Curing Kinetics of Divinyl Ester Resins with Styrene

MARÍA L. AUAD, MIRTA I. ARANGUREN, GUILLERMO ELIÇABE, JULIO BORRAJO

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata,
National Research Council (CONICET), Avenue Juan B. Justo 4302, (7600) Mar del Plata, Argentina

ABSTRACT: The curing reaction of a divinyl ester resin with different proportions of styrene—4, 20, and 40% by weight—was investigated by differential scanning calorimetry (DSC) using isothermal and dynamic modes. The different constraints on the reaction rate was globally considered, taken the reaction as divided in two regimens: below the vitrification regimen and during the vitrification regimen. Below the vitrification regimen, the autocatalytic model developed by Kamal was used to perform the analysis of the curing kinetics of divinyl ester resin with styrene. Experimental data from dynamic and isothermic runs, at a fixed composition, were simultaneously considered, while the actual temperature records (measured during the DSC runs) were also taken into account. The adjusted kinetic parameters took into account the gel effect on the radicals' termination rate and the structure constraints on the reactivity of pendant vinyls groups, present during this stage. During the vitrification stage, the diffusion control due to the low mobility of the reactive groups and molecules was incorporated into the overall rate constant according to the Rabinowitch model, which considers the two regimen contributions to the overall reaction rate kinetic. The Vogel–Fulcher relationship was adopted to express the temperature dependence of the rate constant during the vitrification stage. The method presented here has been satisfactorily applied to dynamic and isothermal curing reactions, allowing a simple and general kinetic expression useful in the design, optimization, and control of the processing of composites based on these thermoset polymers to be obtained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1044–1053, 1999

Key words: divinyl ester resins; styrene copolymers; curing kinetics; diffusion control

INTRODUCTION

Multifunctional vinyl ester resins and their copolymers with vinyl monomers are widely used in industrial and biomedical applications.[1,2] The conjunction of properties, such as excellent resistance to corrosion and solvents, good adhesion, reasonably high glass transition, and adequate electrical properties, are the reasons why these materials have found a wide range of applications such as surface coating varnishes, adhesives, printed circuit board coatings, aircraft, ships, housing, ultraviolet cured inks, medical applications in dental and bone cements, and so on.

The divinyl ester resins (DVER) (diacrylated diglicidyl ether of bisphenol A) used in this work have complete miscibility in the styrene (S) comonomer. Their reacted mixtures show modulus and glass transition temperatures in the range of those of the pure homopolymers.[3]

A wide range of copolymer networks can be made synthetically, leading to materials with different final properties, such as modulus from 2.5 to 3 GPa, glass transition temperatures between 106 and 173°C, and consequently different feasibility for structural modification.[3]

These materials have been the subject of a number of studies due to their poor fracture

toughness, thus, tougher resins have been developed by introducing different elastomeric additives in the formulations, such as carboxyl-terminated butadiene-acrylonitrile (CTBN), epoxy-terminated butadiene-acrylonitrile (ETBN), vinyl-terminated butadiene-acrylonitrile (VTBN),[4,5] or polybutadienes.[6]

The processing conditions of these materials are posed by their chemorheological properties and by the heat transfer during the particular manufacturing process. Therefore, to control the rate of heat evolution and temperature variation during the processing, it is essential to know how the reaction rate and the heat evolved during curing depend on the particular formulation and processing variables selected.

Differential scanning calorimetry (DSC) is a usual method to study the polymerization kinetics of thermosetting resins.[7] The basic assumption realized when calorimetric DSC data are used to calculate the molar conversion is that the heat evolved during the curing reaction is proportional to the extent of reaction. This means that the molar heat of bond formation is constant throughout the curing reaction. As a consequence, the partial heat of polymerization at any reaction time depends only on the molar number of bonds formed up to that time. This is equivalent to saying that the different bonds formed in the copolymerization have the same heat of formation, which is a correct assumption in the special case of a perfectly alternate copolymerization, but is not valid particularly in the divinyl ester resin with styrene (DVER-S) system. Consequently, the calorimetric conversion, calculated as usually from the evolved heat measured with a DSC apparatus, may be different from the molar conversion, and the kinetic analysis from calorimetric data is not possible. A simple model, based in the free radical copolymerization theory of Mayo and Lewis was developed for this system,[8] and both conversions showed a very good match for all the comonomer concentrations.

