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Kinetic and rheological studies of an unsaturated polyester cured with different catalyst amounts

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An unsaturated polyester resin was cured with different catalyst contents. The crosslinking process was followed by static and dynamic viscosimetry and by differential scanning calorimetry (d.s.c.). Activation energies were determined from the gel times obtained by viscosimetry and from the variation in the maximum exotherm temperature obtained by d.s.c. at different heating rates. The existence of a threshold in the amount of catalyst to use is shown by analysis of the gel times. The effect of catalyst content on the glass transition temperatures of the different mixtures has been analysed taking into account the crosslink density, measured by means of the rubber modulus obtained by dynamic mechanical tests.

(Keywords: unsaturated polyester; chemo-rheology; dynamic mechanical properties)

INTRODUCTION

In recent years, the processing of thermosetting resins has received increasing attention from industry, especially from the automotive and aerospace industries. In order to improve the ultimate and/or processing behaviour, other ingredients such as thermoplastic additives (for shrinkage control) and fillers can be added. The processing of thermosetting resins requires a fundamental understanding of the rheology and the polymerization reaction kinetics during cure.

Some researchers[1–5] have used differential scanning calorimetry (d.s.c.) to measure the curing kinetics of unsaturated polyester (UP) resins isothermally. Huang and Chen have carried out these studies at low (40°C), medium (70–90°C) and high (100–120°C) cure temperatures[6–8]. Other researchers[9–11] have studied the effect of temperature not only on the curing kinetics but also on rheological changes. It has been shown[9,12] that the rheological gel point takes place in the early stages of curing reactions, usually at conversions lower than 5%, as a consequence of the formation of microgel particles[13].

The kinetics of curing of polyester resins are normally very complex because many processes occur simultaneously. In the initiation stage, the initiator decomposes chemically, giving out free radicals. In the propagation or polymerization stage, these radicals can react with styrene or the polyester. The chains of polymer will grow and crosslink each other, according to three possible processes: styrene–polyester copolymerization, styrene homopolymerization and polyester homopolymerization, depending on the curing conditions used[14–19].

The aim of this paper is to analyse the effect of temperature on the curing kinetics of an unsaturated polyester using thermal analysis and the effect on the chemo-rheology using static and oscillatory techniques. A time–temperature–transformation (TTT) diagram is proposed. The effect of catalyst concentration on the chemo-rheology and on the dynamic mechanical properties is also studied. The existence of a threshold in the amount of catalyst to use is shown by analysis of the variations in gel times.

EXPERIMENTAL

Materials

The UP resin used (Estratil 1.112) was provided by Plastiform. Nuclear magnetic resonance (n.m.r.) spectroscopy (Varian VXR 300 MHz) was used to characterize the resin. Deuterochloroform ($CDCl_3$) was used to dissolve the resin. The Estratil 1.112 resin consisted of phthalic anhydride (PA), propylene glycol (PG), diethylene glycol (DEG) and maleic anhydride. The n.m.r. peak for maleic anhydride was very small because maleate isomerizes to fumarate (FA) extensively during the synthesis of UP resins. The relative compositions calculated were PA:FA:PG:DEG = 1:0.64:1.02:1.47. The molar ratio of styrene to UP C=C bonds was 1.86:1.

The amount of styrene contained in the UP resin was also determined by evacuating the styrene from the UP resin in an air-circulating oven at 110°C for 2 h. The styrene content, calculated from the weight loss, was 30 wt% (DIN 16945). The acid value of the resin was determined by end-group titration and was found to be 32.6 (ASTM D4662-87).

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The UP resin was used as received. The resin was not accelerated. A 50 wt% methyl ethyl ketone peroxide solution (Diprometil LA-50-R) was used as a catalyst to initiate the reaction. The concentration of the catalyst was 2% by weight of total resin for kinetic measurements. For rheological and dynamic mechanical studies, the concentrations of catalyst were 1.0, 1.2, 1.4, 1.6,1.8, 2.0 and 2.4%. The resin was mixed with the catalyst at room temperature and was then quickly sampled for kinetic and rheological measurements.

All the resin plaques were cast into a mould which consisted of two parallel glass plates separated by a U-shaped 5 mm steel frame spacer and held together by clips. It was necessary to coat all parts of the mould with Freekote 44 release agent before use. Blends were poured into the vertical mould, degassed at 40°C in a vacuum oven for 30 min and cured in an air-circulating oven held at 40°C for 2 h. On completion of this curing schedule, the blends were post-cured at 120°C for 2 h.

