Glass transition temperature-cure temperature--transformation (T_gTT) diagram for EPY® epoxy system

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Abstract: The EPY® epoxy system applied for the production of machine foundation chocks was isothermally cured at varying cure temperatures and times. The thermal behavior during the curing of the system was monitored by means of the glass transition temperature (T_g) and conversion degree (α) measured using differential scanning calorimetry (DSC) and rotational viscometry (ARES). Also, the thermal decomposition was measured by thermogravimetry and differential thermal analysis (TG-DTA). The results were analyzed and summarized in the generalized phase diagram, as well as in the T_g-cure temperature-transformation (T_gTT) cure diagram. The phase diagram has reference to the transformations (in liquid, ungelled glass, gelled glass and rubber state) encountered at time to gelation and vitrification. Whereas the T_gTT diagram shows that there are three types of behavior related to the temperature of cure and makes a useful framework for understanding and analyzing the relations and interdependencies during the curing process of the epoxy system.

Keywords: epoxy system, curing, gelation, vitrification, glass transition temperature, glass transition temperature-cure temperature-transformation diagram.

Diagram temperatura zeszklenia-temperatura sieciowania-przemiana (T_gTT) dla układu epoksydowego EPY®

Streszczenie: Próbki układu epoksydowego EPY®, używanego do wytwarzania podkładek fundamentowych maszyn, sieciowano izotermicznie stosując różne temperatury i różny czas sieciowania. Metodami różnicowej kalorymetrii skaningowej (DSC) i wiskozymetrii rotacyjnej (ARES) zbadano przemiany tak przygotowanych układów pod wpływem zmian temperatury wyznaczając temperaturę zeszklenia (T_g) i stopień konwersji (α). Badano także rozkład termiczny próbek za pomocą symultanicznej termograwimetrycznej i różnicowej analizy termicznej (TG-DTA). Wyniki pomiarów analizy zestawiono w postaci uogólnionego diagramu fazowego oraz diagramu T_g-temperatura sieciowania--przemiana (T_gTT). Pierwszy z diagramów wskazuje odniesienia do transformacji (stan ciekły, szklisty całkowicie nieutwardzony, szklisty niecałkowicie utwardzony i zżelowany) występujących w czasie do momentu żelowania i zeszklenia układu, a diagram T_gTT pokazuje trzy rodzaje zachowań układu w zależności od temperatury sieciowania. Stanowi przydatne narzędzie do zrozumienia i analizowania relacji ujawniających się w procesie sieciowania układu epoksydowego.

Słowa kluczowe: układ epoksydowy, sieciowanie, żelowanie, zeszklenie, temperatura zeszklenia, diagram temperatura zeszklenia-temperatura sieciowania-przemiana.

Epoxy resins are the most common, high-performance, thermoset matrices used today in advanced polymer composites [1–3]. Due to their performance properties, they are extensively applied as coatings, adhesives, laminates, and electronic encapsulants, electrical insulations, as well as structural applications that require lightweight solutions and high strength. The physical, mechanical, and electrical properties of a thermosetting polymer are directly related to the degree of cure. The processability of a thermoset resin critically depends on the rate and extent of polymerization under specific processing conditions. Therefore, the kinetic characterization of the reactive resin is not only important for a better understanding of structure-property relationships, but it is also fundamental in optimizing the process conditions and product quality [1, 4]. To make optimum use of epoxies as structural materials, it is important to know how the curing process evolves, to what extent the transformation proceeds, what is the cured material structure and how all these variables are influenced and limited by temperature.

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Any change in the physical properties of a thermosetting polymer like epoxy resin during the cure process manifests itself through two phenomena: gelation and vitrification. Gelation is a sudden and irreversible transformation of a system from a viscous liquid to an elastic gel. It corresponds to the incipient formation of an infinitely crosslinked network. Vitrification involves the transformation from a liquid or a rubbery state to a glassy state as a result of an increase in the crosslinking density of the system. It is marked by the time at which the reaction mechanism of curing changes from kinetic controlled to diffusion controlled [5].