As in the case of unsaturated polyester resins (UPR), the kinetic of curing of DVER is very complex because many processes occur simultaneously. Detailed mechanistic analysis has been used to explain the reaction of UPR and DVER.[9,10] On the other hand, a phenomenological analysis usually allows obtaining a simplified expression for the reaction rate that does not require the complete understanding of the curing chemistry,[11] unfortunately accompanied by the unavoidable loss of knowledge about the path of reaction.

During the curing of a UPR or a DVER, diffusion constraints present at different stages of the reaction can become the controlling mechanism of the reaction rate. At the early stage of the cure reaction this control manifests itself by an increase in the reaction rate due to the diffusion-controlled termination (the Trommsdorff or gel effect). This initial increment is followed by a continuous diminution due to a specific diffusion control caused by topological constraints produced by the poor accessibility of pendant reactive groups present in the sol molecules or in the gel structure.[12–15] These two effects are present in parallel; the first one is dominant in the early stage of the reaction at very low conversions, the second one sets in at low conversions and remains throughout the cure reaction with increasing influence. At high conversions, an additional overall diffusion control will be present if the reaction temperature is lower than the glass transition temperature of the completely cured thermoset. When the T_g of the reacting system approaches the cure temperature, T_c, many crosslinking reactions become controlled by non-specific diffusion that conduce to a diminished segmental mobility and, as a consequence, the global reaction rate decreases sharply. The reaction still proceeds below the T_g but becomes slow and eventually stops.[14,16]

In the present work, a phenomenological expression for the reaction rate is proposed. The experimental kinetic results measured in dynamic or isothermal DSC runs, with cure temperatures higher than the glass transition temperature of the reactive system, were fitted with the empirical Kamal kinetic model.[17,18] The adjusted rate constants take into account the Trommsdorff effect present at the early stage of the reaction as well as the specific diffusion control determined by the topological structure of the reactive functional groups present in a wide distribution of molecular sizes in the sol and in the gel substructures.

If the cure temperature is lower than the glass transition temperature of the completely cured system, the third overall diffusion control will be present at high conversions when the increasing T_g of the reacting system approaches the cure temperature, T_c. As a consequence, the global reaction rate decreases in several orders of magnitude. To include this additional diffusion control in the kinetic analysis, the "overall" constant of the reaction is calculated using the Rabinowitch[19] eq., where this nonspecific diffusion contribution to the global kinetic constant is coupled

with that calculated previously with the Kamal model.

Thus, the specific goals of this work can be summarized as follows:

1. To study the effect of the composition of the reactive system on the heat evolved during curing and to find the kinetics of the reaction DVER-S, using benzoyl peroxide as initiator.
2. To include the diffusion control caused by the vitrification on the overall reaction rate.

To achieve these objectives, isothermal and dynamic DSC measurements were used to evaluate the kinetic parameters of Kamal's model, which has proved to be able to represent the kinetics of many others similar free-radical crosslinking systems.[20–23]

Since the reaction is highly exothermic, and this feature affects the DSC temperature control, isothermal runs were not truly isothermic, and dynamic runs did not show a linear temperature ramp at the reaction peak. For this reason, experimental data included time, conversion, and temperature records.

Finally, the Rabinowitch model was used to represent the effect of the overall diffusion constraint caused by the vitrification during isothermal cure at T_c less than T_g. The overall crosslinking reaction kinetics of DVER-S systems with different compositions and temperatures were analyzed in all ranges of conversions by combining both complementary kinetic models.

Theoretical Analysis

Different approaches to obtain reaction kinetic models are usually carried out in order to represent the experimental results obtained from any of the different thermal analysis techniques.[24–26] In particular, DSC has been widely used. This technique is based on the implicit assumption that there exists a linear relationship between the heat evolved during cure, ΔH_i, and the extent of reaction α:

$$\alpha = \frac{\Delta H_i}{\Delta H_T} \tag{1}$$

where ΔH_T is the total heat evolved during a dynamic run to reach complete conversion.

The free radical crosslinking reaction that we are dealing with presents the autoacceleration or gel effect, which increases the reaction rate in the very low conversions range, as well as structural or topological constraints that diminish continuously the reaction rate. These two effects are always present in the reactive system. The observed behavior shows that there is also a final declining when the reactive system reaches the vitrification regime.

