DETERMINATION OF GEL AND VITRIFICATION TIMES OF THERMOSET CURING PROCESS BY MEANS OF TMA, DMTA AND DSC TECHNIQUES
TTT diagram

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Abstract

In the present work, gelation and vitrification experimental data are obtained by TMA and DMTA techniques using the same thermoset based on an epoxy-amine system. The results show that the times obtained are not equivalent and depend on the technique used. An attempt has been made to compare both determinations using the degree of cure obtained by means of DSC technique. The principal conclusion that we want to emphasize is that it is the conversion degree and not the time of the phenomenological changes that take place during cure, that is the link to connect and interrelate the results obtained with different techniques. A method is also described for constructing the TTT diagram with only DSC and TMA or DMTA data.

Keywords: curing kinetics, epoxy-amine resin, gelation, TTT cure diagram, vitrification

Introduction

Gillham's [1] adaption of the time-temperature-transformation (TTT) cure diagram to aid the understanding of the cure process of thermosets has been widely utilized for analyzing and designing cure processes of thermosets and thermoset composites. Basically, it is a representation of the time to gel (t_g) and the time to vitrify (t_v) for isothermal cure over a wide temperature range (usually between the glass temperature of unreacted monomer mixture and that of the fully cured resin).

These data like iso-conversion or iso-T_g curves, can be calculated if a kinetic model of the reaction is known. Although a lot of work has been published on the cure kinetics models, theoretical conversion/time curves and theoretical extended kinetic equations, some experimental work is still required in order to obtain the parameters that the model utilizes or to verify that the model is correct. Important experimental results are gelation and vitrification points.

The gel point is defined as the time at which covalent bonds connect across the network and produce a material of infinite molecular weight. As gelation is approached, viscosity increases dramatically, and the weight-average molecular weight goes to infinity although the number-average molecular weight is small. Af-

ter gelation, soluble (sol fraction) and insoluble (gel fraction) materials are present. As the reaction proceeds, the amount of gel increases at the expense of the sol. Several techniques have been utilized to obtain gelation data: torsional braid analysis (TBA), viscosimetry, rheometry (RDA), thermal mechanical analysis (TMA) and dynamical mechanical thermal analysis (DMTA), among others [2].

The vitrification point of a curing system is the time at which the material solidifies and chemical reactions can be quenched permitting only very slow diffusion-controlled reactions. At vitrification point, the glass transition temperature T_g equals the curing temperature T_c due to the transformation from rubbery material to glassy material. The most important experimental techniques used to determine vitrification points are: torsional braid analysis (TBA), dynamical mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) [3].

A key problem in experimental determinations is the assigment of gel time and vitrification time to experimental curves since the transformations occur as functions of time (in a nonequilibrium process), the data obtained with different techniques are usually not interchangeable. See reference [4] for a more detailed discussion. In the present work, gelation and vitrification experimental data are obtained by TMA and DMTA isothermal techniques. Vitrification experimental points are also obtained by curing samples at different temperatures for different times until the material vitrifies and the T_g equals the curing temperature. Experimental cure conversion at gel and vitrification points have been obtained from DSC, TMA and DMTA samples by dynamical DSC experiences, from residual heat or from T_g-conversion master curves.

Experimental

Materials

The system used in this study was composed of Ciba-Geigy's Araldite GY250 epoxy resin which contains, basically, oligomers of the diglycidylether of Bisphenol A (DGEBA) with an epoxy equivalent weight of 188 g/equivalent. The hardener was an aromatic amine adduct HY830, with active hydrogen equivalent weight of 113 g/equivalent. The aminic hardener contained a 40% of di(butyl)phthalate as a plasticizer. Both of the ingredients were used as received. The stoichiometric mixtures were prepared by mixing 100 parts of epoxy resin with 60 parts of hardener with continuous stirring by hand. The total mixing time was approximately 5 min.

Techniques

DSC

The calorimetric measurements were made with a Mettler DSC 30 calorimeter coupled to a Mettler TA4000 thermoanalyzer. The mass of the samples was 10 mg. All samples were cured in a nitrogen atmosphere. Isothermal curing was performed within a temperature range of –20 to 105°C for various periods. After the isothermal curing, the resin samples were cooled and a dynamic scan was performed at a

heating rate of 10 K min^{-1} from −100 to 250°C to determine the residual heat (ΔH_{res}) and the T_g. The degree of conversion was calculated from the ΔH_{res} of the partially cured resin and from the total reaction heat (ΔH_R) associated with the complete conversion of all reactive groups, $\alpha = (\Delta H_R - \Delta H_{res})/\Delta H_R$. The total reaction heat (ΔH_R) was obtained in a similar way by using an uncured sample (freshly prepared resin mixture). Figure 1 shows the DSC dynamic scan of a sample partially cured at $T_c = 95°C$ and the determination of T_g and residual heat.