Thermal analysis

Reaction kinetics were measured by differential scanning calorimetry (d.s.c.) using a Perkin–Elmer DSC-7. All the reactions were conducted in hermetic aluminium sample pans. The weight of the samples ranged between 5 and 10 mg. Isothermal reaction rate vs. time profiles were obtained at 50–80°C. Isothermal runs were carried out at different times. Samples were then reheated from 30 to 250°C in the scanning mode with a heating rate of 10°C min^{-1} to determine the residual reactivity (ΔH_{res}). Runs were also carried out in the scanning mode from 30 to 250°C at a heating rate of 10°C min^{-1} to determine the total heat of reaction (ΔH_{s}). The overall conversion (X) was calculated from $X = (\Delta H_{\mathrm{s}} - \Delta H_{\mathrm{res}})/\Delta H_{\mathrm{s}}$.

The glass transition temperature (T_{g}) of the UP resin mixed with 2 wt% catalyst before reacting was taken as the onset value of the heat capacity change on scanning a sample from −80 to 10°C at 10°C min^{-1}.

The activation energy was determined from the variation in the maximum exotherm temperature (T_{m}) for different heating rates (ϕ) of 1, 2, 5, 10 and 20°C min^{-1}.

Rheological changes measured in a Haake viscometer

Rheological measurements were made with a Haake RV20 viscometer. Tests were conducted to have steady shearing flow values under isothermal conditions at various temperatures specified below. Samples of 60 g were placed in a cylindrical aluminium vessel. Another cylindrical device of 16 mm diameter was immersed in the sample and the viscosity was measured at a 1.03 s^{-1} shear rate. Gelation was assumed to occur at the point at which the viscosity reached a value of 1000 Pa s.

Rheological changes measured in a Metravib viscoanalyser

For rheological measurements, a Metravib viscoanalyser was also employed. The weight of the sample, introduced into a steel cylinder of 10 mm diameter, was around 4 g. Oscillatory shearing flow measurements were made with a device of 1 mm diameter in order to determine the dynamic behaviour at high conversions. The frequency used was 10 Hz for all experiments. The storage modulus (G'), loss modulus (G'') and loss factor (tan δ) values were measured during the isothermal reaction. Several researchers[20–22] have suggested that the crossover of G' and G'' could be an indication of the liquid–solid transition for crosslinking polymers, though for many systems[22,23] the gel point may not be the time value at $G' = G''$.

Dynamic mechanical analysis

Dynamic mechanical tests were carried out with a Metravib viscoanalyser and a three-point bending device with a span length of 44 mm. Specimens were machined to 60 × 12 × 5 mm from plaques prepared as described above. Tests at 10 Hz were made at a heating rate of 3°C min^{-1} over the temperature range 20–250°C. Glass transition temperatures (T_{g}) were taken as the temperatures corresponding to the maximum values of tan δ in the α relaxation.

RESULTS

The activation energy for the samples cured with 2 wt% catalyst was determined from the variation in the maximum exotherm temperature (obtained by d.s.c.) by plotting ln ϕ vs. $1/T_{\mathrm{m}}$ for different heating rates[24]. A value of 60.6 kJ mol^{-1} was obtained for the activation energy.

Figure 1 shows the reaction rate profiles obtained isothermally by d.s.c. over the 50–80°C range on samples containing 2 wt% catalyst. It is assumed that the amount of heat generated through curing is directly proportional to the conversion of the sample at a given time[25]. The reaction rate increased as the temperature increased. This is because a higher temperature increases the mobility of the C=C units. The induction time and the time to maximum rate became shorter with increasing temperature. These results are in agreement with other published data for unsaturated polyester resins[25–27].

Figure 2 shows the isothermal conversion profiles corresponding to *Figure 1*. It can be seen that the higher the temperature, the higher the overall conversion. This is because vitrification occurs at higher temperatures as the curing temperature increases. However, since full conversion was not reached at any curing temperature used, it is possible that many C=C bonds remained buried in the microgel structure, as has been claimed by Yang and Lee[15].

