

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230350027>

Unsaturated polyester resins cure: Kinetic, rheologic, and mechanical-dynamical analysis. I. Cure kinetics by DSC and TSR

ARTICLE in JOURNAL OF APPLIED POLYMER SCIENCE · JANUARY 2001

Impact Factor: 1.77 · DOI: 10.1002/1097-4628(20010118)79:3<447::AID-APP70>3.0.CO;2-M

CITATIONS

32

READS

208

5 AUTHORS, INCLUDING:



J. L. Vilas

Universidad del País Vasco / Euskal Herriko U...

85 PUBLICATIONS 524 CITATIONS

SEE PROFILE



Jose MANUEL Laza

Universidad del País Vasco / Euskal Herriko U...

49 PUBLICATIONS 402 CITATIONS

SEE PROFILE



Moses Rodriguez

Mayo Foundation for Medical Education and ...

42 PUBLICATIONS 406 CITATIONS

SEE PROFILE



L. M. León

Basque Center for Materials, Applications an...

91 PUBLICATIONS 629 CITATIONS

SEE PROFILE

Unsaturated Polyester Resins Cure: Kinetic, Rheologic, and Mechanical-Dynamical Analysis. I. Cure Kinetics by DSC and TSR

J. L. VILAS, J. M. LAZA, M. T. GARAY, M. RODRÍGUEZ, L. M. LEÓN

Departamento de Química-Física, Facultad de Ciencias, Universidad del País Vasco (UPV/EHU),
Apdo. 644-48080 Bilbao, Spain

Received 7 January 2000; accepted 13 March 2000

ABSTRACT: The curing reaction of a polyester resin, using methyl ethyl ketone peroxide and cobalt octoate as promoter, has been studied by differential scanning calorimetry and thermal scanning rheometry under isothermal conditions. All kinetic parameters of the curing reaction, including the reaction order, activation energy, and the rate constant, were calculated and reported using different empirical relationships. The gel time, which is defined by several criteria, was used to determine the apparent activation energy of the process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 447–457, 2001

Key words: unsaturated polyester resin; curing reaction; gel time; DSC; thermal scanning rheometry

INTRODUCTION

Unsaturated polyester resins are widely used as the matrix resin for polymeric composites because of their relatively low cost, good balance of properties, and adaptability to many fabrication processes. They are primarily used in compression molding (sheet molding compounds), injection molding (bulk molding compounds), resin transfer molding, pultrusion, filament winding, and hand lay-up processes.

The resin is normally prepared by the reaction of a saturated diol with a mixture of an unsaturated dibasic acid and a saturated dibasic acid or its corresponding anhydride. It is commonly referred to as general-purpose polyester, and typical examples are orthophthalic, isophthalic, and bisphenol A-fumaric acid polyesters. Commercially, the resin is available in the form of solu-

tions containing 60–70 wt % of the prepolymer in a reactive solvent, usually styrene.

The curing reaction of unsaturated polyester resins is a free radical chain growth polymerization. Before the reaction, the system contains styrene monomer, unsaturated polyester molecules, and curing agents. When the reaction starts, the initiator decomposes, forming free radicals to trigger the polymerization. Free radicals link adjacent unsaturated polyester units and form primary polymer chains through connecting styrene monomers and by both inter- and intramolecular reactions.

The processing of thermosetting resins requires understanding of the rheology and the polymerization reaction kinetics during cure. The kinetic scheme of the cure of unsaturated polyester resins is of considerable importance for the optimization of the many manufacturing processes involving unsaturated polyesters. Not surprisingly, considerable attention has been given to modeling and simulation studies in recent years.^{1,2}

Correspondence to: L. M. León.

Journal of Applied Polymer Science, Vol. 79, 447–457 (2001)
© 2000 John Wiley & Sons, Inc.

The aim of this study was to analyze the effect of temperature and catalyst amount on the curing kinetics of an unsaturated polyester resin by using differential scanning calorimetry (DSC) and thermal scanning rheometry (TSR). In this work, different models are proposed to explain the kinetic of cure.

Modeling the Cure Behavior

The isothermal cure of thermosetting resins is usually characterized by gelation and vitrification: gelation corresponds to the incipient formation of an infinite network of crosslinked polymer molecules, and vitrification involves a transformation from a liquid or rubber state to a glassy state as a result of an increase in molecular weight. The cure of thermosetting resins is complicated by the interaction between the chemical kinetics and the changing physical properties. Near vitrification, the kinetics are affected by the local viscosity, which in turn is a function of the extent of reaction and temperature. Thus, the cessation of reaction is not necessarily an indication that reaction is complete; the reaction may have been quenched because of the vitrification. Subsequent exposure to temperatures higher than the temperature of cure could result in further reaction.

For vinyl polymerizations, a number of kinetic experiments have been performed in an attempt to elucidate the effect of various components on the rate of polymerization.^{3,4} Although all the proposed models achieved different degrees of success in fitting the experimental data, they are, in general, too complex to be used in the reactive polymer processing operations. So, in most studies of reactive polymer processing, researchers prefer the use of empirical models to fit the reaction profiles.

Thus, the overall reaction rate can be expressed as a function of temperature, concentration of the reactants, reaction mechanism, and local microviscosity (which in turn is a function of molecular weight and temperature):

$$\frac{d\alpha}{dt} = kf(\alpha)f(\eta_l) \quad (1)$$

in which α is the degree of conversion, k is a rate constant which obeys the Arrhenius relationship and $f(\eta_l)$ is a function of the local viscosity.