Knowledge of the curing process is required to determine the optimal processing conditions for the epoxy system such as time and temperature of curing so that the ultimate properties of the material can be reached.

One should be aware that the glass transition temperature (T_g) is the most important material parameter in a polymer application because it becomes the upper bound for the service temperature of an amorphous material. At T_g, there are also changes in the thermodynamic properties such as specific heat, thermal expansion coefficient and isothermal compressibility. The T_g of a thermosetting material is first of all a useful parameter to monitor the cure process [5, 6]. As the cure reaction advances, T_g increases nonlinearly with the conversion of the material and reaches a maximum value for a fully crosslinked structure [7].

A unique one-to-one relationship between the values of T_g and chemical conversion degree (α) for epoxy/amine systems was the topic of interest in many studies in the past and finally the empirical DiBenedetto equation [8, 9], reported by Nielsen [10], was broadly used to fit the experimental T_g versus α data [11–16]. Thanks to that, it is possible to carefully analyze the variation of T_g with respect to temperatures and times of isothermal curing and to provide information on cure kinetics (*e.g.*, activation energy) in order to understand cure systems (*e.g.*, state of cure, reaction mechanism) all the better.

A convenient summary of changes occurring during the cure of a thermosetting system, as well as relationships between the conditions of cure and material behavior, are provided by two cure diagrams:

– TTT diagram (time-temperature-transformation) formed by Gillham and Enns [17–19];

– CTT diagram (conversion-temperature-transformation) proposed by Adabo and Williams [20].

Both cure diagrams, *i.e.*, TTT and CTT, developed for the EPY® epoxy system were given in previous articles [21, 22]. Different material states and changes in the epoxy material during the curing, including gelation and vitrification, are shown in these diagrams as a function of time and α value, respectively.

A valuable complement to the above mentioned cure diagrams is the T_gTP diagram (glass transition temperature-temperature-property) where property denotes a specified property of the material [23, 24]. A diagram in

which the loss modulus stands for the specified property of the EPY® material was presented in a previous article [25]. The relationships between the loss modulus and the extent of cure (measured as glass transition temperature) are shown in the T_gTP diagram depending on various temperatures and different material states.

A complement to these three cure diagrams can be other generalized phase diagrams and also the T_gTT cure diagram (glass transition temperature-temperature-transformation) proposed by Gillham and coworkers [26, 27]. The generalized phase diagram for thermoset resins in which the gelation time and the vitrification time *versus* cure temperature (T_{cure}) are shown in Fig. 1. Whereas Fig. 2 presents the curing of thermoset resins by co-ordinates in conversion (measured by T_g) *versus* temperature graph, named the T_gTT cure diagram. Two temperatures: $_{gel}T_g$ (temperature at which gelation and vitrification take place simultaneously) and $T_{g\infty}$ (glass transition temperature of a fully reacted network, at which the conversion degree reaches its maximum value $\alpha = 1$) are critical temperatures in both the diagrams where the four states of materials encountered in the thermosetting process, *i.e.*: liquid, ungelled glass, gelled glass and rubber, are distinguished. It is to be noted here that the unreacted material corresponds to $T_g = T_{g0}$ and essentially no reaction occurs because the reactive species are immobilized in the glassy state; while the fully reacted material corresponds to $T_g = T_{g\infty}$, when the resin is fully cured and it is qualified by $\alpha = 1$. Different changes in the thermomechanical properties of the thermosetting resin during isothermal cure are represented by contours to reach a characteristic, specified state shown in Figs. 1 and 2. The diagrams show that the maximum thermoset conversion is bounded by
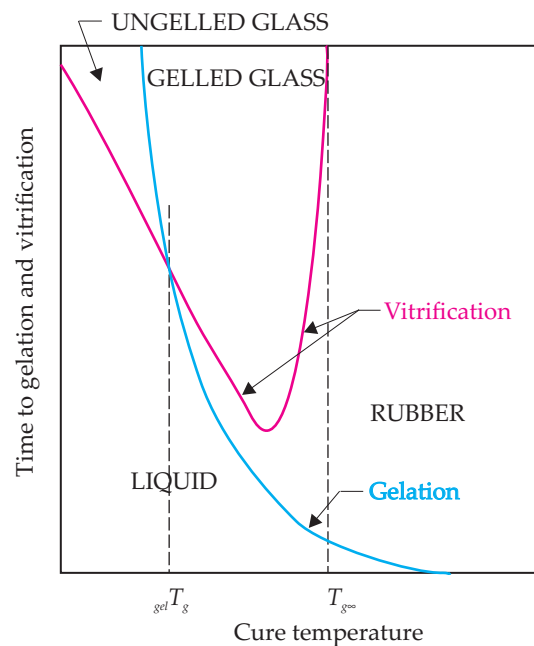

