

Analysis of Kinetic Parameters of an Urethane–Acrylate Resin for Pultrusion Process

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Received 20 May 1999; accepted 16 October 1999

ABSTRACT: An urethane–acrylic resin for a pultrusion processing application was studied. The concentration of Perkadox 16 and methyl methacrylate (MMA) was changed in the formulation mixture. A calorimetric study was performed in a DSC equipment. Isothermal runs from 42 to 60°C were performed to obtain a kinetic model for the polymerization reaction. Conversion of vitrification as a function of temperature was determined and the total heat of reaction as a function of MMA content was also measured. A general kinetic model was applied. An autocatalytic model and master-curve approach with an order of reaction of $n + m = 2$ and an activation energy of 95.9 kJ/mol were found. By the application of the Kissinger model for dynamic runs, an activation energy of 88.8 kJ/mol was obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 355–362, 2000

Key words: urethane–acrylate, kinetics, modeling, pultrusion

INTRODUCTION

Most pultruded composite materials are produced using reinforcements with thermosetting resins and the final quality of the fiber-reinforced composite parts depends on the curing process. Many thermosetting resins are used in pultrusion technology: unsaturated polyester,^{1–5} epoxy resins with low initial viscosity,^{6,7} and phenolic resins.^{8,9} Acrylic resins have been recently introduced in this field, but few kinetic studies have been performed for application of this type of resin in pultrusion technology.

The reaction kinetics and the chemorheological properties of the thermosetting matrix dictate the

processing conditions. Therefore, knowledge of the rate of reaction is essential to control the manufacturing system evolution through the molding process.

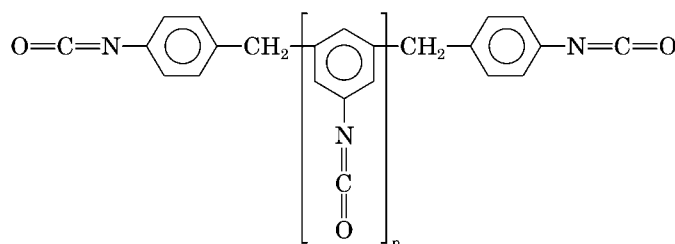
Han and Lee¹⁰ reviewed material characterization in liquid molding. They described different approaches of kinetic models from simple ones or general-purpose models to more complicated kinetic models dealing with a specific resin mechanism of reaction. A mechanistic analysis was also performed to analyze the reaction kinetics¹¹ of vinyl-terminated resins polymerized with similar monomers. Chemical initiation involves decomposition of unstable small molecules into two free radicals, which can rapidly react with the monomer to begin propagation of a polymer chain. Propagation reactions occur between a propagating free radical and a monomer molecule. Trans-

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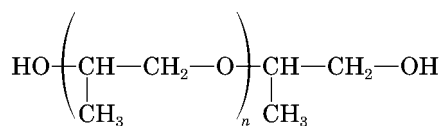
Journal of Applied Polymer Science, Vol. 77, 355–362 (2000)
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Table 1 Chemical Structures of the Used Compounds

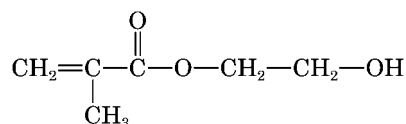
4,4'-methylenebis(phenyl isocyanate) mixture
when $n = 0$, $n = 1$, and $n = 2$



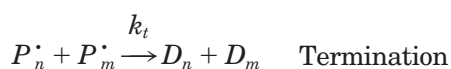
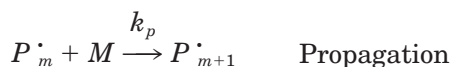
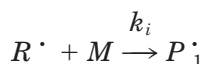
Polymethyl ethylene glycol
When $n = 0$



2-hydroxyethyl methacrylate



fer reactions may take place between a growing radical and initiator, monomer, solvent, polymer, and chain-transfer agent. Propagation and transfer reactions do not change the total number of radicals in the system and, therefore, usually do not influence the rate of polymerization. However, sometimes, a transfer radical has low activity and retardation is observed. Termination can occur by a bimolecular reaction between two polymer radicals or between a radical and a primary radical or a transfer radical. A simplified kinetic scheme for this free-radical chain-growth polymerization in the presence of an initiator can be represented as the following:



where I is the initiator; R , the initiated radical; P_n , the growing length of the polymer chain; D_n ,

the dead polymer of length n ; and M , the monomer.

