

Master Curve and Time–Temperature–Transformation Cure Diagram of a Polyfunctional Epoxy Acrylic Resin

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ABSTRACT: The curing reaction of a well-defined glycidyl methacrylate-*co*-butyl acrylate statistical copolymer, prepared by atom transfer radical polymerization, and a commercial linear diamine (Jeffamine D-230) was studied with the objectives of constructing and discussing a time–temperature–transformation isothermal curing for this system. Thermal and rheological analyses were used to obtain the gelation and vitrification times. Differential scanning calorimetry data showed a one-to-one relationship between the glass-transition temperature (T_g) and fractional conversion independent of the cure temperature. As a result, T_g was used as a measurement of conversion. We obtained a

kinetically controlled master curve for isothermal curing temperatures from 50 to 100°C by shifting T_g versus the natural logarithm time data to a reference temperature of 80°C. We calculated the apparent activation energy by applying two different methods, gel time measurements versus shift factors, suggesting a good agreement between them. Isoconversion contours were calculated by the numerical integration of the kinetic model. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2166–2172, 2011

Key words: atom transfer radical polymerization (ATRP); curing of polymers; glass transition

INTRODUCTION

In recent years, the range of potential applications of thermosetting resins, and especially epoxy resins, has rapidly expanded from classical applications, for example, as cover for surfaces and electronic components, to recent applications, such as advanced composite materials in the automobile and aeronautic industries.

Curing reactions of these thermoset materials produces a three-dimensional network after the chemical reaction of an epoxy resin with an appropriated curing agent, and during this curing, a large variety of complex chemical and physical changes occur as the material changes from a viscous liquid to a hard solid. Therefore, during the isothermal crosslinking polymerization reaction, the two critical phenomena that can take place are gelation and vitrification, which are caused by the transformations from liquid

to rubber and liquid or rubber to the glassy state, respectively.

The gel point of a chemical crosslinking system is defined unequivocally as the moment when the weight-average molecular weight (M_w) diverges to infinity. In the initial stages of the curing, a number of high-molecular-weight particles are formed and are dispersed in a low-molecular-weight phase that constitutes the continuous phase. The number and molecular weight of these particles increase as the curing reaction proceeds, and crosslinking becomes effective. As a result, the crosslinking polymer undergoes a transition from a liquid to a solid state. This first phenomenon is called *chemical gelation*, to distinguish it from physical gelation, in which the network is formed by reversible association mechanisms. Once the gelation of a resin has occurred, the resin loses its fluidity and cannot be shape-altered thereafter. It occurs at a specific point of the chemical conversion called the *gel conversion* (α_{gel}) and at a specific time called the *gel time* (t_{gel}); these depend on the curing system itself and the environment in which the reaction takes place. The gelation point requires study because it is the onset of mechanical strength and curing stress, but it does not involve any chemical changes in the curing process and, therefore, cannot be detected by techniques such as differential scanning calorimetry

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(DSC). However, the rheological properties of the resin change during gelation and can, therefore, be detected by methods based on changes in these properties, but a number of other techniques have been proposed.¹⁻¹²

Vitrification is defined as the transformation of a material from a liquid or rubbery state to a glassy state. At vitrification, the material solidifies, and the chemical reactions can be stopped. Vitrification is a gradual, thermoreversible process and its detection will vary with the technique used, although it can also be determined by both the reaction kinetics and consideration of the system component chemistry. The methodology for the experimental determination of vitrification consists of curing the sample by a technique that is sensitive to vitrification, such as torsion braid analysis or dynamic mechanical thermal analysis.¹³⁻¹⁶ A kinetic investigation of the chemical reaction also allows one to determine the vitrification curve for isothermal curing. Recently, modulated DSC has been also used to directly determine the vitrification^{17,18} and thermodynamic properties during the curing reaction.¹⁹

Another important property of polymeric materials is the glass-transition temperature (T_g). T_g shows a considerable increase with the changes in the chemical conversion during the curing of thermosetting materials. T_g increases nonlinearly with the conversion in crosslinking systems and is, thus, more sensitive in the later stages of curing. Therefore, a better analytical study is required when the reaction rate is low, for example, at the high conversion and after vitrification, because the changes are not entirely distinguishable. The evolution of this property can be linked directly to the conversion via DiBenedetto's equation.²⁰

A good understanding of the curing process that involves time-temperature-transformation (TTT) is of great importance for providing an optimal curing schedule. A graphical representation of the gelation and vitrification phenomena on the well-known TTT diagram provides an intellectual framework for understanding the curing process and the optimization of the processing and the final material properties.