TMA

A Mettler TA4000 thermoanalyzer with a TMA40 measuring cell was used to measure the length of a sample as a function of time. In this way dimensional changes of the sample can be measured. TMA can be used to characterize the change from a liquid resin to a solid (gelation). About 200 mg of liquid resin were placed in a container, which was fixed on the sample support. A periodic force (cycle time = 12 s) of ±0.05 N was automatically applied to the sample, while the temperature was kept constant. 50, 65, 80, 95, 100 and 105°C isothermal experiments were performed. The force changed every 6 s from −0.05 to +0.05 N. Owing to this force, the sensor moved up and down while the resin was still liquid. When the material reached sufficient mechanical stability (gelation), the TMA measuring probe was trapped in the solid sample and the sensor was unable to respond to the force applied. At this moment the sudden decrease in the amplitude of the oscillations revealed that the sample had reached gelation. Then, the samples were quenched by rapid cooling and a dynamic scan was performed from −100 to 250°C at a heating rate of 10 K min^{-1} to determine T_g, the residual heat (ΔH_{res}) and the gel conversion α_g. Figure 2 shows a TMA measurement of the gelation of the epoxy system at $T_c = 95°C$.

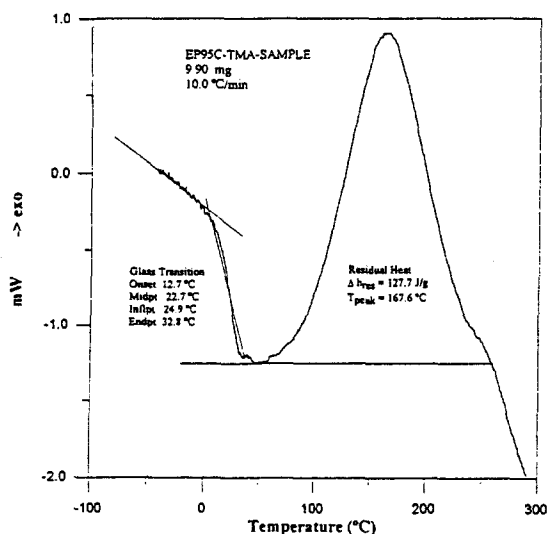

Fig. 1 DSC measurement of the T_g and residual heat ΔH_{res} of a stoichiometric epoxy-amine resin after a TMA measurement of gelation time (t_g) at $T_c = 95°C$

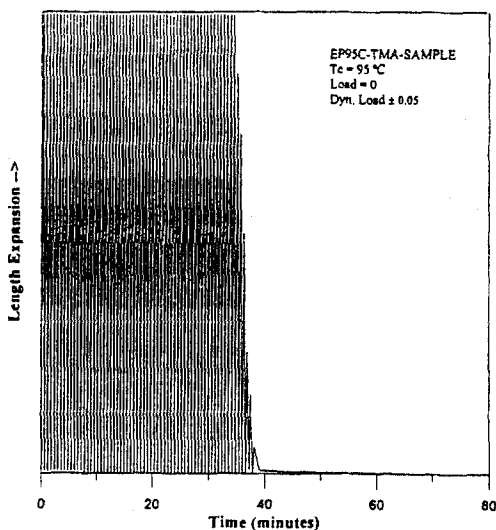**Fig. 2** TMA measurement of the gelation of the stoichiometric epoxy-amine resin under periodic force ($T=95°C$). Gelation is defined when the sensor cannot continue to react to the applied force
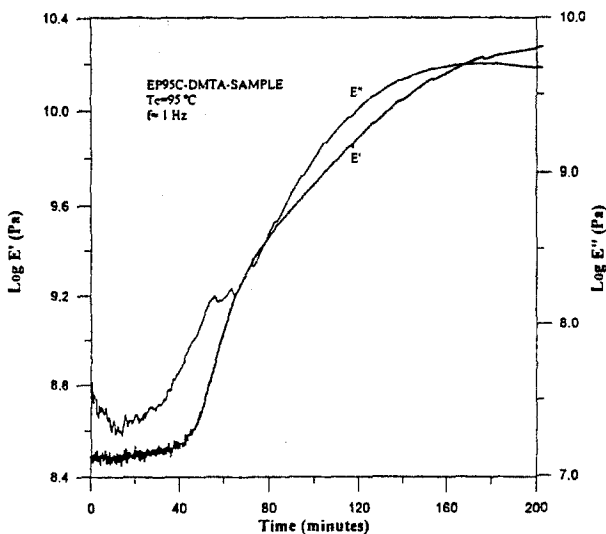