In addition to these three effects and due to the high and fast exothermic reaction, in some cases there is an important thermal contribution that leads to nonisothermal conditions or to a noncontrolled temperature ramp at some time of the reaction for dynamic conditions. In those cases, an extra acceleration of the reaction will take place as the temperature increases with conversion.

The present work takes into account these effects as described in the following:

Kinetics below the Vitrification Regime

The two effects present in this regime are dealt with by the phenomenological model developed by Kamal,[17,18] which has also been applied previously to similar free radical crosslinking systems.[11,24–26] The general model proposes that when the initial rate of reaction is not negligible, the expression becomes

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{2}$$

where k_1 is related to the initial reaction rate and α^m represents, in a phenomenological way, the effects of the different constraints below the vitrification regime.

However, if the initial rate of reaction is negligible, the last expression can be reduced to

$$\frac{d\alpha}{dt} = (k\alpha^m)(1 - \alpha)^n \tag{3}$$

The DVER-S reaction can be described by this kinetic expression, as has been previously proposed by other researchers,[11,24–27] although in these previous works the effects of the high exotherm of the reaction, or the diffusion restriction during vitrification that may appear at relatively low temperatures were not considered.

To take into account the change in the rate of reaction due to temperature, Kamal's eq. was re-

written using an Arrhenius expression for the kinetic constant k:

$$\frac{d\alpha}{dt} = Ae^{(-E/RT)}\alpha^m(1-\alpha)^n \qquad (4)$$

where A is the preexponential factor, E is the apparent overall activation energy, and R is the universal gas constant. The four kinetic constants—A, E, m, and n—take into account all the effects that influence the reaction rate below the vitrification regime, such as the specific chemical reactivity of the functional groups, the autoacceleration or gel effect, and the topological or structural effect.

For the calculations realized with this expression, time zero was taken as that corresponding to an experimental conversion of 0.001. This was also the initial value for application of the estimation method.

Kinetics at the Vitrification Regime

When the reactive system is near the vitrification regime, the growing glass transition temperature of the reactive system approaches the cure temperature, and the reactions between the functional groups become diffusion controlled in such a way that the overall reaction rate is decreased. This effect can be extremely pronounced if the cure temperature is low and, as a consequence, the reaction ends short of full conversion when the reaction temperature is below the final glass temperature of the polymerizing system.

This glass effect on the overall reaction rate can be incorporated using the Rabinowitch model[19] to calculate the overall constant as follows:

$$\frac{1}{k_g(T,\alpha)} = \frac{1}{k(T)} + \frac{1}{k_d(T,\alpha)} \qquad (5)$$

where k is the Kamal rate constant calculated when the reaction is conduced at cure temperatures well upward the vitrification regime, k_d is the rate constant at the final stages of the reaction near the vitrification regime, and k_g is the overall rate constant of the reaction.

Equation 5 shows that k_g becomes governed by the influence of the reduced mobility of the reactive groups, which causes the apparent rate constant to decrease sharply; that is, when $k_d \ll k$ (after vitrification).[28]

While in the initial reaction stage the calculated rate constant of the Kamal model follows an Arrhenius dependence with the temperature; different expressions are used for k_d, which take into account the relaxation processes controlled by diffusion of molecular chain segments in the glass transition region of amorphous polymers.

In this article, k_d, controlled by the temperature molecular relaxations, is described by the empirical eq. known as the Vogel–Fulcher relationship[29]:

$$\ln(k_d) = \ln(k_{d0}) - \frac{E_d}{R}\left|\frac{T_c}{T_g(T_c - T_g + 50)}\right| \qquad (6)$$

where E_d is the activation energy of the diffusion mechanism, T_c is the cure temperature, and T_g is the glass transition of the polymer, which varies with the conversion.

Different eq.s have been proposed to fit experimental data of T_g vs. α, but Di Benedetto's eq. is the most frequently used[28,30]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{[1-(1-\lambda)\alpha]} \qquad (7)$$

where T_{g0} is the glass transition temperature of the system at $\alpha = 0$, and $T_{g\infty}$ is the maximum glass transition temperature attained when $\alpha = 1$. $\lambda = \Delta Cp/\Delta Cp_0$ is the ratio of the isobaric heat capacities of the fully reacted and the initial system ($\lambda < 1$). For the particular case when the ΔCp T_g equals a constant, λ is given by the following eq.[31,32]:

$$\frac{T_{g0}}{T_{g\infty}} = \lambda \qquad (8)$$

This last relationship was used in this work.