In a previous article,²¹ the curing kinetics (determined by DSC) of a poly(glycidyl methacrylate-*co*-butyl acrylate) [P(GMA-*co*-BA)] statistical copolymer synthesized by atom transfer radical polymerization (ATRP) and a commercial linear diamine (Jeffamine D-230) were described. The purpose of this study was to examine the relationship between T_g and the chemical conversion of the curing process of this system. In addition, the gelation and vitrification transitions were examined with rheological measurements and kinetic analysis of the curing reaction, and a detailed TTT diagram is presented and discussed for this novel epoxy acrylic resin.

EXPERIMENTAL

Materials

Statistical P(GMA-*co*-BA) copolymer via ATRP was synthesized to be used as the epoxy resin. For this, the monomers glycidyl methacrylate (GMA; >97%; Fluka; Steinheim, Germany), butyl acrylate (BA; >99%; Fluka; Steinheim, Germany), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich) were purified by vacuum distillation before use. Ethyl 2-bromoisobutyrate (EBrIB; 99%; Aldrich, Steinheim, Germany), copper chloride (CuCl; 99.99%; Aldrich, Steinheim, Germany), and diphenyl ether anhydrous (99.9%; Aldrich, Steinheim, Germany) were used as received.

Statistical GMA-BA copolymerization at a feed monomer composition of 75 : 25 was carried out under ATRP conditions with EBrIB as an initiator, CuCl as a catalyst, and PMDETA as a ligand (both with respect to the initiator) in a 50% (v/v) diphenyl ether solution at 30°C ([GMA + BA]₀/[EBrIB]₀/[CuCl]₀/[PMDETA]₀ = 200 : 1 : 1 : 1). These experimental conditions, with an exchange halide technique, were chosen on the basis of previous GMA homopolymerization and copolymerization results reported by our group.^{22,23} In a typical procedure, the reaction mixture was introduced into a glass ampule, degassed by three freeze-pump-thaw cycles, and then sealed under high vacuum. The ampule was placed in an oil bath with a preset temperature of 30°C. The resulting polymer was isolated as follows. The polymer was dissolved in chloroform and passed through a neutral alumina column to remove the catalyst. The majority of the chloroform was removed by rotary evaporation, and the polymer, dissolved in a minimum amount of chloroform, was poured into a large excess of hexane. The precipitated product was filtered and dried in a vacuum oven at room temperature until a constant weight was reached. The total monomer conversion was measured gravimetrically. The characteristics of this copolymer were as follows: it had a GMA copolymer composition of 0.85; a number-average molecular weight (M_n), as determined by size exclusion chromatography, of 16,800 g/mol; and a polydispersity index (M_w/M_n) of 1.33. The epoxy equivalent weight of the GMA-BA copolymer determined by titration was 171 g/equiv. This value was in agreement with that estimated from the copolymer composition obtained by ¹H-NMR spectroscopy (epoxy equivalent weight = 167 g/equiv). The curing agent was a commercial linear diamine, polyoxypropylene diamine (Jeffamine D-230, Huntsman Corp., Steinheim, Germany), which was used as received.

The epoxy acrylic resin and Jeffamine D-230 were mixed stoichiometrically at low temperature and homogenized by agitation. Isothermal curing reactions

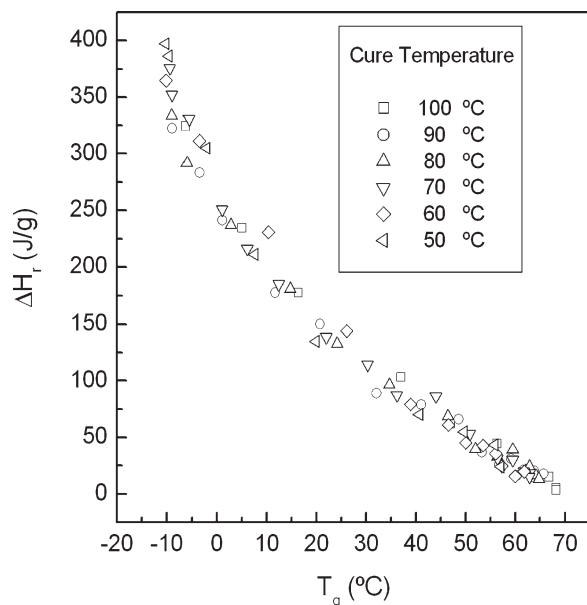


Figure 1 Dependence of ΔH_r on T_g at different isothermal curing temperatures for the P(GMA-co-BA) copolymer with Jeffamine D-230.