Fig. 3 DMTA measurement of the evolution of E' and E'' with the time of the stoichiometric epoxy-amine resin curing process at isothermal temperature of $95°C$. The frequency used was 1 Hz

DMTA

A Rheometrics dynamic mechanical thermal analyzer (DMTA) PL-DMTA MK3 was used to measure the storage modulus (E'), loss modulus (E'') and
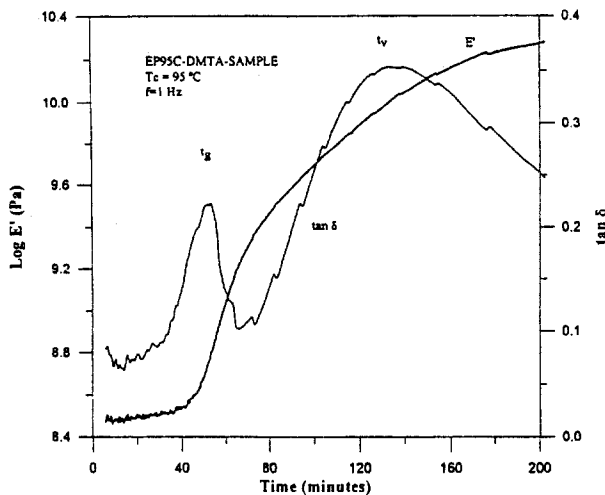
Fig. 4 DMTA measurement of the evolution of E' and tanδ with the time of the stoichiometric epoxy-amine resin curing process at isothermal temperature of 95°C. The frequency used was 1 Hz

tan$\delta = E''/E'$ of curing epoxy samples supported in a glass fibre fabric. Although E' and E'' were calculated from the composite (resin plus glass substrate), it is accepted that changes in E' and E'' were caused basically by the cure process of thermoset resin. 50, 65, 80, 95, 100 and 105°C isothermal experiments was performed in order to obtain E', E'' and tanδ changes with time. The frequency used was 1 Hz. Figure 3 shows the evolution of E' and E'' with time at an isothermal temperature of 95°C. E' and E'' are not in the same scale in order to produce the crossover of storage modulus and loss modulus. Figure 4 shows for the same temperature the evolution of E' and tanδ. While some authors [5–6] assume that the crossover of the E' and E'' (tan$\delta = 1$) indicates gelation and vitrification, others prefer to use the maximum of tanδ to characterise the gel and vitrification times [7–8]. In the present work, after reaching the first tanδ maximum, in some experiments the composite samples were quenched by rapid cooling and a DSC dynamic scan was performed from −100 to 250°C at a heating rate of 10 K min^{-1} to determine T_g and the residual heat (ΔH_{res}). In order to know the gel conversion α_g from residual heat, it was necessary to determinate from DSC samples the exact weight of the resin, by eliminating the resin from the resin-glass fibre composite in an oven.

Theoretical analysis

Applying the gelation theory described by Flory [9] the extent of reaction at the gel point is described by the following equations:

$$\alpha_{E_g} = \left[\frac{m_A f_A}{m_E f_E (f_A - 1)(f_E - 1)} \right]^{1/2} \tag{1}$$

$$\alpha_{A_g} = \left[\frac{m_E f_E}{m_A f_A (f_A - 1)(f_E - 1)} \right]^{1/2} \tag{2}$$

where α_{E_g} is the fraction of the epoxy group that has reacted at the gel point, m_E is the number of moles of epoxy component, and f_E is the functionality of the epoxy component present. The subscript A refers to the analogous quantities for the amine component, whilst subscript g refers to the quantities evaluated at the gel point. If a stoichiometric composition is used, both previous equations can be expressed in function of the functionality only

$$\alpha_{A_g} = \alpha_{E_g} = \alpha_g = \left[\frac{1}{(f_A - 1)(f_E - 1)} \right]^{1/2} \tag{3}$$

α_g is the extension of reaction at gel point. For the case of difunctional epoxy cured with a tetrafunctional amine, $f_E=2$, $f_A=4$ and $\alpha_g=0.577$. Experimental values of α_g are usually greater than the predicted theoretical values due to unequal reactivities of the same functional groups and intramolecular ring formation [10].