Thermal Autoacceleration

At intermediate conversions, which occur at the peak of the reaction rate, the exotherm of the reaction originates an extra increment of the temperature away from the constant value in the case of isothermal runs or from the programmed temperature ramp in the case of dynamic DSC runs. The ΔT originated can be of about 1 to 3°C for the low temperature runs, and up to 10°C for the dynamic runs; thus, it is of paramount interest that this effect is also included in the analysis of the experimental data.

In the present work the input data to the program of estimation of parameters (a multiparametric regression based on the Marquardt algo-
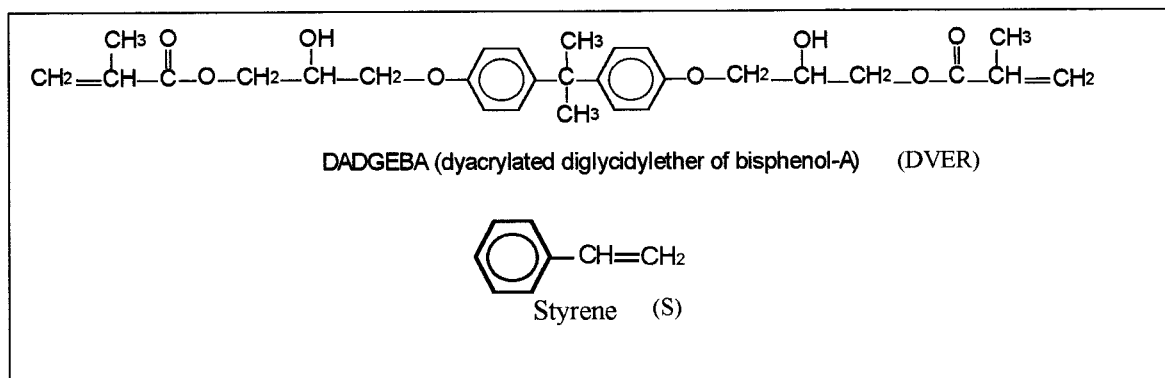
Figure 1 Schematics of the monomers: (a) DVER, (b) S.

EXPERIMENTAL

Materials

A DVER was synthesized by reacting an epoxy resin, diglycidyl ether of bisphenol A (DGEBA MY 790, Ciba Geigy; equivalent weight 176.2 g/eq) with methacrylic acid (Norent Plast S.A.; laboratory grade reagent) using triphenylphosphine (Fluka A.G.; analytical reagent) as the catalyst, in the presence of hydroquinone as stabilizer. The final conversion reached was higher than 93% for all batches, and the formulation was stabilized with hydroquinone. The DVER molecular weight measured by gel permeation chromatography (GPC) was 583 g/mol, using a polystyrene calibration. Details of the synthesis have been reported in a previous publication.[3]

The DVER was mixed with different amounts of styrene monomer using 2% by weight of benzoyl peroxide (BPO) (Lucidol 75%, Akzo Chemicals S.A.) to obtain the final material. The chemical structures of both reactants are included in Figure 1.

Experimental Procedure

All experiments in this study were performed using a Shimadzu DSC-50 calorimeter under continuous nitrogen flow.

The concentration of S in the mixture was varied between 4 to 40% by weight of S. The minimum S concentration, 4%, results from the disso-

lution of the initiator in the monomer before utilization. The DVER and S were mixed with the initiator at room temperature, and then the mixture was quickly transferred into a small DSC aluminum pan, which was subsequently sealed with an aluminum lid (crimped around the edge) to avoid the evaporation during the runs. Samples of 5 and 10 mg were used for the DSC runs and reweighed after the run to check for any weight loss, which was found to be negligible (less than 5%) in all runs.

Isothermal curing was carried out at different constant temperatures in the range of 90 to 110°C. Dynamic runs were done using a constant heating rate of 10°C/min.

The glass transition temperature of the mixtures before curing, T_{g_0}, were measured by DSC (Dupont 990), using liquid nitrogen as the refrigerant fluid. The measurement was taken at the onset of the transition. The ultimate glass transition temperature, $T_{g\infty}$, of the copolymers was measured using a dynamic mechanical analyzer (DMA) (Perkin-Elmer DMA 7e, three point bending, temperature scan, at 1Hz) as the onset of the change in the storage modulus.

