

# NEW APPROACH TO CURE MODELING FOR STEREO LITHOGRAPHY

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## Introduction

Stereolithography systems convert a digital model from CAD (Computer Aided Design) to a plastic 3D model based on the principle of curing of polymer in the liquid state, through the action of visible, ultraviolet or infrared radiation. This system, consists of a computer, a vat containing a polymer, a moveable platform on which the model is built, a laser to irradiate and cure the polymer, and usually a dynamic mirror system to direct and focusing the laser beam. The computer uses the sliced model information (division of the CAD model into a predetermined set of cross sections or layers) to control the mirrors, which direct the laser beam over the polymer surface “printing” the cross section of one slice of the model, by curing of the layer. After drawing a layer, the platform dips into the polymer vat, leaving a thin film from which the next layer will be formed. The next layer is drawn after a wait period to recoat the surface of the previous layer.

The first materials used in Stereolithographic applications were unsaturated polyester resins to production of models and prototypes. The curing reaction of unsaturated polyester involves the formation of a three-dimensional network through of radical polymerization reaction. This reaction is characterized by two main events: gelation and vitrification <sup>1</sup>. Gelation corresponds to the incipient formation of an infinite molecular network, which is associated to an increase in viscosity and a decrease in processability. After gelation, as the reaction further progress, the amount of solid material increases and the polymer becomes more cross-linked increasing its stiffness and strength. Vitrification corresponds to the formation of a glassy solid material, due to an increase in both the cross-linking density and molecular weight of the polymer being cured.

The onset of vitrification occurs when the increasing glass transition temperature ( $T_g$ ) reaches the cure temperature ( $T_{cure}$ ). The rate of the reaction will undergo a significant decrease after vitrification and the reaction becomes very slow as it is controlled by the diffusion of the reactive species. The diffusion-controlled effect, that produces a slow down of the solidification process, will also determine the final degree of conversion.

## Phenomenological model

Many phenomenological models have been developed for the curing simulation of thermosensitive materials. These models assume that only one reaction can represent the whole cure process, and they can be expressed by the following equation <sup>2,3</sup> :

$$\frac{\partial \alpha}{\partial t} = K_c(T) \cdot f(\alpha) \quad (1)$$

where  $\partial \alpha / \partial t$  is the reaction rate,  $f(\alpha)$  is a function of conversion ( $\alpha$ ) and  $K_c(T)$  is the chemical controlled rate constant as function of the temperature. In the case of unsaturated polyester, the curing reaction is usually described through the Kamal model <sup>4,5</sup> :

$$\frac{\partial \alpha}{\partial t} = (k_{c1} + k_{c2} \alpha^m) \cdot (1 - \alpha)^n \quad (2)$$

where  $K_{c1}(T)$  and  $K_{c2}(T)$  are rate constants,  $m$  and  $n$  are constants, the sum of  $m$  and  $n$  represent the overall reaction order. The order of the reaction, according to its definition, indicates the number of atoms, molecules or reactive groups whose concentration determines the reaction rate. Rate constants are supposed to observe an Arrhenius law so can be expressed by the follow equation:

$$K_c(T) = k \exp\left(\frac{-E_A}{R(\Delta + T)}\right) \quad (3)$$

where  $k$  is the pre-exponential factor of the rate constant,  $E_A$  is the activation energy,  $R$  is the gas constant,  $\Delta + T$  is the absolute temperature. However, phenomenological models do not explicitly include the effects of resin composition on the rate of cure and, consequently, the kinetic parameters must be recalculated after each change in the resin formulation. Moreover, these models cannot predict the diffusion control effects after vitrification.

In this paper, a new kinetic model is proposed describing the major events occurring during the curing reaction of unsaturated polyester that will enable us to solve it by the following equations:

$$\frac{\partial \alpha}{\partial t} = \frac{1}{1 + \exp\left[\frac{\xi(a - \alpha_v)}{\xi}\right]} \cdot k \left( \frac{-E_a}{R(\Delta + T)} \right) \cdot \alpha^m \cdot (1 - \alpha)^n \quad (4)$$

where  $\xi$  correspond to the diffusion coefficient,  $\alpha_v$  is the critical value of fractional conversion corresponding to the onset of diffusion-controlled effects or vitrification over the curing reaction,  $a$ , is a constant and  $m$  and  $n$  are the reaction orders. All the kinetic parameters are functions of temperature.