In the absence of diffusion control, the general kinetic equation that describes the reaction is:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

where $f(\alpha)$ can be the simplest expression, a n -order equation:

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where n is the order of reaction; or, for an autocatalytic reaction in which the initial rate is not zero⁵:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

or, if the initial reaction rate is zero:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (5)$$

where n and m are orders of reaction.

Other authors^{3,6} prefer to modify these phenomenological models to account for vitrification as follows:

$$\frac{d\alpha}{dt} = kg(\alpha_{\max})f(\alpha) \quad (6)$$

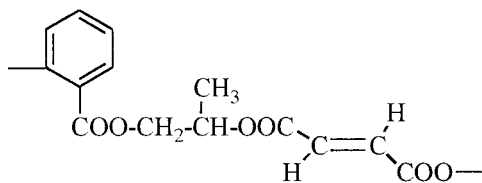
where α_{\max} is the maximum conversion reached for each isothermal experiment. Several equations are proposed as^{3,7}:

$$\frac{d\alpha}{dt} = k \left(\frac{\alpha_{\max} - \alpha}{\alpha_{\max}} \right)^x \alpha^m (1 - \alpha)^n \quad (7)$$

where x is a new adjustable parameter, or:

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_{\max} - \alpha)^n \quad (8)$$

Notice that the different $g(\alpha)$ satisfies the condition of zero reaction rate when $\alpha = \alpha_{\max}$.



Scheme 1

EXPERIMENTAL

Materials

The resin used in this study is an unsaturated polyester resin obtained by polycondensation from maleic anhydride (AM), phthalic anhydride (AP), and propylene glycol (PG) (Stratil 2123; provided by Rio Ródano, S.A.). Nuclear magnetic resonance was used to characterize the resin, with the following molar ratio being obtained: AM/AP/PG = 0.5:0.5:1.1. The nuclear magnetic resonance peak for maleic anhydride was very small because maleate isomerizes extensively to fumarate^{8,9} during the synthesis of polyester resin. The most probable structure of the resin is shown in Scheme 1. The amount of styrene contained in the resin was determined by evaporation of the styrene from the polyester resin in an air-circulating oven at 110°C for 2 h. The styrene content, determined from the weight loss, was 33 wt % styrene (DIN 16945).

Methyl ethyl ketone peroxide (BUTANOX M-50; AKZO Chemicals, S.A) was used as initiator, and cobalt octoate (as a 6 wt % solution of cobalt in dibutylphthalate) (NL51P; AKZO Chemicals) as catalyst. The concentrations of initiator were 0.5, 1.0, and 1.5% by weight of total resin (phr), and the concentration of catalyst was 0.3% by weight of total resin for all experiments.

All materials, unsaturated polyester resin (UPR), methyl ethyl ketone peroxide (MEKP) and cobalt octoate were used as received, weighed, and placed in a flask at the appropriate weight ratio before the experiments.

Experimental Techniques

DSC Analysis

The measurement of the heat evolved during the curing reaction and the residual reactivities were conducted using a Perkin-Elmer DSC-4 differential scanning calorimeter with nitrogen as flushing gas. All the experiments were performed under isothermal conditions to obtain the heat flow

curves. The amount of sample used was between 30 and 50 mg in all cases and Perkin Elmer large-volume capsules, made of stainless steel and fitted with viton o-rings, were used. For the isothermal runs, the DSC cell was allowed to stabilize at each isothermal condition before introducing the sample.

Once an isothermal experiment was completed, the DSC cell was cooled quickly to room temperature and, when stabilized, the residual heat of reaction of the sample was measured under a constant heating rate of 10°C/min, until no further exotherm was observed.

When using DSC to study the isothermal curing kinetics of thermosetting resins, it is assumed that the amount of heat generated is proportional to the degree of cure, α (or the extent of reaction) of the sample at that time. So the rate of curing, $d\alpha/dt$, may be related to the rate at which the heat is evolved, dQ/dt , by:

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \frac{dQ}{dt} \quad (9)$$

By integration of eq. (9), the relative degree of cure, α , can be obtained:

$$\alpha = \frac{1}{Q_{\text{tot}}} \int_0^t \left(\frac{dQ}{dt} \right)_T dt \quad (10)$$

The total heat for the curing reaction (Q_{tot}) is given by:

$$Q_{\text{tot}} = Q_{\text{iso}} + Q_r \quad (11)$$

where Q_{iso} is the heat generated during the isothermal DSC runs at each temperature, and Q_r the residual heat released when the sample is heated to 200°C at a heating rate of 10°C/min.

TSR

The rheological measurements were performed by means of a TSR instrument supplied by Rheometric Scientific. The TSR is designed for monitoring the viscoelastic state of a wide range of materials, particularly the changes in the rheological properties with temperature or time. Because TSR uses a probe and a sample container that can be thrown away at the end of each experiment, the equipment may be used to track the change in viscoelastic properties of a thermoset up to full