Fig. 1. A generalized phase diagram for thermosetting system showing dependence of time to gelation and time to vitrification *versus* isothermal cure temperature (T_{cure}) for an epoxy system
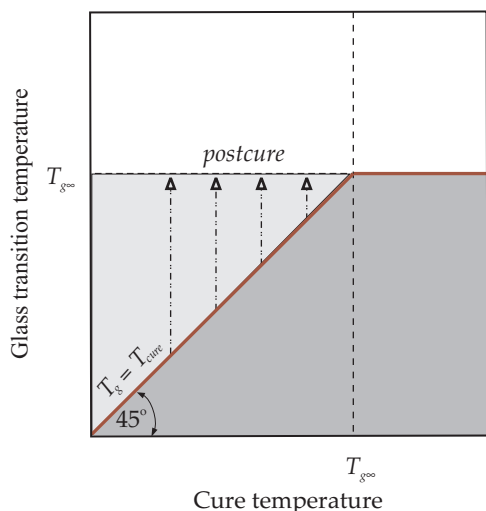
Fig. 2. Schematic diagram of glass transition temperature (T_g) to be expected from curing at isothermal temperature (T_{cure}) [note that the maximum value of the glass transition temperature ($T_{g\infty}$) is obtained only after heating above $T_{g\infty}$]

the vitrification curve $T_g = T_{cure}$ in the temperature range between T_{g0} (glass transition temperature of the unreacted mixture) and $T_{g\infty}$ and that complete reaction may be reached if $T_{cure} \geq T_{g\infty}$.

The research presented in this article was aimed at constructing the T_gTT cure diagram for the EPY® epoxy material over a wide range of isothermal cure temperatures up to the onset temperature of thermal degradation. The EPY® is widely applied as a material for the foundation chocks in the seatings of ship machinery and installations and also for many various heavy land-based machines in mining, power industry and other fields of heavy industry and civil engineering [28].

EXPERIMENTAL PART

Materials

The main components of the investigated material, with the trade name EPY® (from Marine Service Jaroszewicz, Szczecin, Poland), are: epoxy resin Epidian 6 (epoxy number 0.532 mole/100 g) and a curing agent Z-1 (triethylenetetramine), both produced by Chemical Works Organika-Sarzyna in Nowa Sarzyna, Poland. The mass ratio of curing agent/resin was constant and equals 14/100. The epoxy system is completed with additives giving appropriate technological properties and utility of the material.

Sample preparation

System samples for DSC investigations were cast in steel forms in the shape of rectangular bars (50 × 10 × 5 mm) and cured at 23 °C for various periods of time (4, 8, 12, 24, 48, 72 or 168 h). Also, some samples cured at 23 °C for 24 h were postcured additionally at 40, 60, 80 or 100 °C

for 1, 2 or 4 h. Preparation details of the samples used in the investigations of curing and postcuring processes, as well as the samples used in investigations of gelation and thermal degradation were given in previous articles [21, 22].

Method of testing

DSC measurements

The curing and postcuring reactions of the epoxy material were examined using a differential scanning calorimeter DSC Q100 (TA Instruments) in the same manner as defined in a previous article [21].