The kinetic parameters of Eq. (3) were evaluated considering<sup>6</sup>:

- The maximum value of the reaction rate defined by:

$$\frac{d^2 \alpha}{dt^2} = 0 \Rightarrow \alpha_p = \frac{m}{m+n} \quad (5)$$

where  $\alpha_p$  is the fractional conversion that corresponds to the maximum value of the reaction rate.

- The overall reaction order is assumed to be two, thus expressing a second order mechanism:

$$m + n = 2 \quad (6)$$

- The value of the diffusion term is evaluated through the ratio of the experimental values of the reaction rate and those predicted by the kinetic model without diffusion effects.
- As the diffusion controlled regime is approached, the diffusion term decreases, reaching a value of 0.5, which corresponds to the instant where  $\alpha$  equals  $\alpha_p$ .

The diffusion coefficient,  $\xi$ , is determined by non linear regression.

## Experimental

### Material

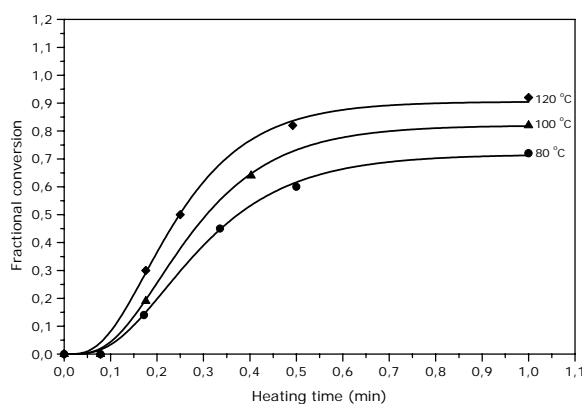
The material chosen for this study consists of an orthofalic unsaturated polyester pre-polymer in styrene monomer (33%). Samples containing 0.5 wt% of methyletilketona peroxide were cured at different Isothermal polymerizations temperatures: 120, 100 and 80°C.

### Method

A gel method to evaluate the fractional conversion through the reaction was used. The insoluble polymer was recovered by filtration at room temperature, and then the solid fraction was evaluated from the weight ratio of the insoluble polymer to the initial sample.

## Results and Discussion

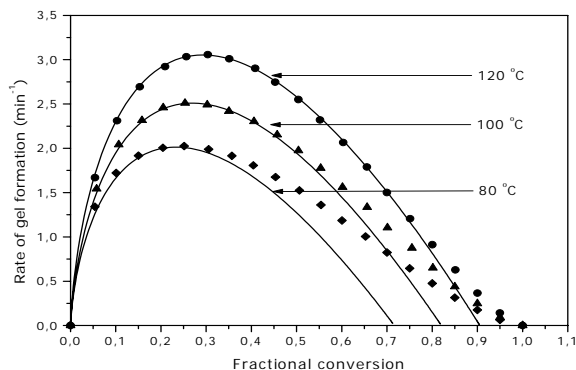
The isothermal curing profiles for the unsaturated polyester reaction measured by experimental method is shown in Figure 1, where the variation of the fractional conversion versus heating time, for different isothermal cure temperatures was investigated. The experimental data (discrete values), was fitted using a sigmoidal equation, because due to vitrification and diffusion limitations over the curing kinetics, the cure profile typically shows a characteristic sigmoidal shape profile. The continuous values obtained by the sigmoidal equation enable to determine the rate of gel formation and the kinetic parameters to model the cure behavior of the resin.