RESULTS AND DISCUSSION

Total Heat of Reaction

The total heat of the copolymerization reaction of the resin with different amounts of styrene (4, 10, 20, 26.4, 40, and 60%) was measured operating a DSC in dynamic mode using a heating rate of 10°C/min. The total heat, ΔH_T, was evaluated as the area under the heat flow curve obtained in dynamical runs.

Figure 2 shows the ΔH_T per mol of double bonds as a function of the S concentration in the
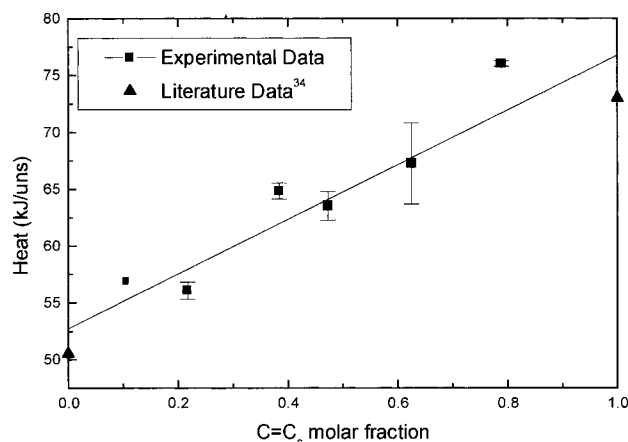
Figure 2 Total heat of copolymerization as a function of the initial molar fraction of S in the reactive mixture.

reaction system. These results show that the heat of homopolymerization of the DVER (per mol of unsaturations) is lower than that corresponding to S. Besides, DVER-S mixtures follow a linear dependence with the concentration of S double bonds and also show good agreement with the literature data for both homopolymers, polystyrene (73 kJ/mol) and poly(2-methyl methacrylate of 2-hydroxy propane) (50.5 kJ/mol).[34]

Kinetic Results

Temperature control is very important while carrying out kinetic experiments because the self-insulating characteristic of polymers leads to a phenomenon called autothermal acceleration. During autothermal acceleration, the heat of curing causes an increment in the sample temperature and rate of polymerization. Three things are generally required for autothermal acceleration: low thermal conductivity and large samples, high heat of reaction, and large activation energies. These criteria are satisfied with the free radical polymerization. Therefore, autothermal acceleration may be important in the cure reaction of a DSC sample, and a uniform sample temperature should not be assumed without careful analysis.[10]

DSC thermograms at typical isothermal and dynamical conditions are presented in Figure 3. The actual temperature history of the sample is also plotted, and in both cases an extra increase of temperature due to exothermic heat flow during polymerization can be seen.

The very fast and highly exothermic polymerization makes it impossible for the apparatus to follow the program imposed. Temperature increase in dynamic runs is much more severe. The

data in Figure 3(a) show that the mean temperature increase at the peak exotherm in dynamic runs is approximately 10°C, clearly a significant increment of temperature. For the isothermal DSC data in Figure 3(b), the mean temperature increase is of course smaller (approximately 3°C).

All the curves present an induction time before the peak of reaction due to the presence of hydroquinone. At end of this period the point at which $\alpha = 0.001$ was taken as time zero of the DSC run.

The experimental data obtained from isothermical runs were fitted up to a point previous to the maximum of the peak to avoid considering simultaneously the glass effect, which was analyzed separately. These isothermal data were considered simultaneously with dynamic DSC measurements to obtain the Kamal kinetic parameters for the curing reaction of a DVER-S system.

The copolymerization of DVER with 4, 20, and 40 % of S was studied. The kinetic parameters were obtained using eq. 4 for the isothermal and dynamic measurements. Table I shows how the parameters of the model vary with the amount of S added. For the three formulations, the exponents m and n do not remain strictly constant. However, their variation with the amount of incorporated styrene is too small to be assigned to a change in mechanism, and it was attributed to small dispersion on the experimental data and usual fluctuations inherent to the fitting method.