at six different temperatures (50, 60, 70, 80, 90, and 100°C) were carried out under dry nitrogen.²¹

Polymer characterization

DSC measurements were made on a PerkinElmer DSC/TA7DX PC series (Norwalk, CT) with an intracooler for low temperatures. The temperature scale was calibrated from the melting point of high-purity chemicals (lauric and stearic acids and indium). After the isothermal curing measurements, dynamic scans were recorded between -40 and 200°C at $10^\circ\text{C}/\text{min}$ under dry nitrogen ($20\text{ cm}^3/\text{min}$) with copolymer samples of about 20 mg. We estimated the total and residual heats of the reaction by drawing a straight line connecting the baseline before and after the peak and integrating the areas under the peak. The actual T_g values were estimated as the temperatures at the midpoint of a line drawn between the temperature of the intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of the intersection of the tangent drawn through the point of inflection with the final tangent. The listed value is the average for several measurements realized for each sample.

The rheological behavior of the curing reaction was studied by dynamic oscillation with a Rheometric RDA II dynamic analyzer (Frankfurt, Germany) with parallel-plate tools. The plate diameter and its gap were 25.0 and 0.50 mm, respectively. The measurements were carried out during isothermal curing in the 50 – 100°C temperature range with an angular frequency of 1 Hz and an initial strain of 10% under

a dry nitrogen atmosphere. As the cure proceeded, the strain was automatically adjusted to maintain the torque response within the range of the transducer. The variation of the viscoelastic properties, such as the shear storage modulus (G') and loss modulus (G''), during curing were registered as a function of the reaction time.

RESULTS AND DISCUSSION

T_g versus the reaction conversion

The T_g determination as a function of conversion was carried out by DSC, where samples were isothermally cured in the calorimetry oven at different curing temperatures (from 50 to 100°C) for various periods of time. In particular, the cured samples were scanned at a rate of $10^\circ\text{C}/\text{min}$ from -40 to 200°C to determine T_g and the residual heat of reaction (ΔH_r). Figure 1 shows the ΔH_r dependence on T_g at different curing temperatures.

The degree of curing (α) is defined as the total heat generated at time t (ΔH_t) with respect to the total heat of reaction (ΔH_T) reached during the polymerization. Therefore, α is determined as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_T} = 1 - \frac{\Delta H_r}{\Delta H_t} \quad (1)$$

DiBenedetto's equation,²⁰ which is indicated for highly crosslinked systems, was used to model the master curve through the treatment of λ as an adjustable structure-dependent parameter:

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2)$$

where T_{g0} is the glass-transition temperature of the uncured material (-11.3°C) and $T_{g\infty}$ is the maximum glass-transition temperature (67.8°C); both were experimentally determined by DSC. According to the model we used, λ varied between 0 and 1, where a high value of λ represented a proportional T_g enhancement with respect to the conversion degree increase and a low value of λ means a very high increase in T_g at high conversion degrees. Figure 2 shows the α dependence on T_g at different curing temperatures and the fitting curve made with DiBenedetto's equation. The obtained λ value was 0.42; this was in agreement with the λ values found for other epoxy-amine systems.^{24,25} Therefore, the relationship between T_g and the degree of conversion, independent of the temperature range explored, was demonstrated.²⁶ This indicated that the molecular structures of the samples cured under different conditions were the same at a given conversion or that the structural differences did not

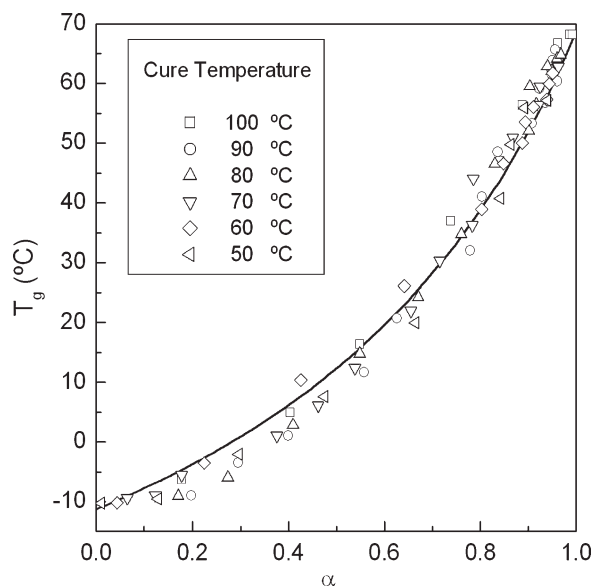


Figure 2 Dependence of T_g on α at different isothermal curing temperatures for the P(GMA-co-BA) copolymer with Jeffamine D-230 according to DiBenedetto's equation.