**Figure 1.** Variation of the fractional conversion vs. curing time for different isothermal curing temperatures.

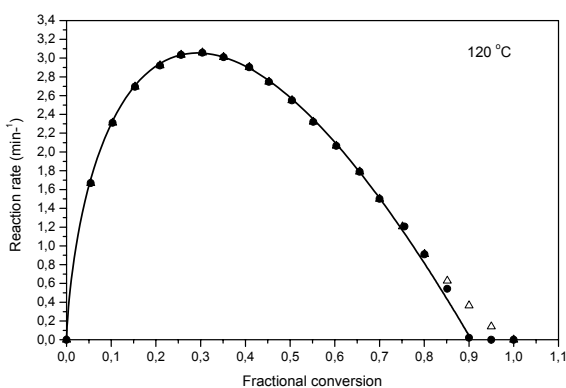
The cure profiles indicated above reveal that, after an induced period, the conversion rate increases rapidly, followed by a progressive slowing down until the cure profile reaches a plateau corresponding to the maximum value of the fractional conversion. This progressive slowing down is due to diffusion limitations on the mobility of the reacting species as the crosslink density increases. As the cure progresses, free volume is consumed by chemical reactions, decreasing the movement of the chains participating in network formation<sup>7</sup>. Consequently, the glass transition temperature  $T_g$  of the system rises, and when reaches the isothermal cure temperature  $T_{cure}$ , the system vitrifies. After vitrification the reaction is very slow as it becomes diffusion controlled (the diffusivity of the reactive groups is seriously reduced). A kinetic model was also proposed to simulate the effects of the temperature and to model curing reactions through the use by Eq. (2). However, as the reaction during its course becomes diffusion controlled, the experimental values of the rate of gel formation and fractional conversion are lower than those predicted by the kinetic model as shown in Figure 2.

From this figure it is possible to observe that both kinetic models describe very well the initial stages of the curing reaction, which correspond to a chemically controlled regime, though the Eq. (2) predicts higher values for the reaction rates in the late stages of the cure reaction. These deviations are particularly important for samples cured at low isothermal curing temperatures.



**Figure 2.** The lines correspond to the experimental values, while the symbols correspond to the values predicted by the equation 2.

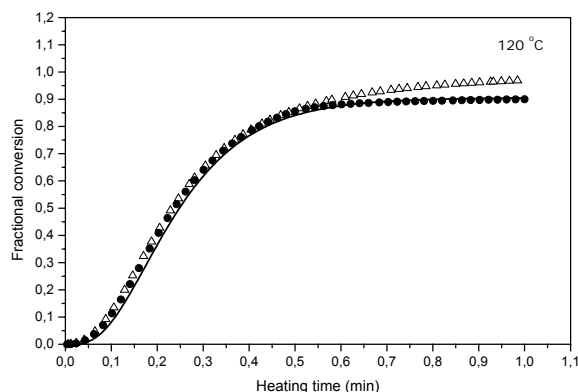
Fractional conversions were computer using the fourth-order Runge Kutta procedure, which numerically integrates Eq. (4). A comparison between experimental values and those predicted by both Eq. (2) and the proposed kinetic model (Eq. 4) for the variation of the rate of gel formation, as a function of fractional conversion is shown in Figure 3.



**Figure 3.** The lines correspond to the experimental values, while the discrete points (●) correspond to the values predicted by the Eq. (2) and the points (Δ) correspond to the values predicted by the kinetic model.

Figure 4 compares the fractional conversion values predicted by both the Eq. (2) and the proposed kinetic model with those obtained experimentally as a function of heating time.

A good agreement is obtained during the initial stages of the curing reaction, afterwards significant deviations are observed. However, a good correlation between experimental and predicted values is observed when the proposed model is used.

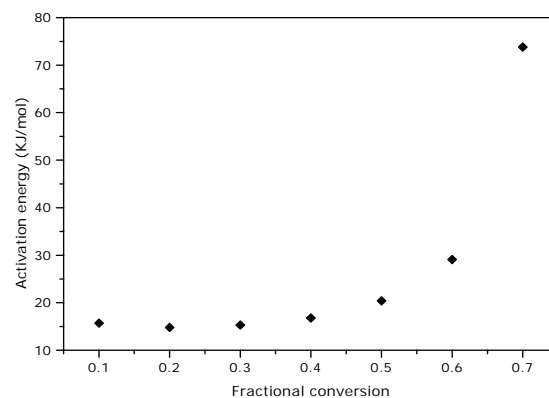


**Figure 4.** The lines correspond to the experimental values, while the discrete points (●) correspond to the values predicted by the Eq. (2) and the points (Δ) correspond to the values predicted by the kinetic model.