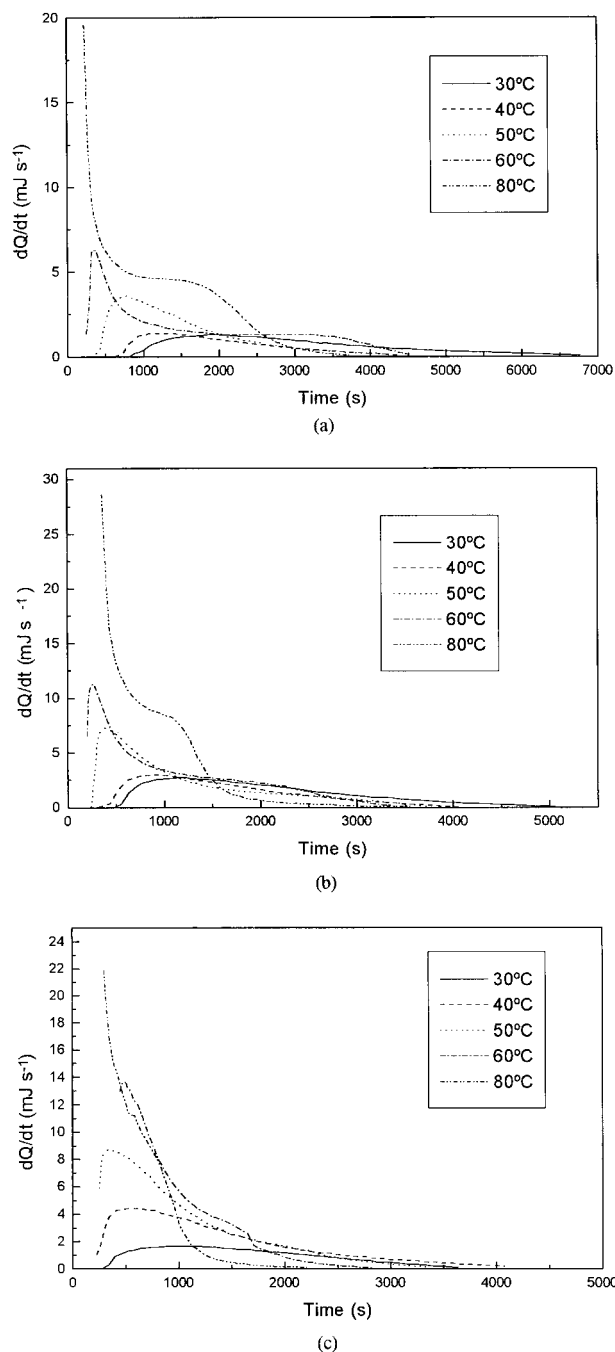


Figure 1 Heat flow versus time: (a) 0.5% MEKP, (b) 1.0% MEKP, (c) 1.5% MEKP.

cure or solidification. The disposable probe is connected via a spring of known force constant to a linear vibrator that is driven at constant amplitude and frequency (2 Hz). As it reciprocates in the sample, the position of the probe is continuously monitored by an accurate transducer. As the viscosity of the sample increases, the motion

of the probe is progressively damped by viscous drag. This change in amplitude and phase of the probe with respect to the drive motion is a function of the viscoelasticity of the material.

After the equipment is calibrated,^{10,11} we can determine the complex viscosity of the system and its components, the storage modulus (G'), the loss modulus (G''), and the loss tangent ($\tan \delta$). The experiments were performed at the same conditions as in DSC measurements.

RESULTS AND DISCUSSION

DSC Results and Kinetic Equation

Figure 1 shows the plots of curing rate dQ/dt versus time obtained from DSC measurements for samples with 0.5, 1.0, and 1.5 phr in MEKP, at 30, 40, 50, 60, and 80°C. Table I shows the data of the induction time, t_z , the cure time at the maximum of dQ/dt , t_m , and the vitrification time, t_v . Vitrification refers to the phase transition from liquid or rubbery state to glassy state, which results in retardation and quenching of the curing reaction. Hence, the vitrification time was defined as the time when cure reaction is completed under isothermal conditions, that is, when the isothermal thermogram returns to the baseline.

The higher the temperature, the faster the reaction rate. The induction time, the time of max-

Table I t_z , t_m , and t_v Values for the Isothermal Experiments

T (K)	t_z (s)	t_m (s)	t_v (s)
% MEKP: 0.5			
303	821	1961	6701
313	624	1284	4524
323	303	783	4410
333	<249	345	4557
353	<224	<224	3776
% MEKP: 1.0			
303	488	1220	5060
313	320	920	4100
323	246	402	3786
333	<204	264	3456
353	<364	<364	3136
% MEKP: 1.5			
303	281	1181	3641
313	<227	599	4250
323	<253	337	3433
333	<448	484	2908
353	<298	<298	2386

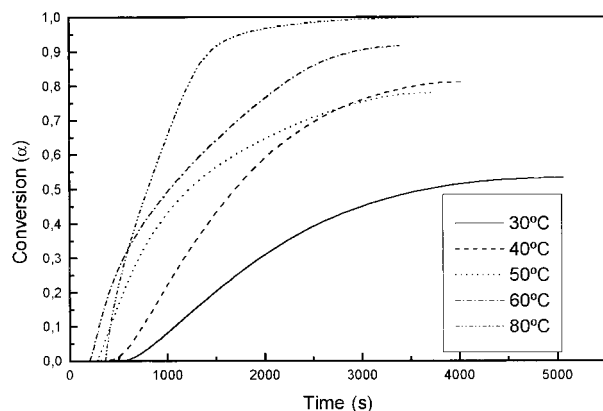


Figure 2 Conversion profile as a function of time at several isothermal temperatures for experiments with 1% MEKP.

imum rate, and the vitrification time are shorter when increasing temperature. Figure 2 shows the corresponding overall conversion profiles for samples with 1.0% MEKP and, as expected, the ultimate overall conversion increases with temperature as shown in Table II. Incomplete cure under isothermal conditions and the increase in the final degree of cure along with cure temperature are due to vitrification, which occurs when the glass transition temperature approaches the cure temperature. These results are in agreement with other published data for unsaturated polyester resins.^{12–14}