However, it is very difficult to obtain the characteristics of the cure reactions of commercial thermosetting resins without a detailed and extensive chemical analysis, since commercial thermosetting materials are a complex mixture of resins, monomer, radical initiators, modifiers, and inhibitors. As a consequence, a general-purpose or phenomenological approach is usually applied to obtain the kinetic model useful for general pultrusion processing design.

In the present study, a differential scanning calorimeter was used to investigate the influence of different quantities of initiator and monomer on the curing of a commercial urethane-acrylate resin as well as to develop a general-purpose kinetic model for pultrusion application of these kinds of materials.

EXPERIMENTAL

A commercial grade of urethane-acrylate (Modar 865, Ashland Chemical), proposed for pultruded profile application, was used for the study. The resin basically is a reaction product of a reaction between the 4,4'-methylenebis(phenyl isocyanate) monomer, dimer, and trimer, prereacted with 2-hydroxyethyl methacrylate and poly(methyl ethylene glycol). Gel permeation chromatography (GPC) was used to determine the molecular weight using the PS standard ($M_n = 1607$

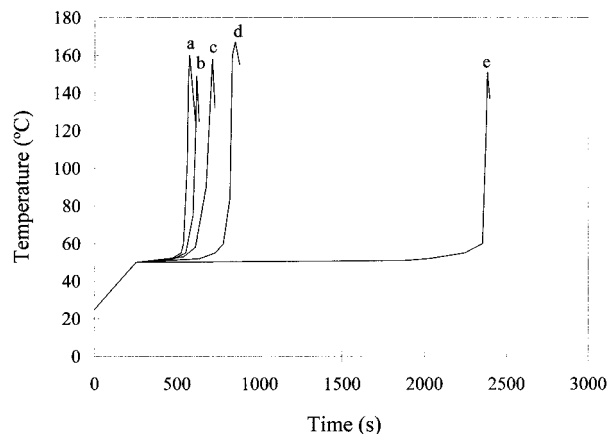


Figure 1 Polymerization temperature as a function of time for 52 wt % of MMA in urethane-acrylic resin for different contents of the initiator, Percadox 16: (a) 4 phr; (b) 3.2 phr; (c) 2.4 phr; (d) 1.6 phr; (e) 0.8 phr.

and $M_w = 8619$). GPC was performed in a Waters device at 30°C with a refractive index detector. THF was used as a solvent at a 1 ml/min flowing rate. Columns of 500 Å were used. Table I shows the chemical structure of the used compounds.

The supplied resin contained 52 wt % methyl methacrylate (MMA). To prevent MMA volatilization during curing, (bis-4-*tert*-butylcyclohexyl)-peroxydicarbonate (Percadox 16, Akzo), with an activation temperature of 40°C, was used.

With the aim to analyze the influence of the MMA amount in the polymerization of the resin, dynamic DSC measurements were conducted for several MMA amounts. For controlling the MMA content, as the raw resin had a content of 52 wt % of MMA, it was necessary to evaporate the MMA under a vacuum at room temperature before the addition of the initiator.

The heat of reaction was measured using a Perkin-Elmer DSC-7, with a nitrogen flux. The sample weights were between 10 and 15 mg. Dynamic experiments were conducted at different heating rates (0.5–20°C/min) from 35 to 180°C. Isothermal tests were performed at temperatures ranging from 42 to 60°C. The residual heat of reaction was also measured under a heating rate of 10°C/min. The total enthalpy used was taken as the sum of the heat generated during the isothermal cure and that for the corresponding residual heat. The induction time was taken as that corresponding to the beginning point of the cure reaction at a given isothermal condition. Conversion was defined for each cure temperature as the enthalpy at a given time divided by the total enthalpy.