For the curing simulation the isoconversional adjustment of Eq. (3) has been used to compute the activation energy. In this case, a linear relation between the logarithm of the time needed to reach a specific value of  $\alpha$  and  $1/(\Delta + T)$  is used <sup>8</sup> :

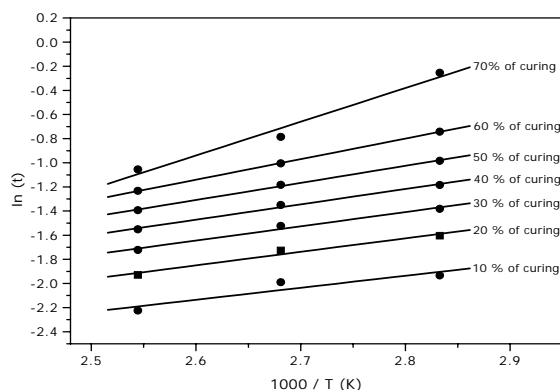
$$\ln t = \text{Constant } t + \frac{E_a}{R(\Delta + T)} \quad (7)$$

Figure 5 shows the variation of the activation energy as a function of fractional conversion. This figure shows that the activation energy remains almost constant during the initial stage of the polymerization reaction and starts to increase due to diffusion limitations for higher conversions.



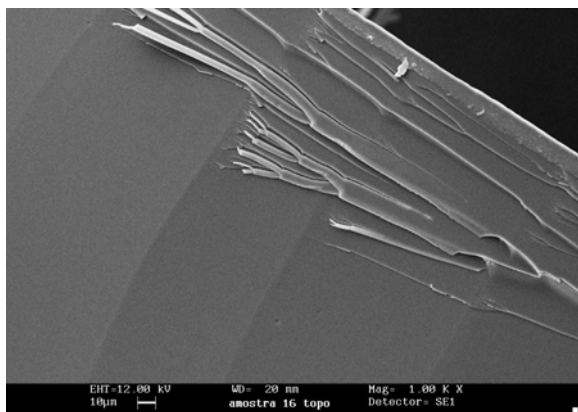
**Figure 5.** Variation of the activation energy with the fractional conversion

Figure 6 shows the variation of the activation energy as a function of temperature for several fractional conversions.



**Figure 6.** Variation of the activation energy.

Finally, Figure 7 shows MEV micrographs of the fractured surface for a sample containing 0.5 wt% of thermal-initiator and isothermally cured at 80°C.



**Figure 7.** MEV micrograph of the reacted sample.

The morphology suggests a flake-like compact microstructure, with microgel structure intimately overlapped via cross-linking.

## Conclusion

The aim of this work is to describe, in detail, factors concerning to the complex physical, chemical and mathematical theory associated with Stereolithographic process. The research described here was undertaken by using an unsaturated polyester resin. A new and more realistic model is proposed. This model describes the major events occurring during the reaction process, including a diffusion factor, showing an excellent agreement with experimental and predicted values.

The morphology of cured sample obtained is correlated with the theory associated with curing reaction. This kinetic model represents an important tool for the curing cycle design. As a result, the amount of experimentation can be minimized and eventually, this will lead to reduce manufacturing cost, shorter lead time and improve control and prediction of the properties of the finished product constructed by Stereolithography.

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## References

1. Li, S., Vatanparast, R. and Lemmetyinen, H., 2000. *Polymer*, 41, 5571.
2. Prime, R. B., 1997. *Thermal characterization of polymeric materials*, Vol. 2, ed. by A. Turi, Academic Press, London.
3. Popescu, C. and Segal E., 1998. *International Chemical Kinetic*, 30, 313.
4. Sourour, S. and Kamal M.R., 1972. *SPE ANTEC Tech. Pap.*, 18, 93.
5. Kamal M.R. and Ryan, M.E., 1989. *Fundamentals of computer modeling for polymer processing*, Edited by Tucker C.L., Hanser, Munich.
6. Bártolo, P.J., 2001. Optical approaches to macroscopic and microscopic engineering, Thesis (PhD), University of Reading, UK.
7. Chern, C.S. and Poehlein, G.W., 1978. *Polymer Eng. Sci.*, 27, 788.
8. Salla, J.M. and Ramis, X., 1995. Effect of the inhibition the curing of an unsaturated polyester resin, *Macromol. Rapid. Commun., Polym. Eng. Sci.*, 36, 3511-3521.