The conversion degree (α) of the curing reaction calculated from the residual enthalpy (ΔH_r) of the partially cured resin and from the total enthalpy of reaction (ΔH_T = 273.8 J/g), corresponding to an "as-mixed" sample without curing treatment, is counted for:

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

ΔH_r and ΔH_T were determined by numerical integration of the area enclosed under the exothermic peak in the thermograms.

Viscoelastic measurements

Parallel plate rheometry was used in order to examine the material behavior below the gel point. Viscoelastic data were obtained using an ARES rheometer (Rheometric Scientific) as defined in a previous article [21].

TG-DTA measurements

The thermal analyzer TG-DTA 92-16 (Setaram) was used to measure the thermal degradation of the material. Thermogravimetry data acquisition was defined in a previous article [22].

Development of cure diagrams

An experimental development of a cure diagram for a thermoset resin performed only on the basis of experimental results involves costly and time consuming experimental measurements. In previous articles [21, 25], it was proven that the number of necessary experimental measurements can be limited to a minimum thanks to numerical modeling. This enables the determination of the conversion at the gel point (α_{gel}) and the temperature at which gelation and vitrification of the investigated system occur simultaneously ($_{gel}T_g$). These results obtained with the use of dynamic and isothermal DSC and rotational viscometry (ARES) (published previously [21]) were completed with new DSC results of the glass transition temperature (T_g), conversion degree at vitrification (α_{vit}) and conversion degree in the glassy state of the EPY®
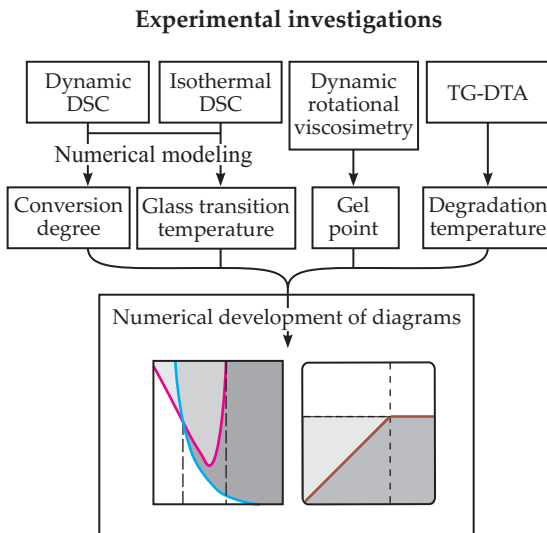
Experimental investigations

Fig. 3. Flow chart of the experimental and numerical development of cure diagrams

Fig. 4. Dependence of limiting conversion degree (α) and conversion degree at vitrification (α_{vit}) on the cure temperature of the EPY® material

material cured at different temperatures and times. The flow chart for the development of a generalized phase diagram and T_gTT diagram is shown in Fig. 3. An appropriate gathering and combining of the experimental results, together with thermogravimetry (TG-DTA) results of onset temperature of thermal degradation (T_d) (published previously [22]), made it possible to develop the T_gTT diagram for the EPY® material.