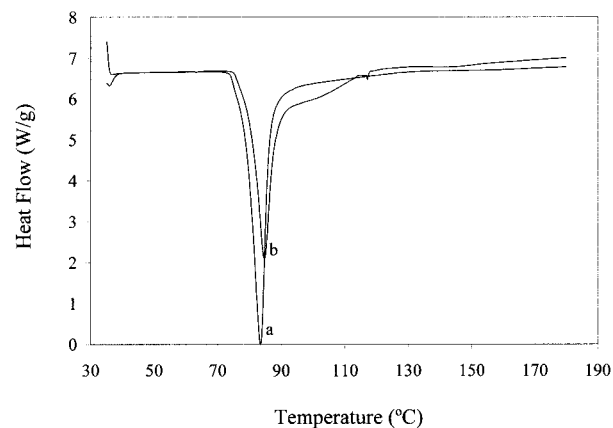


Figure 2 Dynamic runs in DSC for different pans: (a) pan without holes; (b) pan with holes.

RESULTS AND DISCUSSION

To study the more suitable formulation, the quantity of the initiator Percadox 16 was varied from 0.8 to 4 phr. The maximum temperature through polymerization was measured using a thermocouple. Results shown in Figure 1 allowed us to use 1.6 phr of the initiator for polymerization of the resin because higher contents did not substantially modify the time to gelation and so the lubrication network effects could be avoided.

As test-accuracy problems were observed for hermetic aluminum pans, ones with holes were used. Figure 2 reports the dynamic scans obtained during curing of the reactive mixture (resin + MMA + initiator) for both types of pans. For hermetic pans, a slight delay in polymerization as well as a shoulder in the high-temperature side of

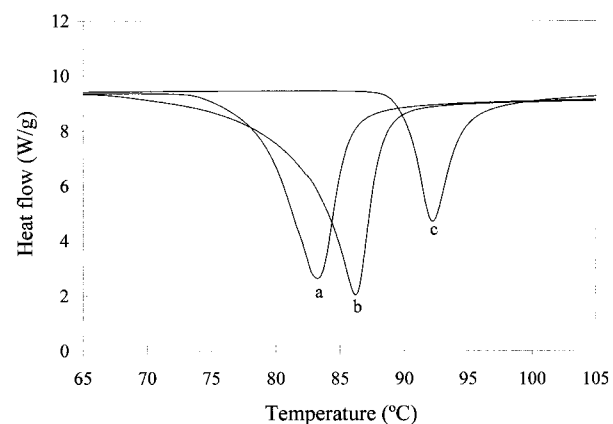


Figure 3 Dynamic runs in DSC of three MMA weight contents in the reactive mixture: (a) 51.2% wt; (b) 73.0% wt; (c) 20.2% wt.