The activation energy calculated is practically constant for all formulations, as it has been pre-
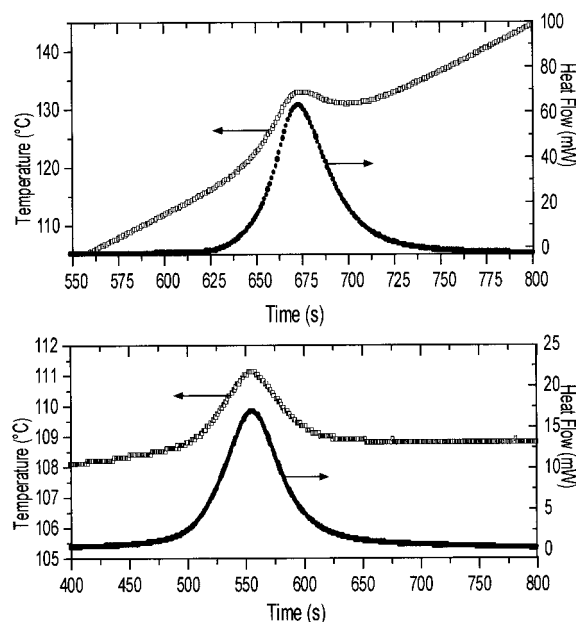

Figure 3 Typical (a) dynamic and (b) isothermal DSC thermograms. Temperature history is also included.

Table I Model Parameters Considering the Simple Kamals Equation (Equation 4, Below the Vitrification Regime)

Styrene (wt %)	ln (A)	E (kJ/mol)	m	n
4	20.7	78	0.94	1.21
20	22.5	81	1.02	1.52
40	22.0	81.2	0.96	1.43

viously found by Lee and coworkers,[11] whereas the frequency factor increases slightly when the S content increases. This overall activation energy is also in agreement with values reported for most polymerizations initiated by thermal initiator decomposition (80 to 90 kJ/mol).[35]

Since only minor variations were observed in the kinetic parameters, the reaction rates for all the formulations were finally fitted with an average of the particular kinetic parameters. Then, the kinetic reaction rate was expressed as

$$\frac{d\alpha}{dt} = 2.74 \ 10^9 \ e^{(-80(\text{kJ/mol})/RT)} \alpha^{0.97} (1-\alpha)^{1.39} \quad (9)$$

Figure 4 shows the experimental advance of reaction as a function of time for the copolymerization of 60/40 of DVER-S at different isothermal conditions and also in dynamics runs. The predictions of the model are also shown in the figure as continuous lines. It can be seen that the agreement of the model to the experimental results is quite good.
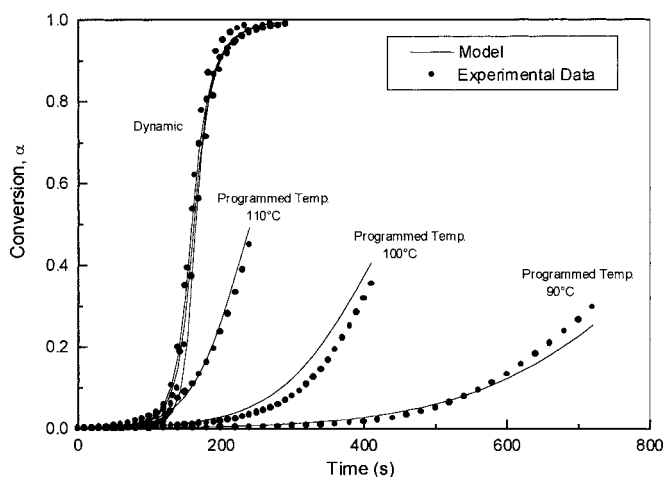
Similar results were obtained for the other two systems tested (4 and 20% of S). In all cases, the Kamal model provides a good representation of the experimental DSC data in the range of conversions below the vitrification regime, that is, for the whole range of conversions in the dynamic DSC runs and the conversions lower than the conversion at the glass transition in the isothermal runs with T_c less than T_g. From the beginning of the vitrification stage, where the restrictions caused by the decreasing mobility of the reactive groups becomes the controlling mechanism for the propagation, it is necessary to calculate the T_g value as function of the extent of the reaction to be included in the Vogel–Fulcher equation. This was done using eqs. 7 and 8, and the calculated results are shown in Figure 5.

The procedure used for the determination of k_{d_0} and E_d from eq. 6, at constant temperature is 1. the evaluation of the overall rate constant (k_g) from the experimental data of α and $d\alpha/dt$; 2. determination of k_d using eq. 5, since k is already known from fitting the first part of the reaction peak; 3. plotting of $\ln(k_d)$ versus $[T_c/T_g (T_c - T_g + 50)]$ to yield a straight line whose slope and y-intercept are used to calculate E_d and k_{d_0}, respectively.

The obtained values are summarized in Table II for different compositions at each measured temperature.

