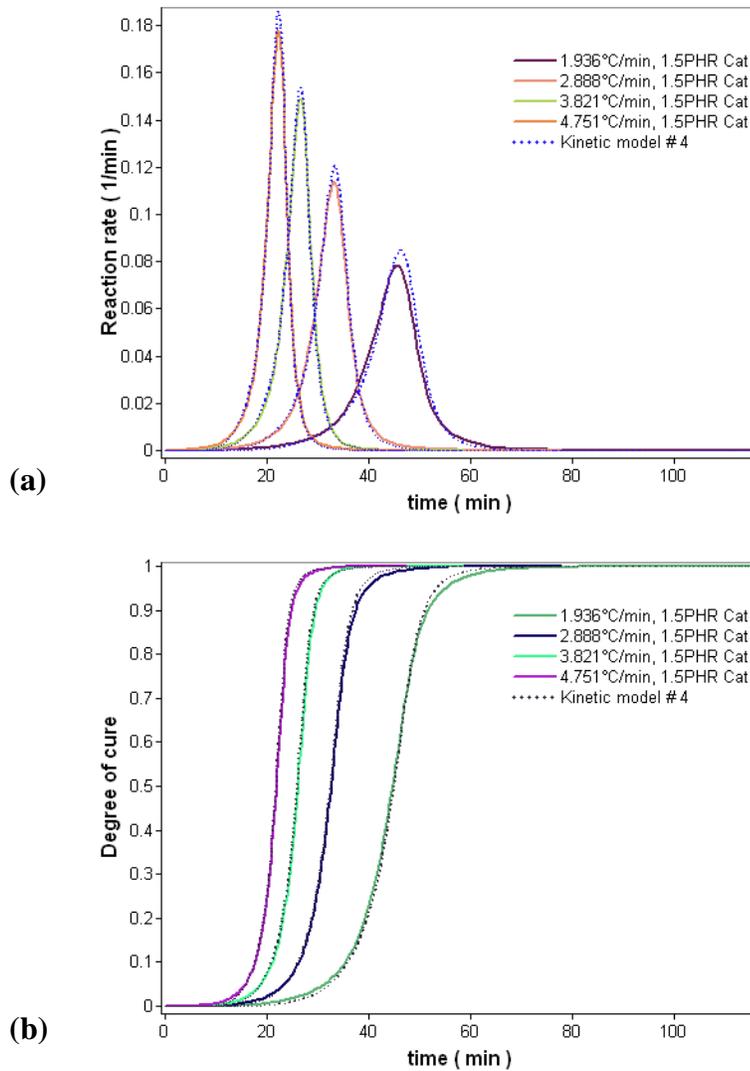


Figure 2. Evolution of reaction rates (a) and degrees of cure (b) and predictions of the fitted Kamal-Sourour model (kinetic model 4) for various heating rates