have a significant influence on T_g (the possible structural variation occurred in a range that could not be measured by T_g). Consequently, a master curve could be built, which helped to understand the molecular characteristics and thermodynamic properties of this material.

Time-temperature superposition

Assuming that the polymerization reaction was kinetically controlled and that a unique apparent activation energy (E_a) could be defined, we established a relationship between the time and temperature by taking the time-temperature superposition principle. Figure 3(a) shows T_g values as a function of the curing time at different isothermal curing temperatures. As shown in Figure 3(b), the master curve was made up by a horizontal shift of the different curves and with the curve obtained at 80°C as the curing temperature of reference. This curve matched well at T_g values lower than 50°C, which were below vitrification point.

E_a of the curing reaction was obtained as the slope of the shift factor (a_T) at various isothermal curing temperatures for this system versus the reciprocal of the temperature ($1/T$) because a_T , Arrhenius-like, was dependent on temperature as follows:

$$E_a = -RTa_T \quad (3)$$

where R is the ideal gas constant and T is the absolute temperature.

The representation of a_T is plotted in Figure 4, where a value of $E_a = 60 \pm 1$ kJ/mol was found.

This value was in agreement with that obtained from the t_{gel} measurements (as is described later) and also with other bifunctional epoxy resin systems. Wisanrakkit and Gillham²⁶ determined an E_a value of 63.5 kJ/mol for systems based on diglycidyl ether of bisphenol A (DGEBA) and bifunctional amines; when DGEBA was used with diethylenetriamine, values between 56 and 59 kJ/mol were found.^{18,27-30} Previously, Kissinger³¹ determined an E_a value of 51.8 kJ/mol for the same reaction. This was in good agreement with that reported for DGEBA epoxy systems,^{6,7} even when anhydride cured agents⁸⁻¹⁰ were used, with values from 73 to 75 kJ/mol. On the other hand, Xie et al.³² calculated E_a values near 224 kJ/mol for tetrafunctional resins, such as N,N,N',N' -tetraglycidyl-4,4'-diaminodiphenylmethane cured with 4,4'-diaminodiphenyl sulfone, whereas Spadaro et al.³³ obtained values close to 169 kJ/mol for the