It is of great interest to note that the values of Q_{tot} are constant, independent of the temperature chosen for the isothermal cure. Therefore, the total heat (Q_{tot}), the sum of isothermal heat and residual heat, was determined as the average of the values measured at various isothermal temperatures and initiator concentrations, the obtained value being 231 Jg^{-1} , in agreement with those reported by other authors.^{3,7,15–18}

The scanning calorimetry traces shown in Figure 1 appear to be composed of at least two exothermic peaks that vary in size and position as the concentration of MEKP and isothermal temperature change. This indicates that the polymerization kinetics are quite complicated and may

suggest the occurrence of two separate reaction processes, as it has been pointed out by other authors,^{19,20} or these apparently anomalous data may be due to the complex variation in rate constants^{21,22} (k_p and k_t) as the polymerization proceeds.

Figure 3 describes the rate of cure versus degree of curing for the polyester resin at various cure temperatures. It can be observed that rate maxima exhibit increasing values when increasing cure temperature. From these plots, we have determined the parameters in the kinetic expressions, defined by eqs. (4), (5), and (7). To compute the different parameters in these equations, several methods have been proposed.^{23–26} In this study, we have used a nonlinear multiple regression through the Levenverg-Marquardt algorithm without constraints on the kinetic parameters by fitting the experimental data to eqs. (4), (5), and (7). The results obtained from this method are summarized in Tables III, IV, and V. In Figure 4 the experimental values of $d\alpha/dt$ are compared with those calculated using the different kinetic models for the experiments with 1.0% MEKP. Good agreement has been found over the whole curing temperature range for conversions lower than 0.6, except in the cases in which the temperature is above 50°C , as the reaction rate is very high which makes it impossible to get the initial values for $d\alpha/dt$, so that kinetic parameters have been determined without this information. As a consequence, the agreement is poor.

The deviations observed for conversions higher than 0.6 can be attributed to vitrification where the mobility of the reactive groups is hindered, and the rate of conversion is controlled by diffusion rather than by chemical factors.^{27,28} Notice that the values of the empirical reaction orders (n and m) change with the reaction conditions, so we can suggest that the mechanism for the curing reaction depends on conditions used.

In an ideal condition, a successful model should describe the experimental data well throughout the whole range of cure, but in this work, we have not taken into account the diffusion in the kinetic

Table II Maximum Conversion Reached for Each Temperature and Initiator Concentration

% _w MEKP	303 K	313 K	323 K	333 K	353 K
0.5	0.39	0.42	0.39	0.81	0.96
1.0	0.53	0.81	0.78	0.92	1.0
1.5	0.51	0.78	0.90	0.94	0.97

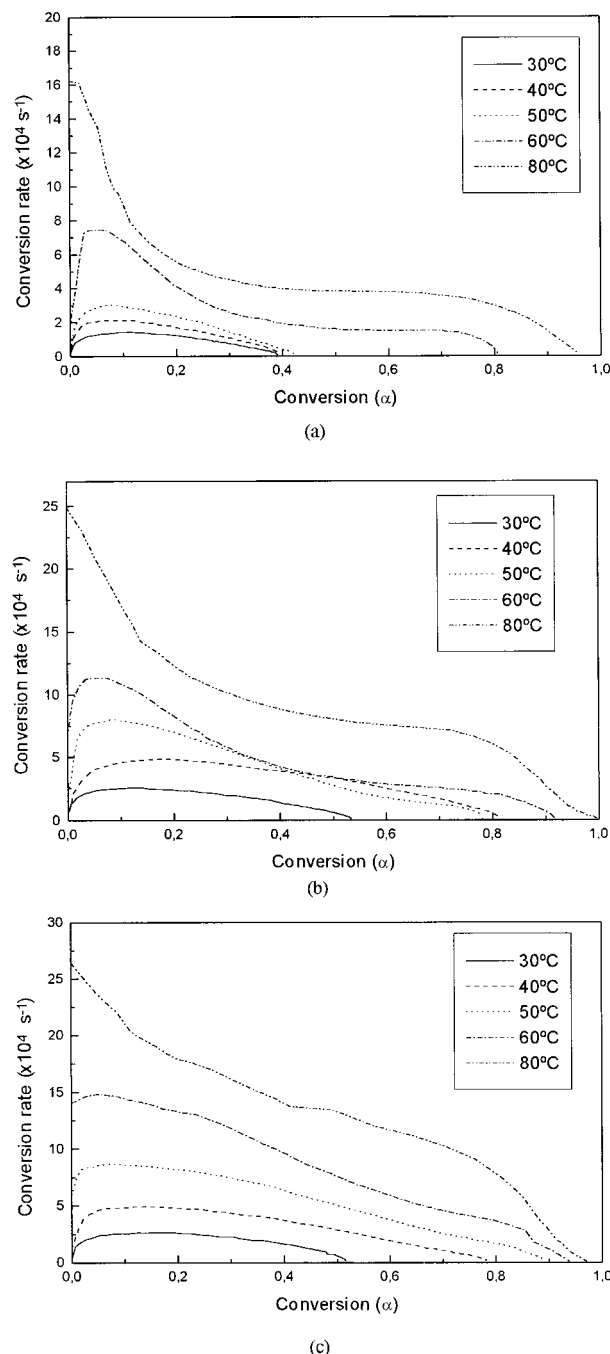


Figure 3 Isothermal conversion rate as a function of conversion: (a) 0.5% MEKP, (b) 1.0% MEKP, (c) 1.5% MEKP.