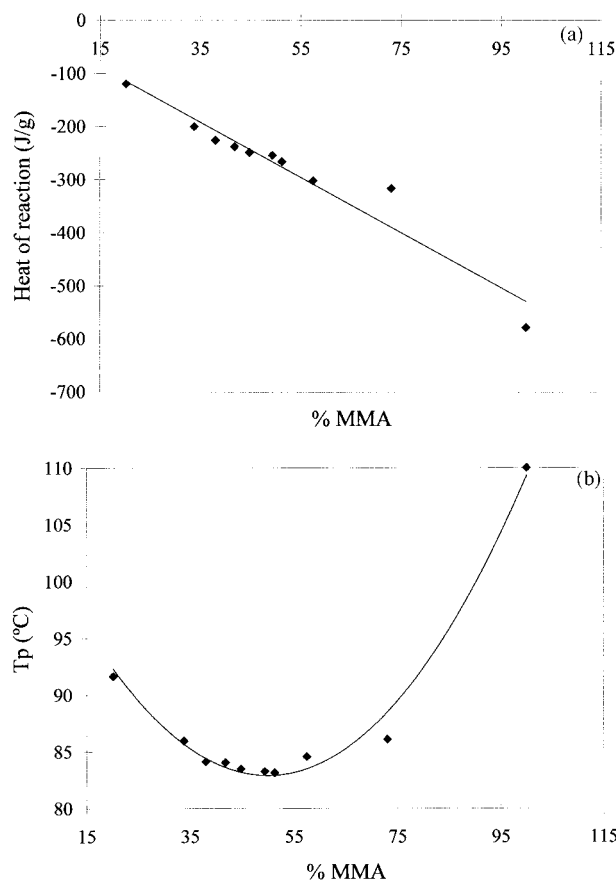


Figure 4 DSC results of a reactive mixture with different contents of MMA: (a) heat of polymerization; (b) temperature of exothermic peak, T_p .

the exothermic peak were observed, possibly due to the trapped oxygen in the pan.

Figure 3 shows calorimetric dynamic scans for three MMA weight contents in the reactive mixture. As inferred from Figure 4(a), the polymerization enthalpy data as a function of the MMA content were fitted by a straight line. The heat of polymerization data for MMA pure was taken from the literature¹² and it is included in Figure 4(a). The heat of reaction increases with the content of MMA, indicating that the heat of reaction depends on the quantity of the double bonds. The maximum temperature of the exothermic peak (T_p) is also shown in Figure 4(b). The peak shifts to higher temperatures for a low content of resin or a low content of monomer, because, in both cases, the reaction between the resin and monomer is less probable and it needs more activation energy to occur.

In the following, the only mixture analyzed was that containing 52 wt % of MMA (commercial

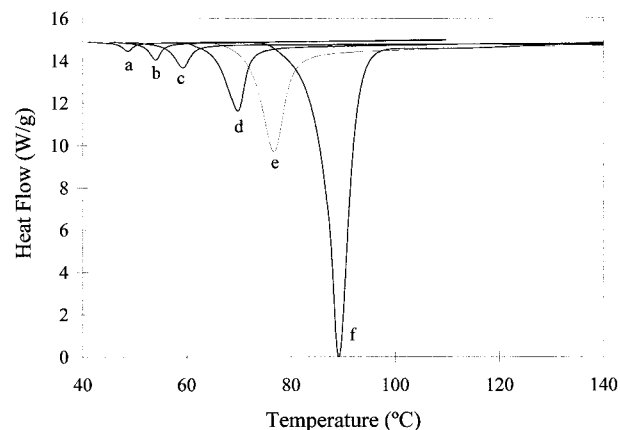


Figure 5 Flow evolved during curing reaction in DSC experiments for different heating rates: (a) 0.5 °C/min; (b) 1 °C/min; (c) 2 °C/min; (d) 4 °C/min; (e) 10 °C/min; (f) 20 °C/min.

resin). Figure 5 shows the heat flow evolved during cure at different heating rates. For constant heating-rate experiments, the extent of cure at the exothermic peak is a constant, although the temperature at which the exothermic peak occurs depends on the heating rate. The relation between the heating rate and the exothermic peak temperature was expressed by Kissinger.¹³ The plot of $\ln(\text{heat rate})$ versus $(1/T_p)$ is shown in Figure 6; the apparent activation energy value calculated is 88.8 kJ/mol.

Figure 7 gives plots of conversion versus time minus the induction time ($t - t_i$) for the isothermal thermograms. Final conversion increased as the temperature increased. This behavior is reflected in Figure 8. The cure reactions stopped at each temperature before complete conversion was

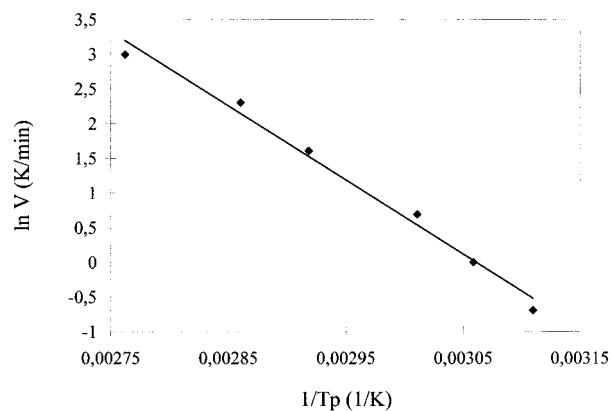


Figure 6 Kissinger's graphic for the dynamic runs of DSC experiments.