In order to obtain the vitrification point from T_g and conversion data, it is necessary to obtain a relationship between T_g and the extent of conversion at vitrification. Then, the time to vitrification can be calculated from the kinetics of the reaction.

One way of calculating T_g vs. α_v relationship is by DiBenedetto's equation [11]

$$\frac{T_g - T_{go}}{T_{go}} = \frac{(\varepsilon_x/\varepsilon_m - F_x/F_m)\alpha_v}{1 - (1 - F_x/F_m)\alpha_v} \tag{4}$$

where T_{go} is the glass transition temperature of the uncrosslinked polymer, $\varepsilon_x/\varepsilon_m$ is the ratio of lattice energies for crosslinked and uncrosslinked polymers, F_x/F_m is the ratio of segmental mobilities and α_v is used instead of X_c, the mole fraction of monomer units which are crosslinked in the polymer at vitrification. In a previous work [12], we fitted Eq. (4) to experimental α vs. T_g data for the same stoichiometric system and $\varepsilon_x/\varepsilon_m=0.64$ and $F_x/F_m=0.43$ were found. With these values, the DiBenedetto equation can be used to calculate α_v and then to determine the time to vitrification from the assumed kinetic rate law.

Under conditions far from diffusion control, the rate of a kinetically controlled reaction can be expressed by an Arrhenius rate expression:

$$\frac{d\alpha}{dt} = kf(\alpha) = k_o \exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

where α is the extent of reaction, k is the reaction rate constant, k_o is the Arrhenius frequency, E is the activation energy and $f(\alpha)$ the conversion-dependence function. By rearranging and integrating Eq. (5) for a curing time of $t=0$ where $\alpha=0$ for a time t with a degree of curing α, we obtain:

$$\ln t = \frac{E}{RT} + \left[\ln\left(\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} \right) - \ln(k_0) \right] \tag{6}$$

For a fixed conversion, the terms in the square brackets are constant. Equation (6) can be expressed as:

$$\ln t = A + \frac{E}{RT} \tag{7}$$

where constant A is only a function of α, or equivalently, only a function of the glass transition temperature T_g if there is a unique relationship between α and T_g. By applying Eq. (7) at a series of isothermal experiments for a constant conversion, it is possible to determine the activation energy E and the constant A from the slope and the intercept of the linear relationship $\ln t$ vs. T^{-1}. Alternatively, Eq. (7) can be applied to different degrees of conversion in order to see how the reaction evolves or whether the activation energy changes with the degree of conversion.

Results and discussion

Figure 5 shows the extent of reaction at gel point vs. temperature for a series of TMA and DMTA determinations. It has already been stated that gelation was determined by TMA and DMTA in both experiments. At the moment the material gelled, the experiment was stopped, the sample was cooled rapidly and T_g, the residual heat, and degree of gel conversion were determined by DSC. As can be seen
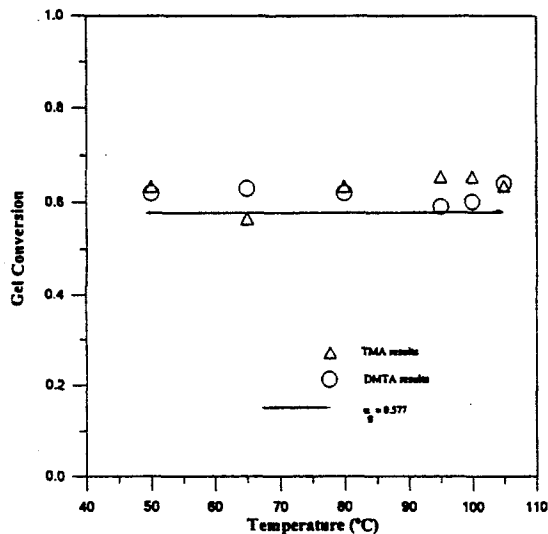