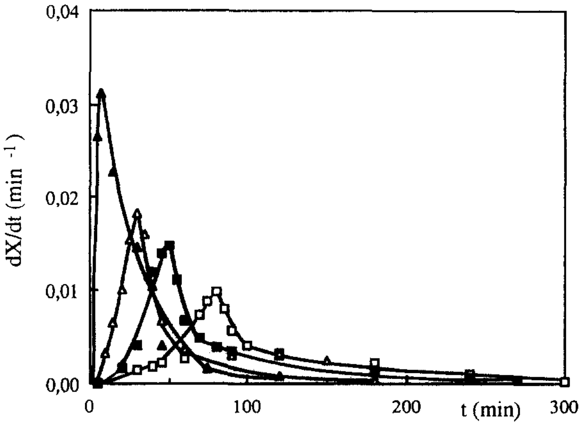

Figure 1 Reaction rate profiles at different temperatures: (□) 50°C; (■) 60°C; (△) 70°C; (▲) 80°C

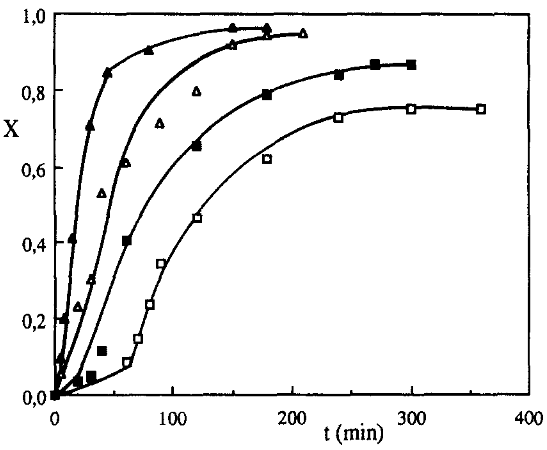

Figure 2 D.s.c. conversion profiles in the range 50–80°C. Symbols as in *Figure 1*

Steady and oscillatory rheological studies were made in order to correlate the viscosity changes during curing with the changes in overall conversion. *Figure 3* shows the variations in steady viscosity, dynamic modulus and loss modulus with time for a mixture containing 2 wt% catalyst at 50°C. Both G' and G'' increase as crosslinking reactions progress to give a maximum value for G'', corresponding to the vitrification time, after which G' remains practically constant. Gelation is defined as the point at which the curing system transforms suddenly from a viscous liquid to an elastic gel. Tung and Dynes[28] reported that the time at which the crossover of G' and G'' occurs during isothermal curing can be taken as the gel time. Winter and Chambon[21] also took this point as the gelation time, though indicating that for many systems the gel point may not be equal to the one calculated at $G' = G''$. A well-accepted indicator for the occurrence of gelation is a rapid increase in viscosity. When the viscosity increases to infinity, the gel point is considered to have been reached. However, it is not practical to measure an 'infinite' viscosity. An accepted method[2] is to define the gel point when the viscosity reaches a value of 10^4 or 10^3 Pa s. In fact[11], the gel points determined from $G' = G''$ for UP resins appear somewhat earlier than those determined from $\mu = 10^4$ or 10^3 Pa s. In this study, the rheological gelation times taken from steady ($\mu = 10^3$ Pa s) and dynamic ($G' = G''$) shearing measurements were similar. As shown by Hsu and Lee in studies on the curing of UP resins[12], these major changes in rheological properties occur at the very beginning of the curing reactions for a conversion lower than 5% in a way completely different to what happens for other thermosetting resins like epoxides. This premature gelation may be attributed to the spherical structures formed among the polyester molecules in the early stages of the curing reactions[2].

As shown in *Figures 4–6*, a similar behaviour was found for all curing temperatures analysed. For all cure conditions, rheological gelation happened much earlier than the chemical gel point and the overall conversions corresponding to the rheological gel points were very low in all cases. It has been shown[29–33] that microstructure formation, caused by intramolecular crosslinking between the double bonds of the polyester molecules, is the main feature in the curing of unsaturated polyester resins at low curing temperatures such as those used in this study. The microgels so formed would be involved in the next curing reaction steps, via inter- or intramicrogel crosslinking reactions, leading to the final structure of a crosslinked network in a complicated way in which the dominance of intermicrogels crosslinking reactions over intramicrogel crosslinking reactions would change with the extent of curing at constant temperature and may vary at other curing temperatures[6–8].