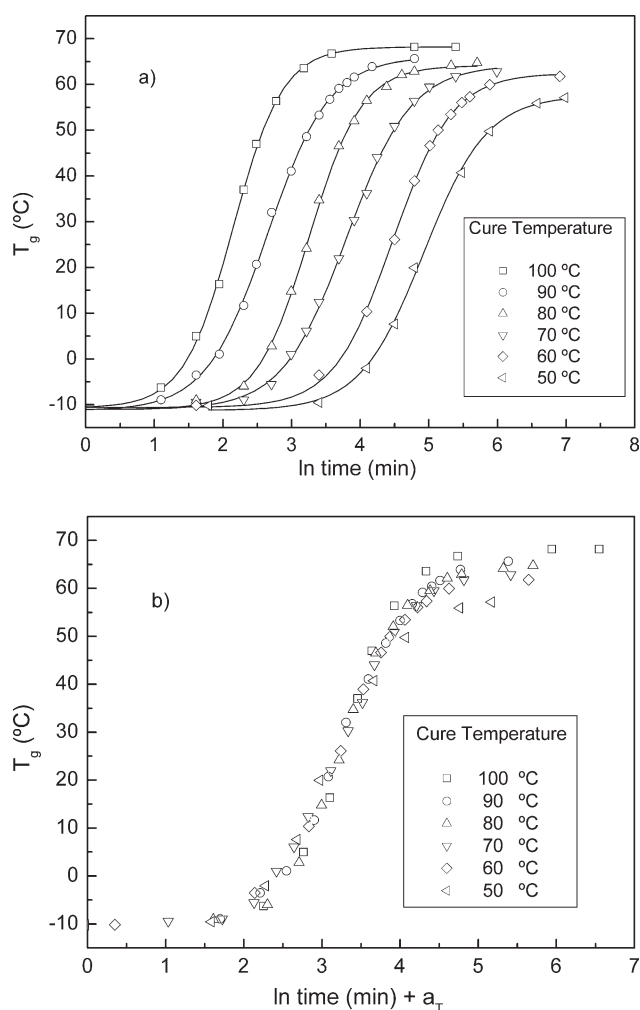


Figure 3 (a) Dependence of T_g on the cure time at different isothermal curing temperatures for the P(GMA-co-BA) copolymer with Jeffamine D-230 and (b) superposition of T_g as a function of time by horizontal shifting of the original curves to form a master curve with 80°C as the reference cure temperature.

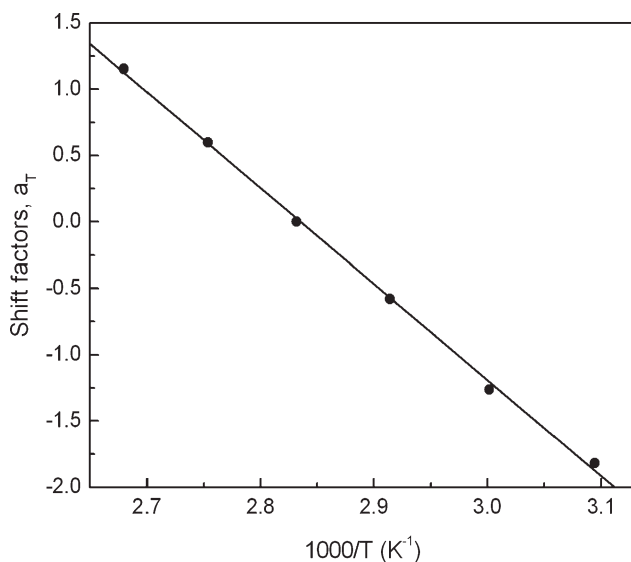


Figure 4 Arrhenius plot of a_T as a function of $1/T$.

same reaction. In this study, the resin based on P(GMA-co-BA) copolymer showed a total E_a similar to that attained with bifunctional epoxy resins, although higher values were expected because they presents relatively elevated amounts of glycidyl groups. Also, E_a was quite similar to those obtained by both isothermal and dynamic curing methods from DSC measurements.²¹

Gelation and vitrification measurements

The gel point of an epoxy system is most commonly determined with rheological methods, although other measurement methods, such as solubility, can be also used.¹² Therefore, different criteria have been proposed in the literature for determining t_{gel} by the monitoring of variations in the material dynamic mechanical properties. In this study, the t_{gel} values were determined from the G' and G'' crossover point, and their values are summarized in Table I. Figure 5 depicts the dynamic mechanical characterization of the 70°C isothermal curing of the resin. As shown, the dynamic moduli increased sharply and then gradually leveled off as the cure approached

TABLE I
 t_{gel} and t_{vit} Values at Various Isothermal Cure Temperatures for the P(GMA-co-BA) Copolymer with Jeffamine D-230

Temperature (°C)	t_{gel} (min)	t_{vit} (min)
50	26.0	167.3
60	10.5	107.7
70	4.5	62.8
80	1.9	37.3
90	1.0	24.0
100	0.5	14.5

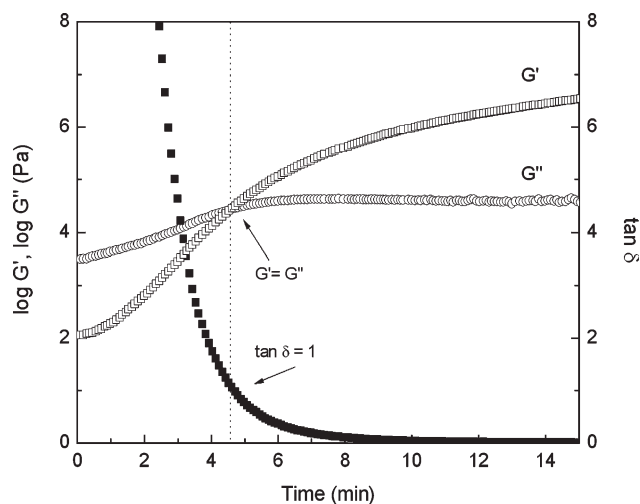


Figure 5 Evolution of different dynamic properties for the 70°C isothermal curing of the P(GMA-co-BA) copolymer with Jeffamine D-230.