In the vitrification regime, the constant k_d, given by eq. 6, and the Kamal rate constant, k, are substituted in eq. 5 to evaluate the overall rate constant k_g at each cure temperature T_c. As a consequence, k_g becomes a function of the T_g,

Figure 4 Conversion versus time for a copolymer made from a mixture 40/60 by weight of DVER-S.
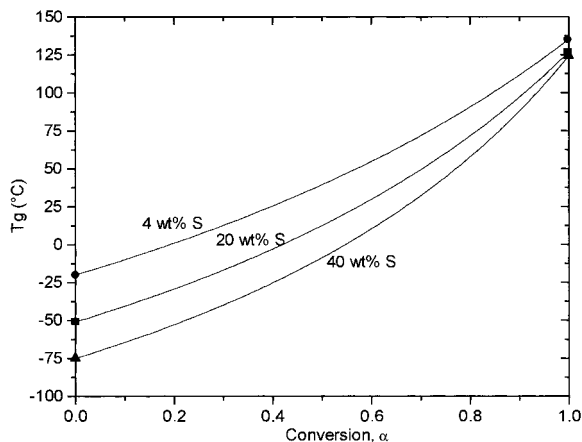
Figure 5 Glass transition temperature, T_g, versus conversion of unsaturations for different feed compositions.

which varies with the conversion α and the T_c. The expression for the global rate constant is then substituted in eq. 9, which can be integrated numerically using a differential finite method to obtain the conversion as a function of time. The numerical method was performed for different compositions of S and cure temperatures. Figure 6(a–c) shows the experimental conversion of double bonds versus time, and the corresponding calculated values at different isothermic temperatures and DVER-S compositions, using the overall constant, k_g (eq. 5). The predictions of the complete model (continuous line) are compared with the results calculated using only the rate constant obtained below the vitrification regime, k (eq. 9, dotted line). Comparison between experimental and predicted data was made taking that for a conversion of 0.05, experimental and theoretical time were the same (to avoid considering the inhibition time, which was not taken into account in this model). Predictions using k_g or k gave the same result in the conversion range where the T_g of the reactive system is below the reaction temperature. However, at the vitrification regime, the lower mobility of the reactive groups delays the reaction substantially and the simple Kamal model cannot represent the experimental results up to complete conversion. In this stage, only the complete model can account for the observed experimental behavior.

The overall rate constant, k_g, allows the correlation of the complete evolution of the free radical curing reaction because it takes into account, in a phenomenological way, all the constraints that can be present in this system. The diffusion controls caused by the gel and the topological effects,

which influence the kinetic from the beginning, are included in the Kamal propagation constant, k. For a given isothermal cure temperature, k does not change with the conversion. On the other hand, k_d is conversion dependent through the difference between the T_g of the reactive system and the cure temperature T_c. In the earlier stages of the reaction, when $T_g \ll T_c$, k_d is much greater than k; consequently, the reaction in the early stages is primarily controlled by the gel and topological effects. As the reaction advances, T_g rises and approaches to T_c; thus, the value of k_d becomes smaller. After vitrification, T_g is higher than T_c, and k_d is much smaller than k, resulting in the reaction being controlled by the lower mobility of the molecules or structures at which the reactive groups are attached.

Previous kinetic studies on a DVER-S similar system[11] and on a UPR-S system[36] have been performed applying the simple Kamal model at different isothermal cure temperatures in the whole range of conversions, including the vitrification regime. In those cases, the Kamal kinetic eq. was modified by introducing the maximum conversion reached by the system at each cure temperature, α_{max}, as a new parameter. In this way, the resultant kinetic eq. can only be used to model processes that operate at the same isothermal conditions.

CONCLUSIONS

The simple Kamal kinetic model used in this work described reasonably well the initial stages of the cure reaction of a DVER with different proportions of S. The predictions obtained from this

Table II   Model Parameters Obtained Using the Complete Model (Considering Vitrification Effects) at Different Curing Temperatures and Initial Compositions