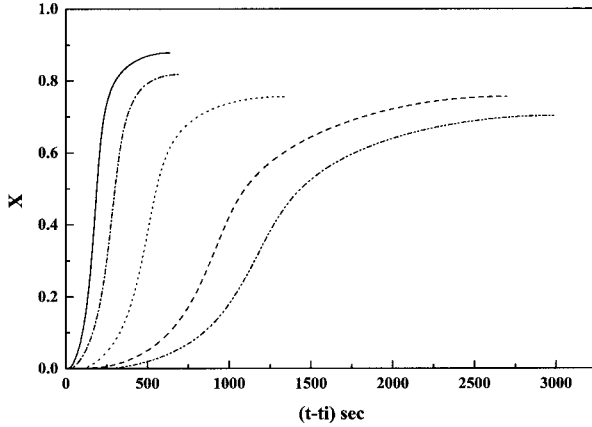


Figure 7 Conversion as a function of time ($t - t_i$) for isothermal runs of DSC at different temperatures: (---) 42°C; (-·-·-) 45°C; (·····) 50°C; (- - - -) 55°C; (—) 60°C.

achieved. Although after vitrification a diffusion-controlled reaction can occur, conversion to vitrification was taken as corresponding to the achieved maximum conversion, x_f , for each cure temperature.

By taking into account vitrification, the phenomenological autocatalytic model proposed by Kamal and Sourour^{14,15} for the polymerization of thermosetting resins is the following:

$$\frac{dx}{dt} = kx^m(1-x)^n \quad (1)$$

where x is the conversion; t , the time; and k , the constant rate. Equation (1) can be written as

$$\frac{dx}{dt} = k \frac{x^m}{x_f} (1-x)^n \quad (2)$$

As shown for other vinyl-terminated resins,¹⁶ by assuming an overall reaction order equal to 2 over all the cure temperature range, and integrating eq. (2) with respect to real time, $t - t_i$, one obtains

$$\frac{1}{(1-m)} \left(\frac{x_f}{x} - 1 \right)^{m-1} = k(t - t_i) \quad (3)$$

t_i being the induction time.

By defining 50°C as a reference temperature, and using the Arrhenius expression for the reaction rate constant,

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (4)$$

All the conversion curves can be referred to the reference conversion curve versus time by a defining time-shift factor, A_t , as

$$\frac{(t - t_i)}{(t_{\text{ref}} - t_{i\text{ref}})} = A_t = \exp\left(\frac{E}{R\Delta T}\right) \quad (5)$$

where $1/\Delta T = (1/T - 1/T_{\text{ref}})$.

Figure 9 presents a plot of $\ln A_t$ versus $1/\Delta T$. From the straight line obtained, the activation energy was evaluated as 95.9 kJ/mol. This activation energy is close to the one obtained in the application of Kissinger equation for dynamic runs (88.8 kJ/mol).

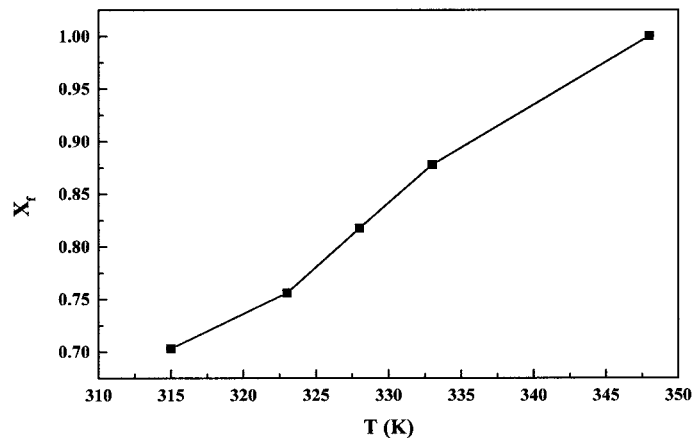


Figure 8 Final experimental conversion versus temperature.