the finishing point. G' presented a lower initial value and attained a higher maximum at the end of the cure cycle. Consequently, the two modulus curves intersected ($G' = G''$ or $\tan \delta = 1$) at $t_{gel} = 4.5$ min. When we associated the extent of the reaction with the t_{gel} obtained, we observed that gelation occurred at roughly 6% conversion, independently of the curing temperatures imposed. The fact that the extension of the reaction at gelation was independent of the curing temperature is a common observation, and similar results have been obtained for other epoxy systems.^{12,34}

The temperature at which the measurement is performed is an important factor for the validity of this criterion for gelation. Because gelation represents a specific extent of reaction, the temperature dependence of the time to gel can be described by the Arrhenius equation, as follows:

$$\ln t_{gel} = C + \frac{E_a}{RT} \quad (4)$$

where C is a constant factor.

The t_{gel} , as determined from the time at which $G' = G''$, against $1/T$ is plotted in Figure 6. A linear relation in the curing temperatures range studied was found and defined an E_a of 78 ± 1 kJ/mol.

Applying the gelation theory described by Flory,^{35,36} we defined the extent of the reaction at the gel point as follows:

$$\alpha_{gel} = \left[\frac{r}{(f_e - 1)(f_a - 1)} \right]^{1/2} \quad (5)$$

where f_e and f_a are the epoxy and amine functionalities, respectively, and r is the amine/epoxy stoichiometric ratio. In this case, with an epoxy-resin system

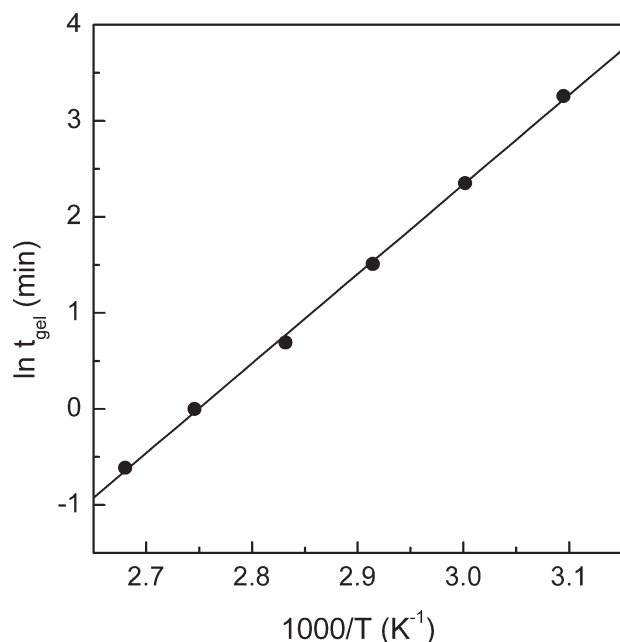


Figure 6 Arrhenius plot of t_{gel} as a function of $1/T$.

based on a P(GMA-co-BA) copolymer and a linear aliphatic amine, Jeffamine D-230, where at $f_e = 100$, $f_a = 2$ and $r = 1$, the theoretical gelation took place at a conversion value of 10% ($\alpha_{gel} = 0.10$). This theoretical value agreed with the value obtained experimentally ($\alpha_{gel} = 0.06$); however, it was lower than the one calculated by Flory's theory for bifunctional resins with tetrafunctional amines,³⁶ which was approximately $\alpha_{gel} = 0.58$ (58%), probably because of the elevated epoxy content in the copolymer.

The gel-point T_g was determined with DiBenedetto's equation with $\alpha_{gel} = 0.06$ and $\lambda = 0.42$. The obtained value was -9.2°C .