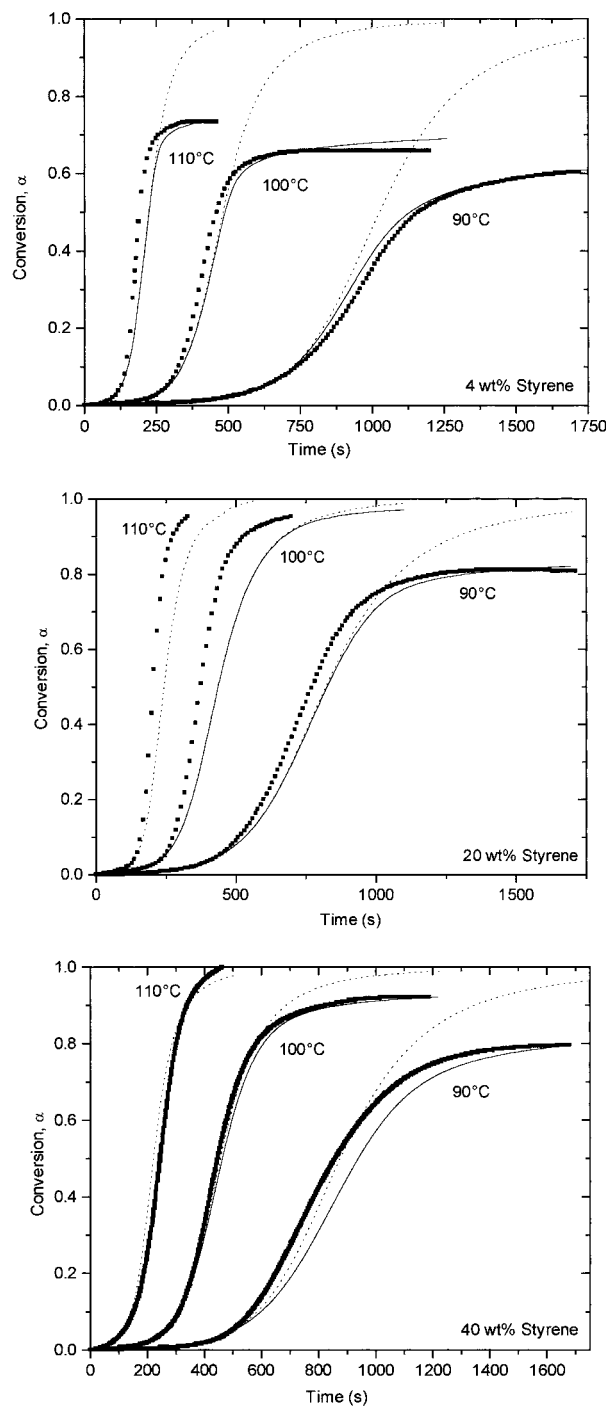| Styrene (wt %)	T_c (°C)	K (1/seg)	$\ln (k_{d_0})$	E_d (kJ/mol)
4	90	$8.44\ 10^{-3}$	10.54	11.54
	100	$17.17\ 10^{-3}$	17.52	15.70
	110	$33.68\ 10^{-3}$	19.11	15.93
20	90	$8.44\ 10^{-3}$	7.66	7.66
	100	$17.17\ 10^{-3}$	5.74	3.08
	110	$33.68\ 10^{-3}$	no vitrification	
40	90	$8.44\ 10^{-3}$	4.42	7.13
	100	$17.17\ 10^{-3}$	3.61	4.51
	110	$33.68\ 10^{-3}$	no vitrification	

Figure 6 Conversion versus time for reactive mixtures of different initial composition: (a) 4% wt, (b) 20% wt, and (c) 40% wt of S. The black square curve represents experimental data, the solid line represents the complete model (considering the vitrification effects), and the dashed line represents the prediction considering the simple Kamal model (below the vitrification regime).

expression show very good agreement with the experimental results obtained from the isothermic and dynamic runs. In the initial stages of the

reaction, only the gel effect and the effects of the topological constraints were considered in the phenomenological model.

At later stages of the reaction, a diffusion control due to vitrification was incorporated into the reaction kinetics by modifying the overall rate constant. During the course of the isothermal curing, the overall rate constant was assumed to be a combination of the Kamal kinetic constant obtained in the initial stages of the reaction and the vitrification-controlled rate constant. The developed model and the calculated parameters were used to predict the behavior of the reacting system under different isothermal conditions. A good agreement between predictions of the model and experimental data, expressed as degree of cure as a function of time, was found, confirming the ability of the complete model to represent the DVER-S copolymerization and that of the proposed method to determine the model parameters.

The total heat of copolymerization increases linearly as the S concentration is increased, and this dependence must be considered in any kinetic model proposed to represent the system behavior. From the linear regression of the experimental data, the homopolymerization heat of DVER and S are in reasonable agreement with the literature data.

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