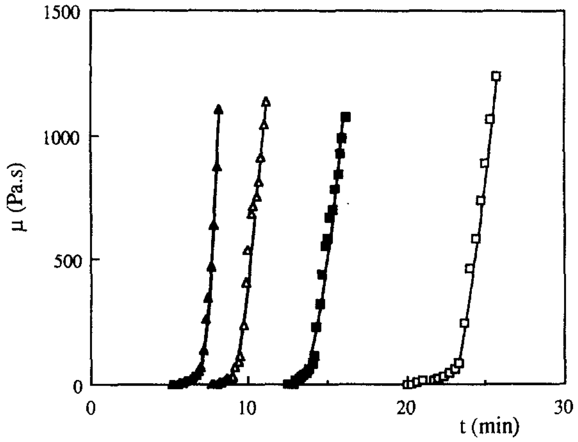

Figure 4 Changes in viscosity in the range 50–80°C. Symbols as in *Figure 1*

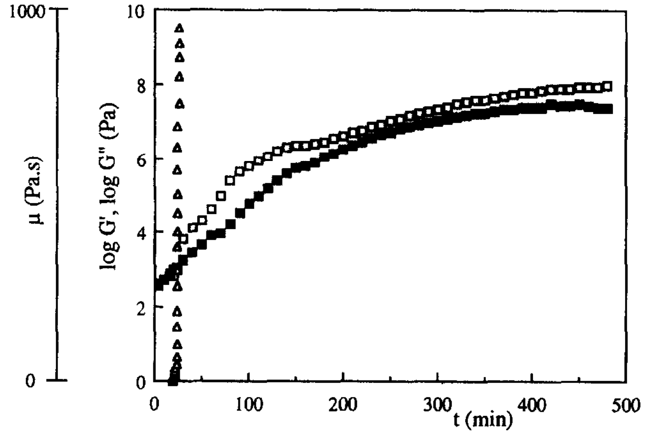

Figure 3 Changes in steady viscosity (△), dynamic modulus (□) and loss modulus (■) with time at 50°C

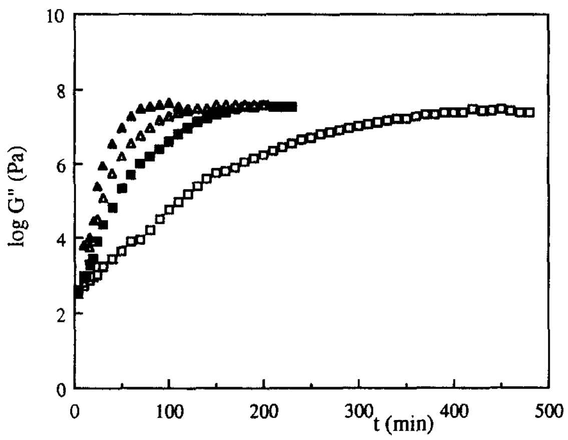

Figure 5 Variations in loss modulus in the range 50–80°C. Symbols as in *Figure 1*

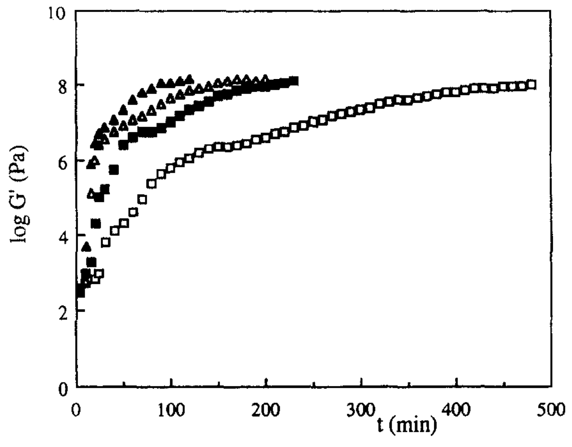

Figure 6 Variations in dynamic modulus in the range 50–80°C. Symbols as in *Figure 1*