model. When the reactive system is near the vitrification region, the growing glass transition temperature approaches the cure temperature and the reaction between the functional groups becomes diffusion controlled in such a way that the overall reaction rate is decreased. It is ob-

Table III Kinetic Parameters Obtained by Application of Eq. (4)

Temperature (K)	k_1 (s ⁻¹)	k_2 (s ⁻¹)	m	n
% _w MEKP: 0.5				
303	2.00E-05	2.04E-03	0.85	7.0
313	3.44E-06	2.69E-03	0.62	6.7
323	3.68E-06	1.61E-03	0.58	6.2
333	8.00E-05	1.26E-03	0.23	3.0
353	1.26E-03	3.06E-09	3.6	1.9
% _w MEKP: 1.0				
303	8.55E-06	1.32E-03	0.52	3.9
313	0	1.54E-03	0.45	1.8
323	0	2.15E-03	0.32	2.6
333	6.60E-04	2.50E-04	0.00	1.2
353	2.32E-03	1.21E-01	6.0	2.5
% _w MEKP: 1.5				
303	3.00E-05	1.47E-03	0.59	3.7
313	1.00E-04	1.46E-03	0.45	2.1
323	6.00E-04	1.08E-03	0.40	1.5
333	1.39E-03	7.60E-04	0.47	1.3
353	2.36E-03	1.53E-12	60576.6	0.91

served that this effect is extremely pronounced at low temperatures and, as a consequence, the reaction stops at low conversion. This glass effect on the overall reaction rate can be incorpo-

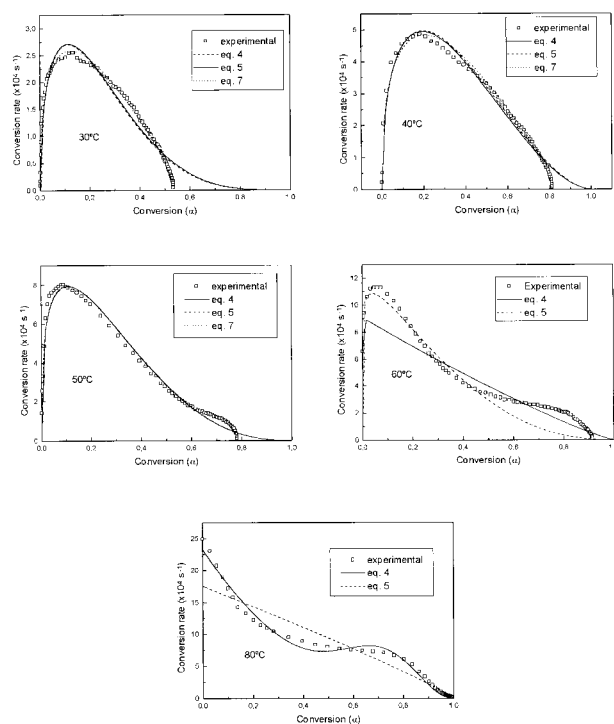
Table IV Kinetic Parameters Obtained by Application of Eq. (5)

Temperature (K)	$k/10^{-3}$ (s ⁻¹)	m	n
% _w MEKP: 0.5			
303	1.38	0.67	6.5
313	2.64	0.62	6.6
323	1.57	0.56	6.1
333	1.35	0.21	3.0
353	0.9	1.01E-17	2.4
% _w MEKP: 1.0			
303	1.27	0.50	3.8
313	1.53	0.45	1.8
323	2.17	0.32	2.6
333	1.65	0.10	2.4
353	1.75	5E-19	0.9
% _w MEKP: 1.5			
303	1.29	0.51	3.5
313	1.40	0.35	2.1
323	1.41	0.14	1.4
333	1.93	0.07	1.2
353	2.23	5E-23	0.9

Table V Kinetic Parameters Obtained by Application of Eq. (7)

Temperature (K)	$k/10^{-3}$ (s $^{-1}$)	α_{\max} (1 - M_{∞}/M_0)	x	m	n	$n + m$
% _w MEKP: 0.5						
303	0.52	0.39	0.82	0.42	1.0	1.4
313	1.37	0.42	0.50	0.45	3.2	3.6
323	0.89	0.39	0.36	0.42	3.2	3.6
333	1.40	0.81	-0.40	0.22	3.6	3.8
353	—	0.96	—	—	—	—
% _w MEKP: 1.0						
303	0.78	0.53	0.45	0.37	1.6	2.0
313	1.26	0.81	0.30	0.39	1.1	1.5
323	2.19	0.78	-0.042	0.32	2.7	3.0
333	—	0.92	—	—	—	—
353	—	1.0	—	—	—	—
% _w MEKP: 1.5						
303	0.65	0.51	0.50	0.32	0.76	1.1
313	1.19	0.78	0.34	0.31	1.3	1.6
323	1.30	0.90	0.34	0.12	0.85	0.97
333	1.81	0.94	0.35	0.048	0.71	0.76
353	—	0.97	—	—	—	—

rated using different models,^{4,29,30} but it would be difficult to obtain a model useful for industrial purposes.