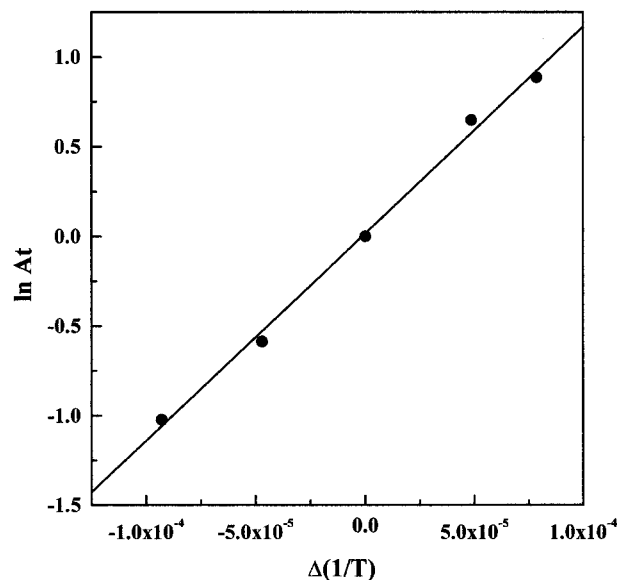


Figure 9 Shift-factor temperature in function of temperature. The solid line was made using a linear fit.

For building a master curve, eq. (3) can be modified by using the time-shift factor:

$$\ln\left(\frac{x_f}{x} - 1\right) = \left(\frac{1}{m - 1}\right)\ln[(1 - m)kA_t] + \frac{1}{m - 1} \ln \frac{(t - t_i)}{A_t} \quad (6)$$

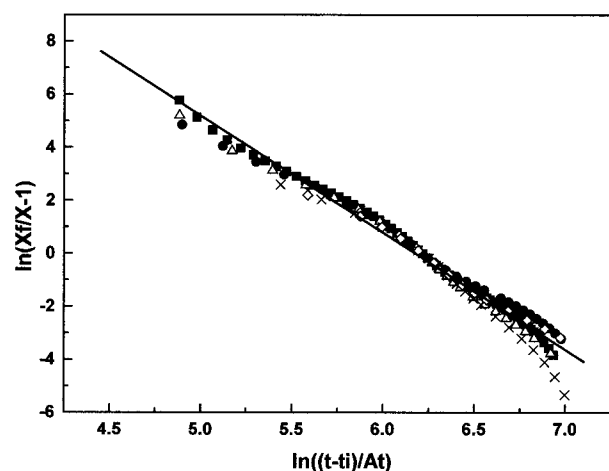


Figure 10 Master curve: Logarithmic graphic of the normalized conversion versus reduced time at various isothermal temperatures: (■) 42°C; (●) 45°C; (△) 50°C; (×) 55°C; (◇) 60°C. The solid line was made using a linear fit.