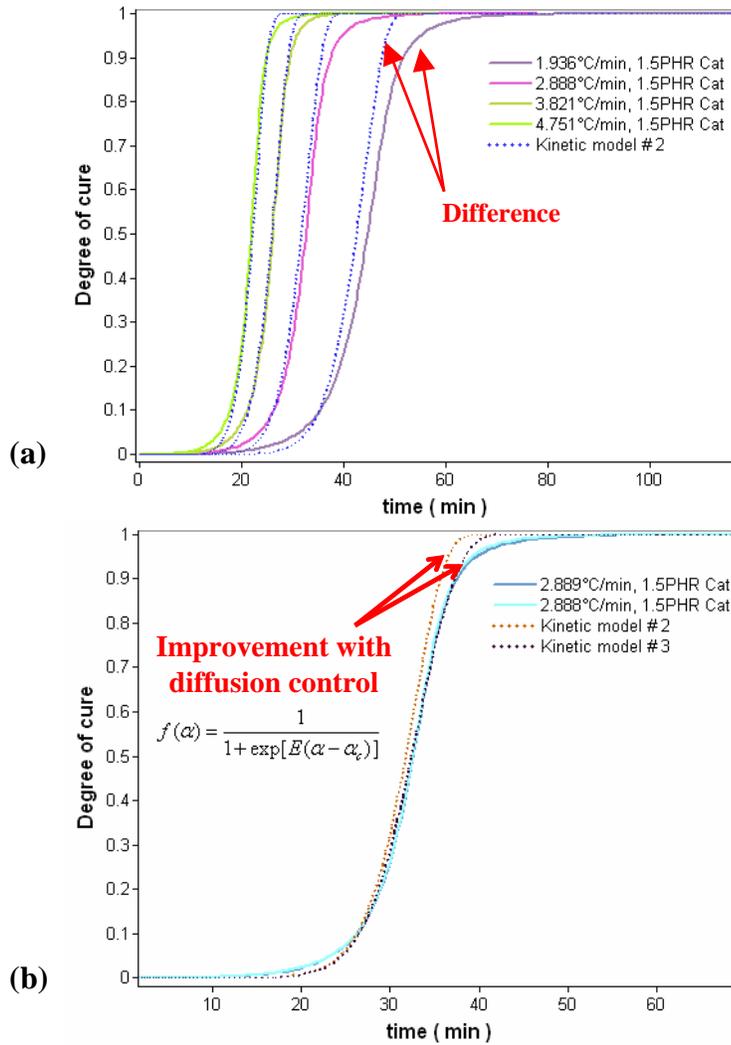


Figure 3. Degrees of cure versus time for different heating rates: a) comparison of experimental data with Riccardi's model predictions (kinetic model 2); b) improvement of Riccardi's model with diffusion control.

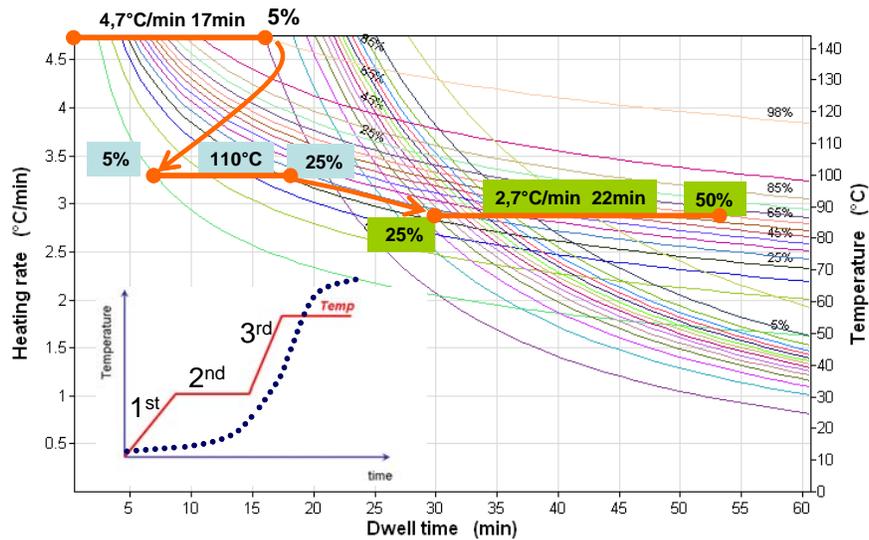


Figure 4. IsoConversion Map used to predict the degree of conversion.