**Figure 4** Results obtained in modeling the curing reaction for the experiments with 1.0% MEKP.

Gel Time and Apparent Activation Energy (E_a) from TSR Measurements

The cure of a thermosetting reactive “prepolymer” usually involves transformation of low molecular weight monomers or oligomers from the liquid to the solid state as a result of the formation of a polymer network by chemical reaction of the reactive groups. Two stages, which are divided by a gel point, are usually distinguished in this process; it is accepted that growth and branching of the polymer chains occur in the liquid state where the reactive system is soluble and fusible. An infinite network of polymer chains appears and develops only after gel time. The reactive system then loses its solubility and fusibility, leading to the final reactions, which take place in the solid state.

The change in dynamic-mechanical properties of a curing system is directly proportional to the extent of the reaction. From the study of these dynamic-mechanical properties, a kinetic parameter, as for example the gel time (t_g), can be determined and from it kinetic studies of the curing system can be made.

The gel time is one of the most important kinetic characteristics of curing, because it describes the attainment of a certain critical conversion responsible for the transition from the first to the second stage of the process.³¹ The gel point is

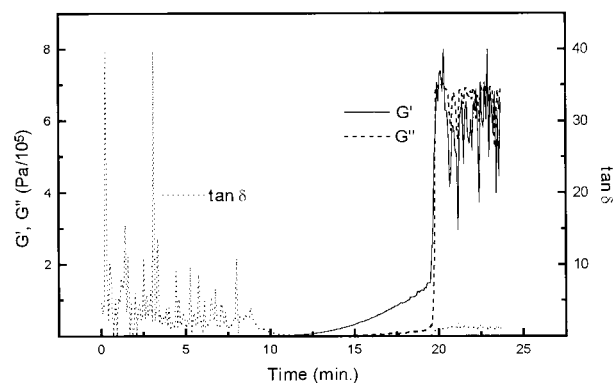


Figure 5 Storage modulus (G'), loss modulus (G''), and $\tan \delta$ versus time for the UPR system from TSR.

characterized by the appearance in the reactive system of a macromolecule with an infinitely large molecular weight, $\bar{M}_w \rightarrow \infty$.

Generally, rheologic and mechanical techniques are used to determine the gel time by means of extrapolation to infinite viscosity. The shear rate and the vitrification affect the gel time determination. The dynamic-mechanical tests are the best methods for the rheologic study during the polymerization. Considering a linear viscoelastic behavior²²:

$$G^* = G' + i \cdot G''$$

$$\tan \delta = \frac{G''}{G'} \quad (12)$$

where G' is the shear storage modulus, G'' is the shear loss modulus, and $\tan \delta$ is the loss tangent.

Figure 5 shows a typical result obtained in a TSR experiment, in which three different regions are apparent. In the first region, the G' modulus is low because of the low crosslinking. In the second region, where the gel time is reached, this modulus increases exponentially versus time. In the last region, the modulus increases more rapidly, and the TSR is not able to measure it because of the high medium viscosity, highly disperse data being obtained, which indicates that the resin has been cured.

Several methods have been proposed to determine the gel point during isothermal cure. Thus, Tung and Dynes³² proposed a correlation between the gel point and the intersection point of the curves of storage and loss modulus. In the liquid state the viscous properties are predominant ones, so $G'' > G'$ and $\tan \delta > 1$, whereas in the

solid state, the elastic properties are the predominant, $G'' < G'$ and $\tan \delta < 1$. Therefore, in the gel point $G'' = G'$ and $\tan \delta = 1$. Chambon and Winter^{33,34} proposed that G' and G'' curves are parallel or coincident in a narrow range of frequencies near the gel point. Harran and Landourd³⁵ determined the gelation by means of the decrease in the rate of growth of G'' during the cure. The

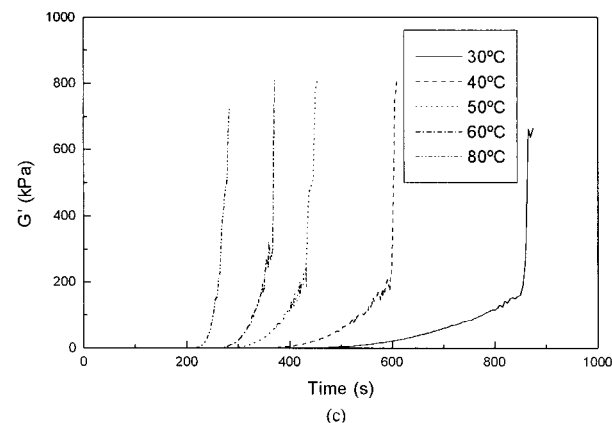
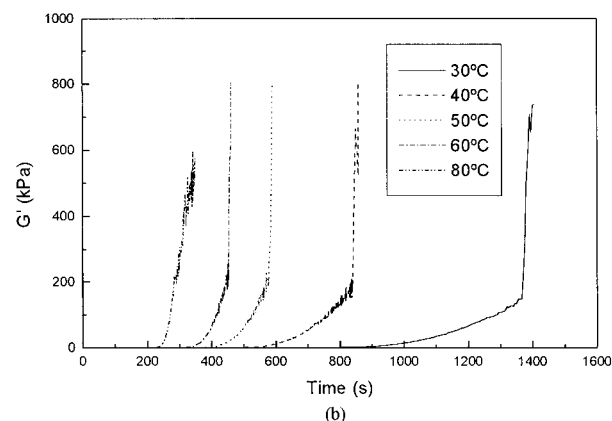
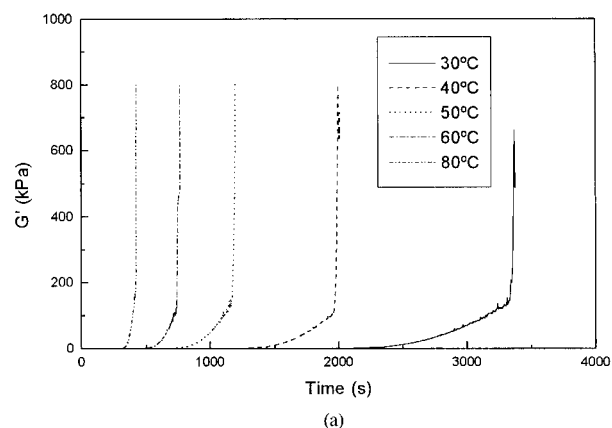