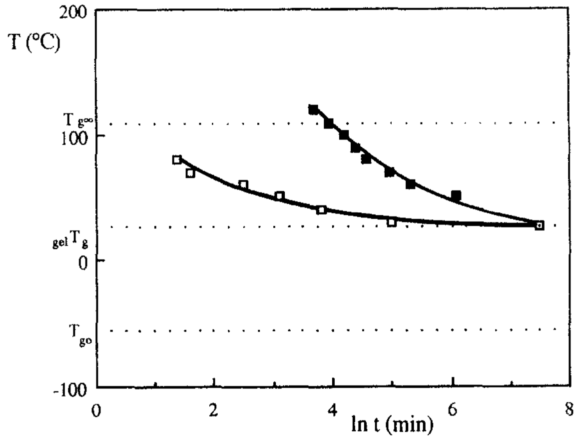

Figure 8 The isothermal time–temperature–transformation diagram: (□) gelation times; and (■) vitrification times

From an analysis of *Figures 5* and *6*, it becomes evident that crosslinking reactions occurred for a long time after the rheological gel point (occurring at log G' and log G'' values of around 3) had been reached since both G' and G'' increase continuously after this time. This increase in G' and G'' is similar to the increase in overall conversion (*Figure 2*) up to the vitrification point. The slight increase in G' and overall conversion after this point could be explained in terms of a diffusion-controlled mechanism of crosslinking taking over after the mixture has vitrified.

Figure 7 shows the times corresponding to gelation of the mixture cured with 2 wt% catalyst as a function of temperature. Rheological gelation times determined by the dynamic technique were slightly lower than those obtained from steady rheometry. From an Arrhenius approach, activation energies were calculated from the gelation times using a multiple-regression technique. The values calculated from the gelation times obtained by steady and dynamic viscosimetry were 61.8 and 64.5 kJ mol^{-1}, respectively. These values are similar to the one found by d.s.c.

Gillham and coworkers[34–36] have developed a diagram for thermosetting resins in an attempt to understand the curing phenomena. They have summarized the physical transformations, i.e. gelation and vitrification, of a thermosetting resin at different curing temperatures by means of a time–temperature–transformation (TTT) diagram. A TTT diagram for the UP resin is proposed in *Figure 8*. T_{g0} is the T_g corresponding to the initial, uncured mixture. $_{gel}T_g$ is the T_g when the processes of vitrification and gelation occur together. This was calculated from static viscosimetry results. The slopes of the viscosity vs. time profiles in the regions before and after the sharp rise in viscosity during curing were measured and plotted against reciprocal absolute curing temperature. The experimental values were well fitted by straight lines, which means that, within experimental error, the method was adequate to obtain the $_{gel}T_g$ values[37]. $T_{g\infty}$ is the maximum T_g attained by the system. This was found to be around 110°C by dynamic mechanical analysis. The sample was cured at 130°C for 90 min and then reheated from 20 to 250°C at 3°C min^{-1} in order to obtain the T_g value. As the T_g value measured for another sample cured at 150°C for 90 min was, within experimental error, the same, 110°C can be taken as the $T_{g\infty}$ value for this system. If $T < {}_{gel}T_g$, only vitrification will be observed. If $_{gel}T_g < T < T_{g\infty}$, both gelation and vitrification will be observed. It can be seen in *Figure 8* that the vitrification times continue to decrease at temperatures above $T_{g\infty}$, in contrast to the diagrams obtained for other thermosets like epoxides. On the other hand, the gel points at the higher temperatures do not appear in the diagram because gelation takes place too soon, before the curing temperature is reached in the viscoanalyser under the test conditions used.

The influence of the catalyst content on the crosslinking process and on the properties of the cured mixtures was also analysed in order to discover if there was any boundary in the amount to use. Gelation times at different curing temperatures as a function of catalyst content are displayed in *Figure 9*. An increase in catalyst concentration results in a decrease in gelation time for all curing temperatures employed owing to the higher rate of microgel formation during the early stages of the reaction[6–8,11]. Furthermore, the difference in gelation time for the same temperature becomes smaller as the catalyst concentration increases, indicating that there is a critical catalyst concentration beyond which the gelation time is practically constant. This fact has to be taken into account when choosing the optimum amount of catalyst