Fig. 5 Degrees of gel conversion against temperature determined by DSC from the TMA and DMTA experimental curing processes of the stoichiometric epoxy-amine system

in Fig. 5, the α_g is independent of the curing temperature and of the experimental technique used. A constant value of $\alpha_g = 0.62 \pm 0.03$ has been obtained that only differs slightly from the theoretical value of 0.577 for the system used. This indicates, as predicted by the theory, that gelation is an isoconversional phenomenon.
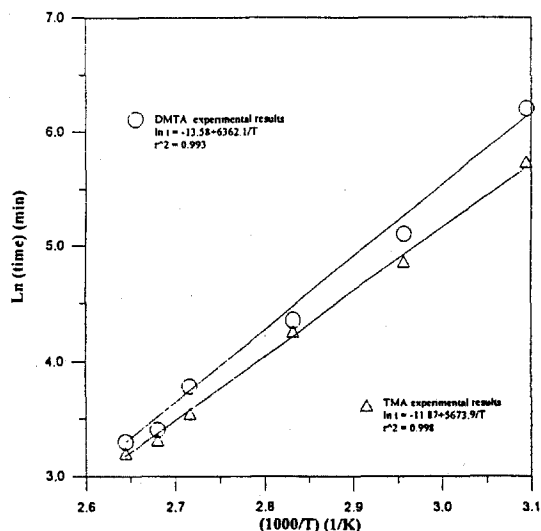

Fig. 6 Logarithm of gel times *vs.* the inverse of the temperature for different TMA and DMTA experimental curing processes of the stoichiometric epoxy-amine resin
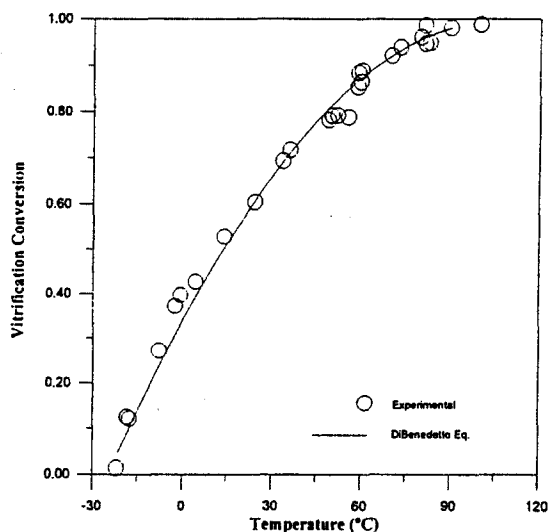

Fig. 7 Degrees of vitrification conversion against temperature from the DSC and DMTA experimental curing processes of the stoichiometric epoxy-amine system. The solid line represent the values obtained by Eq. (4)

The times of gelation at different temperatures for TMA and DMTA experiments are shown in Fig. 6. It can be seen that the time taken by the material to gel in the TMA does not coincide with the time taken in the DMTA (even if they have the same α_g). Neither do they coincide with the time taken in the DSC calorimeter to reach the same degree of conversion. The gel time depends on experimental process. It can be also seen from Fig. 6 that at low temperatures the differences are more important than at higher ones. Thus, if we wish to obtain the t_g, knowing α_g, we must use some kinetic procedure to obtain the time taken to reach α_g. From
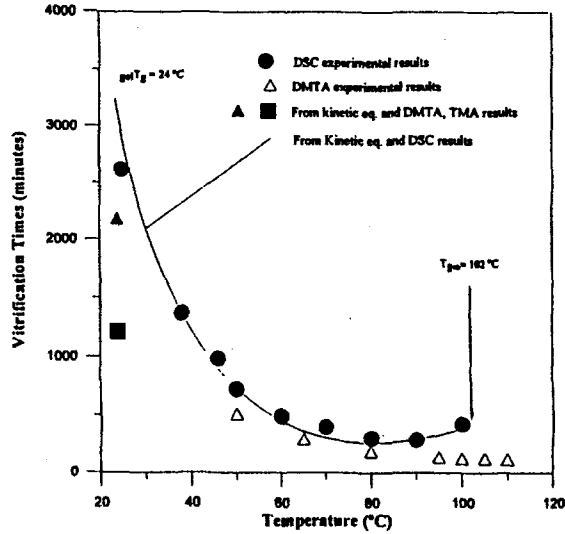