Figure 6 Isothermal shear modulus versus time: (a) 0.5% MEKP, (b) 1.0% MEKP, (c) 1.5% MEKP.

Table VI Gel Time for the UPR System for all the Criteria Used [tg_1 , Criterion of Tangent Line to G' Curve tg_2 , tg_3 , tg_4 , and tg_5 , Criteria of the Viscosity (500, 1000, 2000, and 5000 Pa · s, Respectively)]

Temperature (K)	tg_1 (s)	tg_2 (s)	tg_3 (s)	tg_4 (s)	tg_5 (s)
0.5% MEKP					
303	3338	2874	3012	3222	3246
313	1970	1734	1848	1854	1866
323	1173	954	996	1044	1056
333	733	586	612	618	630
353	411	276	289	301	306
1.0% MEKP					
303	1366	1026	1134	1170	1182
313	840	630	666	714	720
323	578	394	411	443	459
333	452	284	299	316	329
353	264	160	164	172	189
1.5% MEKP					
303	855	612	660	720	732
313	597	423	433	475	481
323	433	261	281	297	312
333	367	208	215	227	241
353	246	131	136	139	146

change in the slope between the two linear zones of $\log G''(t)$ is used to determine the gel point (independently of the experiment frequency). White³⁶ correlated the gel point with the intersection between the two tangent lines at the beginning and at the end of the viscosity curve; Gillham³⁷ considered the gel point when the loss modulus G'' is maximum; Willard³⁸ proposed the crossing point between the tangent line at G' curve and the baseline ($G' = 0$); and Malkin and Kulichikhin³¹ considered the gel point to be that for which a maximum in the loss tangent is attained.

We performed TSR isothermal experiments at different temperatures (30, 40, 50, 60, and 80°C) (see Fig. 6) and the gel time was determined according to the following criteria:

- Criterion of the tangent line to G' curve: the gel time has been taken at the point corresponding to the crossing between the tangent drawn at G' , when G' reaches a maximum rate of variation, and the baseline ($G' = 0$).
- Criterion of the viscosity: at this point the real dynamic viscosity η' reaches several determined values (500, 1000, 2000, and 5000 Pa · s).

The results obtained can be seen in Table VI.

The cure reaction of a UPR is a free-radical polymerization among active chains generated by the rupture of the double linkages and styrene molecules, which act as a bridge between the chains. Depending on the amount of active chains and their generation rate, the crosslinking will be more or less fast and the gel time will be major or minor. In our system, the effect of two variables was found, as shown in Figure 7:

- The gel time decreases when the cure temperature increases. It can be explained by

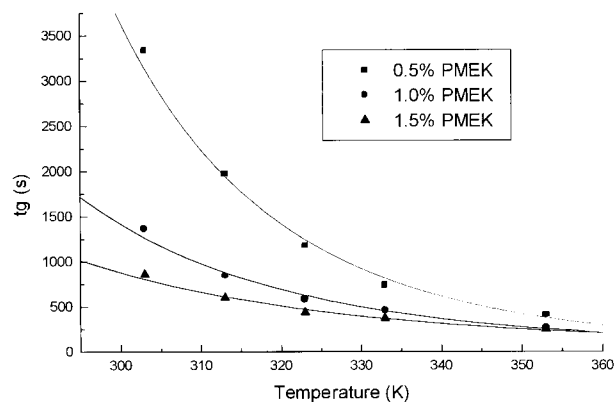
**Figure 7** Gel time (from criterion 1) versus temperature.

Table VII Apparent E_a from Eq. (15) (tg from Criterion 1)

% MEKP	E_a (kJ · mol ⁻¹)
0.5	37.7
1.0	28.6
1.5	21.8

considering that the increase of the temperature implies an increase in the mobility of the active chains, leading to a faster cure reaction as expected considering the positive activation energy usually accompanying these reactions.

- The gel time decreases when the MEKP wt % increases. It can be attributed to the major amount of active chains generated, which leads to a faster cure reaction.

Apparent Activation Energy (E_a)

The chemical conversion obtained at the gel time is considered constant for a given system.³⁹ Therefore, the gel time (tg) can be related to the apparent kinetic constant (k') of the reaction through the equation:

$$tg = cte \cdot \frac{1}{k'} \quad (13)$$

Assuming that the apparent kinetic constant of the reaction k' is related to temperature by an Arrhenius relationship:

$$k' = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (14)$$

from which it can be obtained:

$$\ln tg = cte' + \frac{E_a}{R} \cdot \frac{1}{T} \quad (15)$$

There is a linear relationship between $\ln(tg)$ and the inverse of temperature for isothermal cure reactions. From the slope of this plot, the apparent activation energy (E_a) can be obtained. It has been verified that E_a values are similar independently of the criterion used for its calculation. In Table VII are shown the values obtained for our system according to the first criteria used. From these results, an interesting fact

can be observed— E_a decreases when MEKP wt % increases, so the initiator concentration modifies the reaction mechanism, as previously reported.⁴⁰

CONCLUSIONS

The reaction kinetics and the rheological behavior of an unsaturated polyester resin were studied by using thermal techniques as a function of cure temperature and initiator concentration. It has been found that the reaction rate (determined by DSC) increases and the gel time is reduced when increasing concentration of MEKP and/or cure temperature.