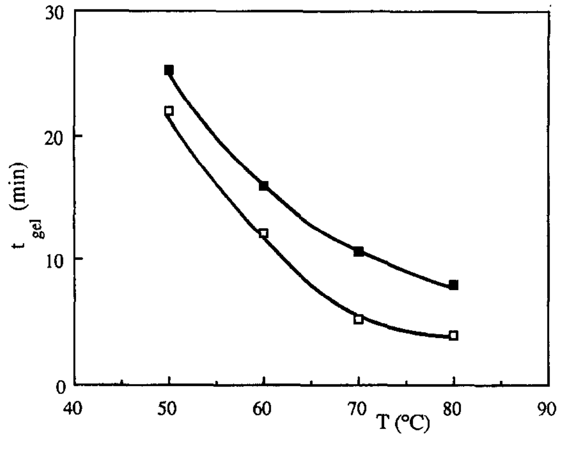

Figure 7 Gelation times determined by steady (■) and dynamic (□) viscosimetry

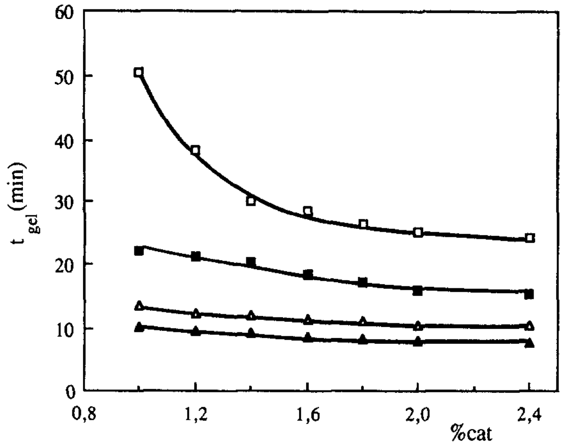

Figure 9 Gelation times at various temperatures for systems cured with different catalyst contents. Symbols as in *Figure 1*

to use. This knowledge may be important because an excess of catalyst can act as a plasticizer and modify the final properties of the cured resin. It is also worth noting that as the catalyst concentration changes the rate of microgel formation, it might also affect the dominance of intermicrogel or intramicrogel crosslinking reactions during curing, as shown by other authors[29].

In order to discover the influence of catalyst content on the ultimate behaviour of the cured resin, the glass transition temperatures of the plaques, crosslinked with the above-defined curing schedule, were studied by dynamic mechanical measurements. The glass transition temperature were found to be around 100°C for all mixtures, indicating that the variation in the amount of catalyst employed in this work did not influence the T_g of the network formed. It is worth noting that the T_g of each plaque was lower than the one obtained when the sample was isothermally cured at high temperatures and then reheated from 20 to 250°C at $3°\mathrm{C\,min^{-1}}$. This is probably because of the importance of the curing temperature in the early stages of the reaction when the dominance of inter- or intramicrogel crosslinking reactions may vary.

The crosslink density was determined from the average molecular weight between strands of the network (M_c) as a function of catalyst content. For estimation of M_c, an approximation of the simple rubber elasticity theory used by several authors[38–42] was employed. M_c was calculated from the rubbery modulus (E_r), obtained at $T_g + 50°\mathrm{C}$, by means of $M_c = 3dRT/E_r$, where d is the density of the material and T is the temperature in kelvin. The values obtained can be used in order to make comparisons, but they cannot be taken as absolute values because E_r is a function of the test conditions and usually the value obtained from dynamic techniques is higher than that from static measurements[43]. It was found that the average molecular weight between crosslinks was around $200\,\mathrm{g\,mol^{-1}}$ in all cases, indicating that the crosslink density of the cured samples does not depend on the catalyst content.

CONCLUSIONS

The rheological properties and glass transition behaviour of an unsaturated polyester cured with different catalyst amounts have been studied. The activation energies determined by different techniques for the mixtures cured with 2 wt% catalyst were similar at approximately $60\,\mathrm{kJ\,mol^{-1}}$.

The different catalyst amounts added to the mixtures did not significantly modify the glass transition temperature or the crosslink density in the studied range. Nevertheless, an increase in catalyst concentration resulted in a decrease in gelation time, probably because of the higher rate of microgel formation. Moreover, the difference in gelation time for the same curing temperature became smaller as the catalyst concentration increased, which indicates the existence of a critical catalyst concentration beyond which the gelation time remains practically constant. This fact has to be taken into account when choosing the optimum amount of catalyst because an excess could act as a plasticizer and modify the final properties of the cured resin.

An isothermal time–temperature–transformation (TTT) diagram was proposed. This diagram is very useful when choosing a convenient curing schedule for a particular application. The temperature at which gelation and vitrification take place simultaneously (${}_{gel}T_g$) is 26°C.

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