RESULTS AND DISCUSSION

Dependence of conversion degree on curing conditions

In a diagram of conversion degree *versus* curing temperature for the EPY® epoxy system, presented in Fig. 4, two stages can be seen. When $T_{cure} < T_{g\infty}$, isothermal curing of the epoxy system undergoes two different stages. The first stage is controlled by the chemical reactivity of the functional groups; the curing reaction takes place in the liquid state and the T_g of the system is lower than the T_{cure}. The reaction rate depends on T_{cure} until $T_g = T_{cure}$. At this point, the second stage of curing starts. The system vitrifies and the reaction decreases considerably until the reaction becomes practically inhibited by restricted the reacting groups' mobility, which prevents full conversion. When the system reaches the glassy state, the chemical reaction becomes controlled by diffusion and α tends to a practically constant limiting value, α_∞. The value of α_{vit} (when $T_g = T_{cure}$) for the EPY® system was calculated using the DiBenedetto equation as shown in a previous article [21]. The results obtained in this way are marked in Fig. 4 by solid squares whereas the maximum value of conversion degree (α_∞) obtained in DSC investigations for the EPY® system at given curing temperatures (23, 40, 60, 80 and 100 °C) were marked in Fig. 4 by solid circles. Progress of the curing reaction is con-
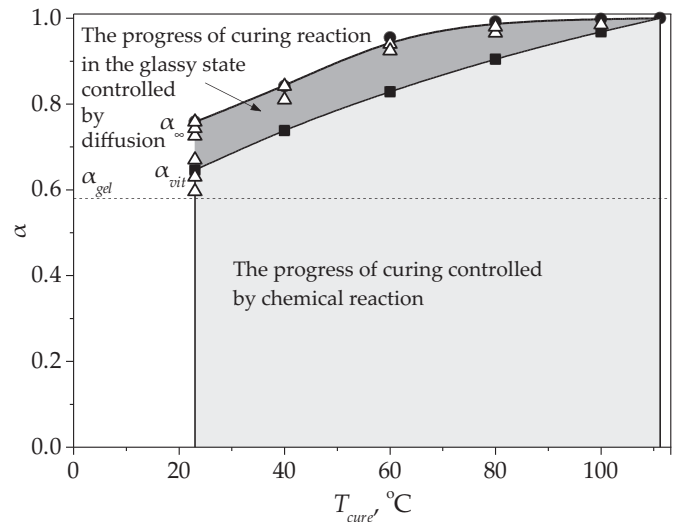
trolled by chemical processes when $0 < \alpha < \alpha_{vit}$ whereas in the glassy state, between α_∞ and α_{vit}, it is controlled by diffusion. The DSC results for conversion degree in the glassy state of the EPY® material cured at different temperatures and times were marked with open triangles in Fig. 4.

Generalized phase diagram

The experimental results for the cure of the EPY® epoxy system at a series of constant temperatures were used in order to obtain the gelation time and the vitrification time *versus* T_{cure}. These transformation times were measured using ARES [21] and DSC methods, respectively. The results derived from investigations are summarized by means of the phase diagram in Fig. 5, which shows the types of behavior depending on the T_{cure} value. At high temperatures, the liquid gels but does not vitrify. At low temperatures, the liquid vitrifies and need not gel if the chemical reactions are quenched by vitrification. At intermediate temperatures, the liquid first gels and later vitrifies. The time to gelation (t_{gel}) and time to vitrification (t_{vit}) during isothermal cure can be calculated using equations [18, 29, 30]:

$$t_{gel} = A^{-1} \exp(E_A / RT) \int_0^{\alpha_{gel}} d\alpha / f(\alpha) \qquad (2)$$

$$t_{vit} = A^{-1} \exp(E_A / RT) \int_0^{\alpha_{vit}} d\alpha / f(\alpha) \qquad (3)$$

where: A – the kinetic Arrhenius pre-exponential factor, T – isothermal curing temperature, E_A – activation energy for the overall curing reaction, R – the universal gas constant, $f(\alpha)$ – the conversion function.

Under the assumption of homogeneous curing kinetics in the range from T_{g0} and $T_{g\infty}$ the values of t_{gel} and t_{vit} can be expressed according to equations [18, 31]:

$$t_{gel} = \frac{1}{A} \cdot \frac{\exp\left(\dfrac{Ar \cdot T_{g0}}{T}\right)}{1+B}\left[\left(\frac{X_{gel}}{1-X_{gel}}\right) + \frac{1}{1+B}\cdot \ln\left(\frac{X_{gel}+B}{B\,(1-X_{gel})}\right)\right] \tag{4}$$

$$t_{vit} = \frac{1}{A} \cdot \frac{\exp\left(\dfrac{Ar \cdot T_{g0}}{T}\right)}{1+B}\left[\left(\frac{\dfrac{T_{cure}}{T_{g0}}-1}{E-F\cdot\dfrac{T_{cure}}{T_{g0}}}\right) + \frac{1}{1+B}\cdot \ln\left(\frac{\dfrac{\left(\dfrac{T_{cure}}{T_{g0}}-1\right)}{B}+E-1+(1-F)\cdot\dfrac{T_{cure}}{T_{g0}}}{E-F\cdot\dfrac{T_{cure}}{T_{g0}}}\right)\right] \tag{5}$$