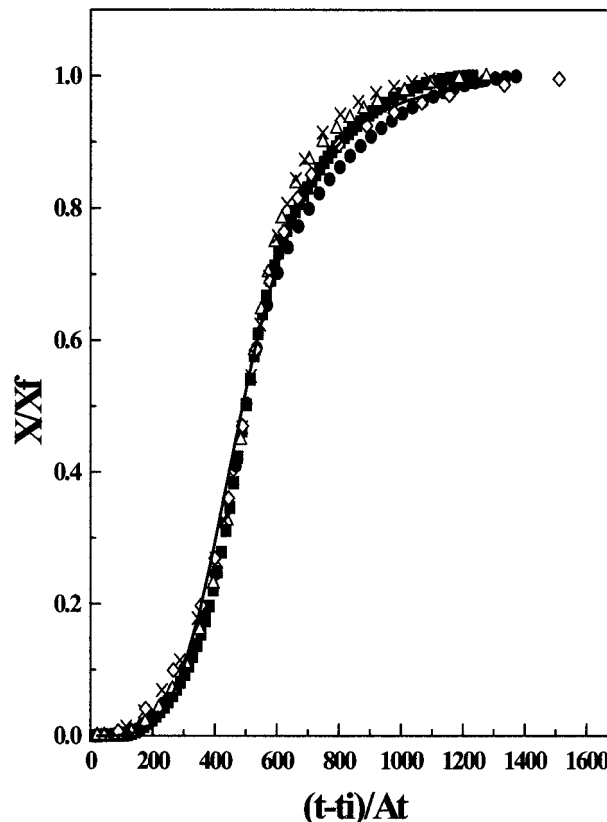


Figure 11 Normalized conversion versus reduced time for various temperatures: (■) 42°C; (●) 45°C; (△) 50°C; (×) 55°C; (◇) 60°C. The solid line was made using the kinetic parameters estimated.

The variation of $\ln(x_f/x - 1)$ against $\ln[(t - t_i)/A_t]$ is depicted in Figure 10. The experimental results were fitted to a straight line up to conversions in the vitrification region. Taking into account the Arrhenius approach, k_0 and m were calculated as follows:

$$k_0 = 2.965 \times 10^{13} \text{ s}^{-1}, \quad m = 0.773 \quad \text{and} \quad n = 1.227$$

The values obtained are similar to those reported in the literature survey¹⁶ for other similar vinyl-terminated resins.

When normalized conversion, x/x_f , was plotted against reduced time, $(t - t_i)/A_t$ (Fig. 11), using the kinetic parameters estimated above, a good correlation between the experimental data and theoretical findings was obtained, meaning that the reaction mechanism does not change regardless of the isothermal cure conditions used.

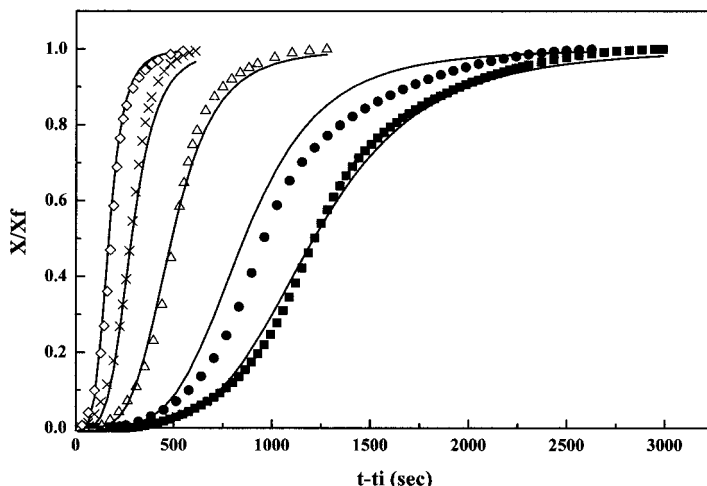


Figure 12 Normalized conversion versus real time for various temperatures: (■) 42°C; (●) 45°C; (△) 50°C; (×) 55°C; (◇) 60°C. The solid lines were made using the kinetic parameters estimated for each temperature.

The good correlation can also be seen when plotting for each cure temperature the normalized conversion versus the real time, $t - t_i$, as reported in Figure 12.

Figure 13 gives plots of the rate of cure versus the real time at various isothermal cure temperatures. Some deviation from the modeling to the experimental data was observed after microgelation had occurred. However, the small deviations observed in Figure 12 (normalized conversion) and in Figure 13 (reaction rate) seem to indicate that it becomes necessary to consider phenomena

other than chemical reactions occurring through curing.

As is well known for unsaturated polyester resins cured with a monomer such as styrene (or MMA),¹⁷ gelation occurs at low conversions because microgels appear at the early stages of curing. Polymerization after microgelation in those vinyl-terminated resins follows by means of inter- and intramolecular reactions within those microgels. This possibility can also be tested for the analyzed reactive mixture. Thus, formation of those microgels allows us to consider two steps for