The reaction process was shown to be complex, as indicated by the presence of various peaks in DSC traces, and by the change of different kinetic parameters, reaction orders, and activation energy, with the reaction conditions.

The gel time depends on the criterion used for its determination, indicating that the gelation process occurs during a period of time. However, the E_a values determined from different criteria are the same.

REFERENCES

1. Zetterlund, P. B.; Johnson, A. F. *Thermochim Acta* 1996, 289, 209.
2. Auad, M. L.; Aranguren, M. I.; Elicabe, G.; Borrajo, J. *J Appl Polym Sci* 1999, 74, 1044.
3. Stevenson, J. F. *Polym Eng Sci* 1986, 26, 746.
4. Huang, Y. J.; Lee, L. J. *AIChE J* 1985, 10, 1585.
5. Kamal, M. R. *Polym Eng Sci* 1974, 14, 23.
6. Hale, A.; Makosko, C. W.; Bair, H. E. *Proc ANTEC'87* 1987, 1110–1115.
7. Lee, J. H.; Lee, J. W. *Polym Eng Sci* 1994, 34, 742.
8. Curtis, L. G.; Edwards, D. L.; Simons, R. M.; Trent, P. J.; Von Bramer, T. T. *I & EC Prod Res Dev* 1964, 3, 218.
9. Paci, M.; Crescenzi, V.; Supino, N. *Makromol Chem* 1982, 183, 377.
10. PL-TSR Operators Manual. Rheometric Scientific Ltd.: UK.
11. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodríguez, M.; León, L. M. *Polymer* 1998, 40, 35.
12. Grentzer, T. H.; Kitchen, K. E.; Lo, S. K.; Spencer, C. J.; Rust, D. A. 45th Ann Conf Comp Inst, SPI 1990, 2-B.
13. Tollens, F. R.; Hill, R.; Lee, L. J. 47th Ann Conf Comp Inst, SPI 1992, 17-B.
14. de la Caba, K.; Guerrero, P.; Eceiza, A.; Mondragon, I. *Polymer* 1996, 37, 275.
15. Kubota, H. *J Appl Polym Sci* 1975, 19, 2279.

16. Rojas, A. J.; Borrajo, J.; Williams, R. J. J. *Polym Eng Sci* 1981, 21, 1122.
17. Abadie, M. J. M.; Sakkas, D. *Revue Compos Nouveaux Matér* 1991, 1, 95.
18. Azaar, K.; Brouzi, E.; Granjer, R.; Verghaund, J. M. *Eur Polym J* 1991, 27, 1431.
19. Lem, K. W.; Han, C. A. *Polym Eng Sci* 1984, 24, 175.
20. Salla, J. M.; Ramis, X.; Martín, J. L.; Cadenato, A. *Thermochim Acta* 1988, 134, 126.
21. Horie, K.; Mita, I.; Kambe, H. *J Polym Sci Part A-1* 1970, 8, 2839.
22. Cook, W. D.; Simon, G. P.; Burchill, P. J.; Lau, M.; Fitch, T. J. *J Appl Polym Sci* 1997, 64, 769.
23. Moroni, A.; Mijovic, J.; Pearce, E. M.; Found, C. C. *J Appl Polym Sci* 1986, 32, 3761.
24. Khanna, V.; Chanda, M. *J Appl Polym Sci* 1993, 49, 319.
25. Kenny, J. M. *J Appl Polym Sci* 1994, 51, 761.
26. Kim, W. G.; Nam, T. Y. *J Polym Sci Part A Polym Chem* 1996, 34, 957.
27. Chern, C. S.; Poehlein, G. W. *Polym Eng Sci* 1987, 27, 782.
28. Hang, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. *J Appl Polym Sci* 1998, 68, 1125.
29. Chiu, W. Y.; Canot, G. M.; Soong, D. S. *Macromolecules* 1983, 16, 348.
30. Wisanrakkit, G.; Gillham, J. K. *J Coating Technol* 1990, 62, 35.
31. Malkin, A. Y.; Kulichikhin, S. G. *Adv Polym Sci* 1991, 111, 217.
32. Tung, C.; Dynes, P. J. *J Appl Polym Sci* 1982, 27, 569.
33. Chambon, F.; Winter, H. *Polym Bull* 1985, 13, 499.
34. Chambon, F.; Winter, H. *J Rheol* 1987, 31, 683.
35. Harran, D.; Landourd, A. *Rheol Acta* 1985, 24, 596.
36. White, R. P. *Eng Sci* 1974, 14, 50.
37. Gillham, J. K. *Polym Eng Sci* 1979, 19, 676.
38. Willard, P. E. *Polym Eng Sci* 1974, 14, 273.
39. Babayevsky, P. G.; Gillham, J. K. *J Appl Polym Sci* 1973, 17, 2067.
40. Cuadrado, T. R.; Borrajo, J.; Williams, R. J. J.; Clara, F. M. *J Appl Polym Sci* 1983, 28, 485.