On the other hand, for the vitrification point, no general criterion has been defined or accepted so far for its determination, and several methods based on different criteria are used arbitrarily. Consequently, a strong dependence of the measured values on the methodology used is observed. In our previous article,²¹ the critical conversion (the conversion value where the diffusion process starts to be predominant) was calculated from the reaction kinetics obtained by DSC measurements. It is well-known that the vitrification process induces a modification of the kinetics by prohibiting further reactions, although a very slow diffusion-controlled reaction may occur in the glassy state. As a result, the curing reaction kinetics go from chemistry-driven to diffusion-controlled. In this study, T_g at these critical conversions was estimated throughout the obtained T_g -conversion degree relationship. The values of the vitrification time (t_{vit}) are also summarized in Table I. To determine the reliability of these data, the vitrification points of this epoxy system under study were also determined

with rheological measurements. In this case, the criterion adopted for its determination was the $\tan \delta$ peak at a frequency of 1 Hz by a dynamic time sweep test because this method provided better correspondence with the DSC data.²⁹ Thus for example, the rheological vitrification observations for the curing isotherm temperatures of 80 and 90°C were at 36.8 and 26.9 min, respectively. The t_{vit} values obtained by this approach revealed that the correlation between both methods was quite good.

TTT cure diagram

The TTT cure diagram of P(GMA-co-BA) copolymer and Jeffamine D-230 is shown in Figure 7. This diagram shows the gelation and the vitrification contours at different conversion degrees. As shown, both vitrification and gelation took place rapidly, so the TTT diagram for this system had a very difficult construction. In this diagram are plotted the T_g contours of the uncured system (T_{g0}) and the totally cured resin ($T_{g\infty}$) and the gel-point T_g obtained from DiBenedetto's equation for $\lambda = 0.42$ and $\alpha_{gel} = 0.06$ (gel-point $T_g = -9.2^\circ\text{C}$). Moreover, the gelation and vitrification points at different curing temperatures are plotted, and the isoconversion curves, obtained by the integration of DiBenedetto's equation, are also fitted. This sort of diagram allows the establishment of a borderline between the gel state and the glassy state. When $T < T_{g0}$, the unreacted blend prepared with the resin and hardener was in the glassy state. Likewise, when $T > \text{gel-point } T_g$ and $t < t_{gel}$, the blend behaved as a thermoplastic fluid, so it was supposed that the resin and hardener had still not reacted. These conditions of time and temperature could be ideal settings for the use of the blend in

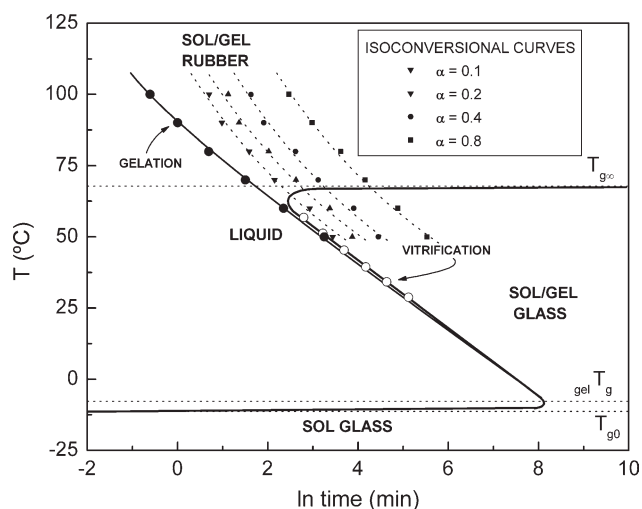


Figure 7 Generalized TTT isothermal curing diagram with isoconversion contours. Gelation, vitrification, and isoconversion contours, as well as the various states of the material, are shown.

any real application and could delimitate the pot-life time. The t_{gel} and t_{vit} values limited the border area where the blend changed from a thermoplastic prepolymer to a solid thermosetting material. The rapidity and proximity with which both actions took place showed the high reactivity of the copolymer used as a resin, whose α_{gel} even appeared at $\alpha = 0.1$. As a result, because the curing kinetics of acrylic resins were very fast, the system under study required working temperatures lower than T_{g0} and short periods of time to retain its preservation.

CONCLUSIONS

The curing reaction of a polyfunctional epoxy resin based on a GMA copolymer, synthesized by ATRP, and Jeffamine D-230 was investigated, and a general relationship between T_g and the conversion was achieved for this system. The results suggest that the reaction path and the relative reaction rates were independent of the curing temperature. Consequently, T_g was used to measure conversion. This was of practical importance because T_g could be measured more easily and accurately than the conversion from ΔH_r , especially at high conversion, where T_g was increasing, but there was little or no measurable change in the residual heat data from the DSC scans. The t_{gel} and t_{vit} values and the corresponding conversions at different curing temperatures analyzed were determined from the rheological and kinetic parameters, which controlled the crosslinking process. Finally, the TTT diagram was constructed and allowed the selection of optimal curing conditions for this novel epoxy acrylic system.

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