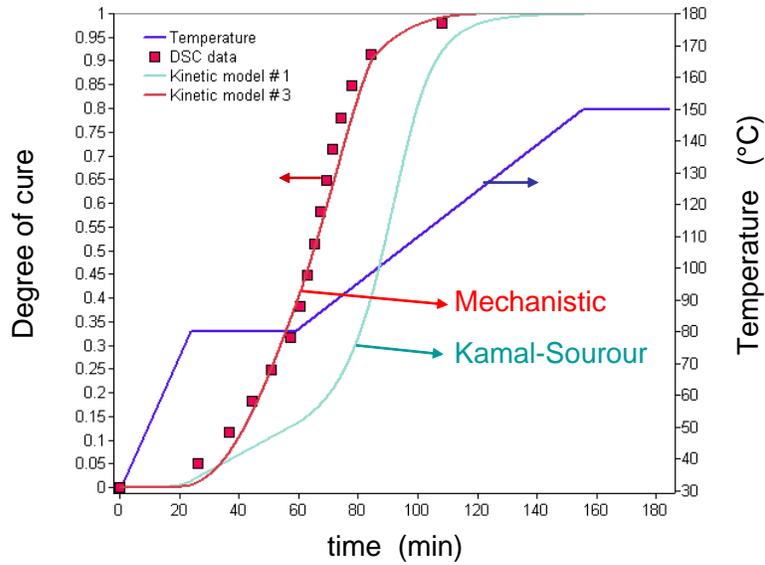


Figure 5. Comparison of experimental data obtained by isoconversion with Kamal-Sourour and Riccardi mechanistic models.

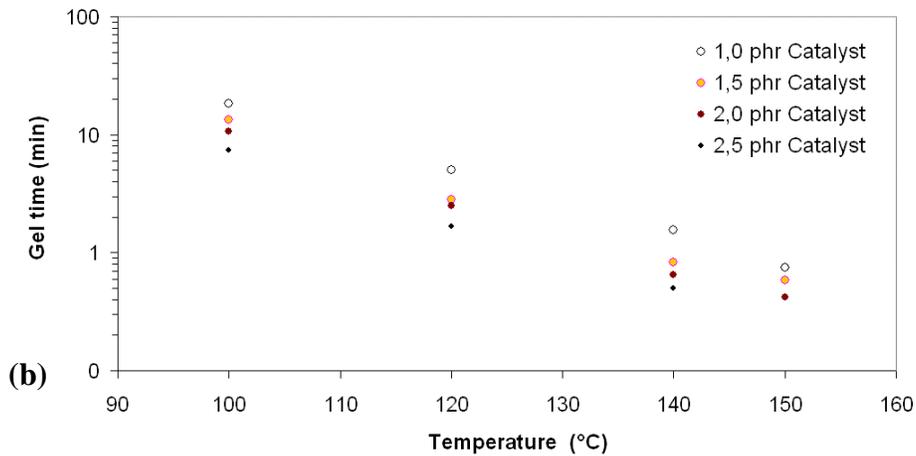
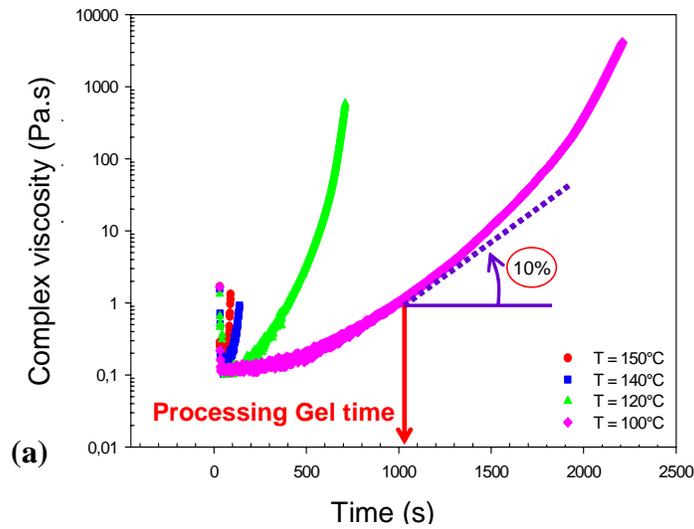


Figure 6. Rheological data for isothermal cures: a) viscosity evolution during cure; b) gel times for various isothermal temperatures and different percentages of catalyst.