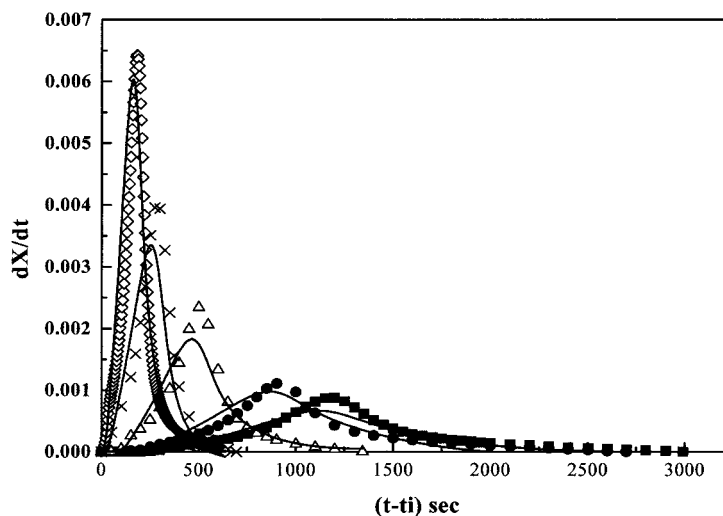


Figure 13 Rate of cure versus real time for various temperatures: (■) 42°C; (●) 45°C; (△) 50°C; (×) 55°C; (◇) 60°C. The solid lines were made using the kinetic parameters estimated.

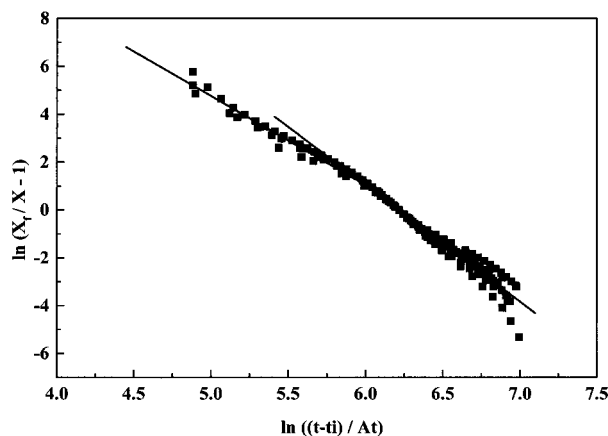


Figure 14 Master curve: Converted conversion versus reduced time for two cure paths.

polymerization up to vitrification: one prior to the microgelation region and the other after that region. In this work, $x \approx 0.20$ was taken as an arbitrary conversion in the transition zone, because a slight variation in the slope of $\ln(x_i/x - 1)$ can be detected in Figure 10. Therefore, the experimental data were computed again for the determination of the kinetic parameters in both regions. Figure 14 presents the findings so attained. From the straight lines plotted in this figure, we obtained $k_0 = 2.06 \times 10^{13}$, $m_1 = 0.717$ ($n_1 = 1.283$), and $Ea_1 = 95.9$ kJ/mol for the first region and $k_0 = 3.13 \times 10^{13}$, $m_2 = 0.792$ ($n_2 = 1.208$), and $Ea_2 = 95.9$ kJ/mol for the region between microgelation and vitrification. The lower value of the reaction rate constant before microgelation is possibly a consequence that, for this region, the linear radicals in formation have a higher probability to find other growing radicals, while in the second region, via inter- and intramolecular reactions, the propagation rate becomes essentially the same¹¹ and termination is not favored because of the lower mobility of the polymer chains.

CONCLUSIONS

A study of the kinetic parameters of a commercial thermosetting resin suitable for pultrusion processing was performed. The urethane-acrylic

resin kinetic model was not found in the literature of this kind of material. However, it is an important equation necessary for developing a processing model.

The resin formulation was optimized by study of the quantity of the initiator and the MMA content. The activation energy of the polymerization process as well as the order of the reaction was obtained by thermal measurements. An autocatalytic model was applied and it fitted the experimental results.

It was shown that for conversion higher than 0.20 microgelation produces a delay in the reaction rate. Before and after microgelation occurs, the activation energy is the same (95.9 kJ/mol); however, the preexponential factor and the m_i and n_i values slightly vary from low to higher conversions. This fact can be a consequence of some changes that occurred in the radicals' growing process through polymerization of these resins.

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