Fig. 8 Experimental DMTA and DSC vitirification times *vs.* the cure temperature of the stoichiometric epoxy-amine resin. The solid line represent the values obtained by Eq. (7) and DSC isothermal experiments
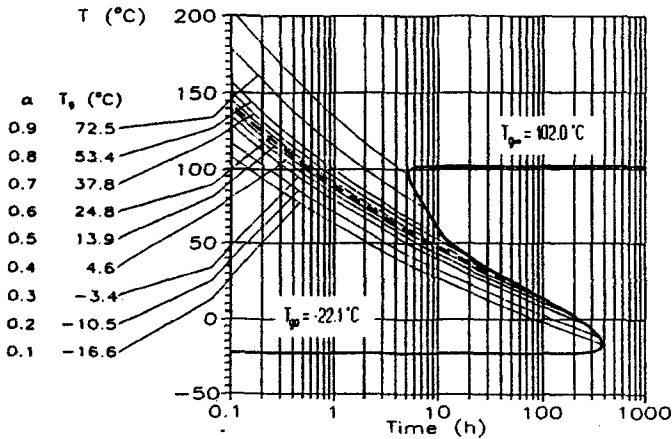

Fig. 9 TTT cure diagram for epoxy resin, showing the isoconversional lines, the vitrification curve and the gelation line (----)

Fig. 6 it is possible to determine the activation energy E and the constant A from the slope and the intercept of the linear relationship $\ln t$ vs. T^{-1}. The TMA kinetic process is characterised by values of $E=47.2$ kJ mol^{-1} and $A=-11.87$ min and the DMTA kinetic process by $E=52.9$ kJ mol^{-1} and $A=-13.59$ min.

Figure 7 shows the experimental degree of conversion at vitrification in function of the curing temperature. The continuous line is a representation of α_v-T using Eq. (4) that coincides fairly well with the values obtained experimentally, the only exception being a slight discrepancy at high conversion. The α_v-T relationship is independent of the curing temperature and of the technique used.

The experimental times of vitrification at different temperatures for DSC and DMTA experiments are shown in Fig. 8. As with gelation time, the vitrification time depends on the process and technique used. In order to determine the vitrification time for specific process, it is necessary to known the conversion at vitrification and a kinetic equation to determinate from that the t_v.

For a specified experimental process, in order to apply the preceding comments to establish gel and vitrification times and to construct the TTT diagram, the next methodology is proposed:

a) Gel point (α_g, t_g). The samples can be gelled in the TMA or DMTA techniques. The T_g or residual heat of the gelled samples can be used to determine the α_g. Then, the values for t_g can be taken as the times needed to reach a conversion of α_g, using an isoconversional adjustment such as $\ln t = A + E/RT$. Previously, A and E must have been obtained for different conversions.

b) Vitrification point (α_v, t_v). From experimental data or using an analytical expression, it is necessary to establish the $T_g-\alpha_v$ relationship. The values for t_v can be taken as the times needed for the material to reach the conversion α_v at which $T_g=T_c$, and it is calculated from the isoconversional kinetic adjustment.

c) Other points such as T_{go}, the glass transition temperature of the uncured reactants, and $T_{g\infty}$, the glass transition temperature of the fully reacted system, can be obtained calorimetrically. Values for T_{go} and $T_{g\infty}$ of -22.1 and 102°C has been obtained for the system studied.

d) The $_{gel}T_g$, the temperature at which the material gels and vitrifies simultaneously, can be determined as the temperature at which the material vitrifies on reaching a conversion equal to α_g. For the system studied, a value for $_{gel}T_g$ of 24°C has been obtained. The maximum time taken for the material to gel and vitrify simultaneously can be determined from the α_g isoconversional line.

Figure 9 shows the TTT curve diagram for epoxy resin obtained with the preceding methodology. The dashed line corresponds to gelation times. The wider solid curve corresponds to vitrification times.

Conclusions

The gel and vitrification times depend on the experimental kinetic process (the experimental technique). The experimental times obtained with different techniques are not interchangeable and the differences increase at experimental isothermal process at low temperatures.

The principal conclusion that we want to emphasize is that it is the conversion degree and not the time of the phenomenological changes that take place during cure, that is the link to connect and interrelate the results obtained with different experimental procedures.

Times must be obtained from a conversion degree and a well-known kinetic equation that describes the process at different curing stages. A method is also proposed to construct the TTT diagram for a specific process by knowing only DSC and TMA or DMTA data.

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