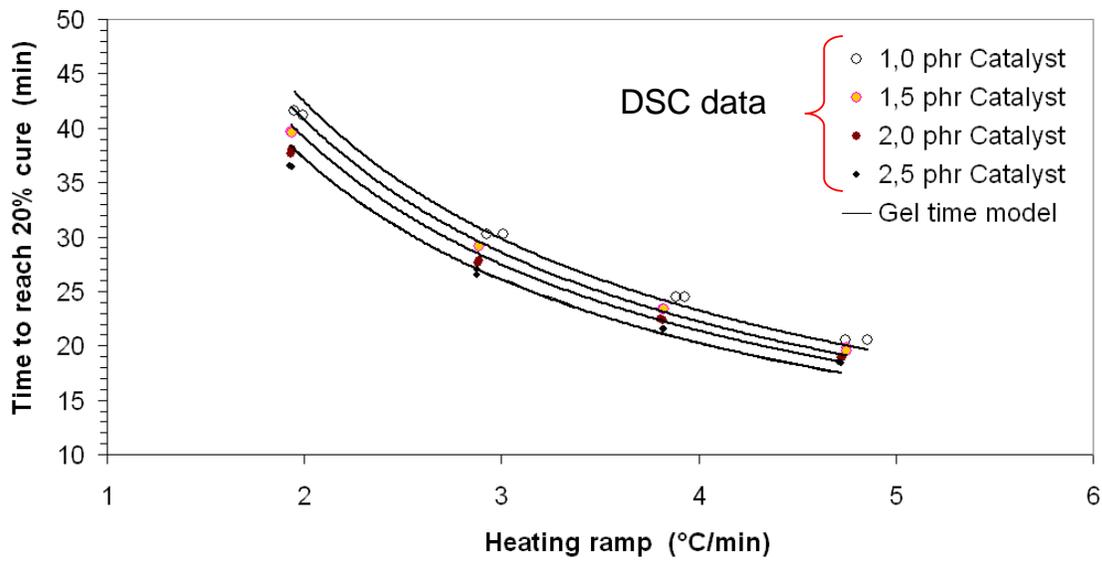


Figure 7. Gel times calculated for 20% of conversion from dynamic DSC data and predictions of the proposed gel time model.

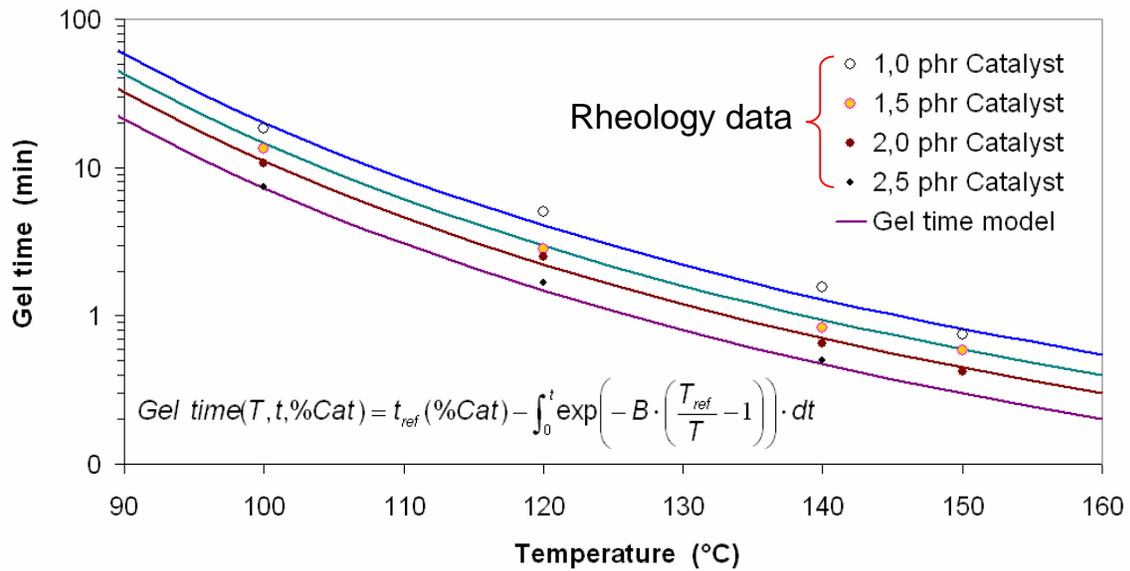


Figure 8. Comparison of experimental gel times from rheological data with predictions of the proposed gel time model for various percentages of catalyst.