where: Ar – the Arrhenius number ($Ar = E_A / RT_{g0}$), B – the ratio of rate constants ($B = k_1 / k_2' = 0.5$), X_{gel} – the conversion at gelation, E – the ratio of lattice energies for crosslinked and uncrosslinked polymer ($E = E_x / E_0$), F – the ratio of segmental mobilities ($F = F_x / F_0$).

The t_{gel} decreases exponentially with temperature since the degree of reaction at the point of gelation is constant. In contrast, the t_{vit} value passes through a minimum, which occurs at intermediate temperatures of cure. This reflects competition between the increased rate constants for reaction and the increased degree of reaction required to overcome the thermal motions for vitrification at higher temperatures. The temperature at which gelation and vitrification occur together is defined as $_{gel}T_g$ (Fig. 5). For the EPY® system $_{gel}T_g$ equals 12.5 °C [21]. Vitrification can occur before gelation ($T_{cure} < {}_{gel}T_g$) simply by an increase of molecular weight. Gelation occurs without vitrification when the cure is performed above the maximum softening point, the maximum T_g value, which $T_{g\infty} = 111.2$ °C [21] for the EPY® system is marked in Fig. 5. It is also apparent that if reactions cease at vitrification ($T_{cure} < T_{g\infty}$), the T_g

value of the system after cure will equal the temperature of cure. The vitrification curve therefore gives the time to reach the softening temperature, which the system can achieve by curing at T_{cure}.

A diagram such as Fig. 5 summarizes much of the behavior of the thermosetting process for the EPY® system and in particular shows that it is characterized by two temperatures $_{gel}T_g$ and $T_{g\infty}$. Both $_{gel}T_g$ and $T_{g\infty}$ are critical temperatures of the phase diagram (Fig. 5), which shows the four types of materials encountered in the thermosetting process, *i.e.*, liquid, ungelled glass, gelled glass and rubber.

T_gTT cure diagram

The T_gTT cure diagram developed for the EPY® epoxy system is presented in Fig. 6. The diagram distinguishes three types of behavior with respect to the curing temperature of the epoxy system.

Region of $T_{g0} < T_{cure} < {}_{gel}T_g$

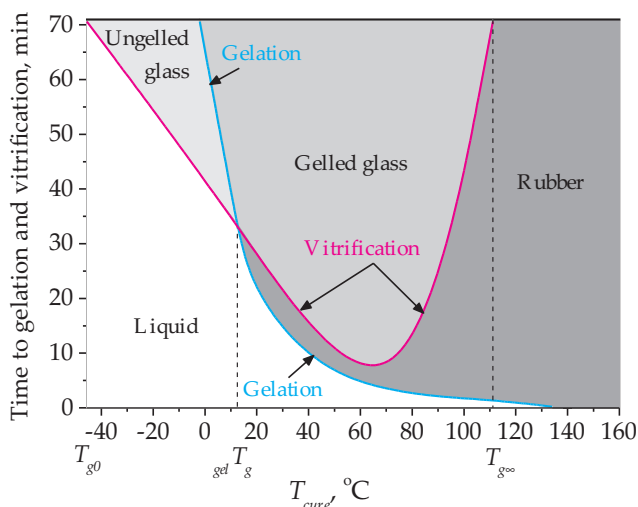Below $T_{g0} = -45.6$ °C [21], the EPY® system is a glassy solid, soluble in suitable solvents and its conversion de-

Fig. 5. Generalized phase diagram for the EPY® epoxy system – time to gelation and time to vitrification *versus* cure temperature ($_{gel}T_g$ and $T_{g\infty}$ are critical temperatures in the phase diagram, which shows the four states of materials encountered in the epoxy process, *i.e.*: liquid, ungelled glass, gelled glass and rubber)
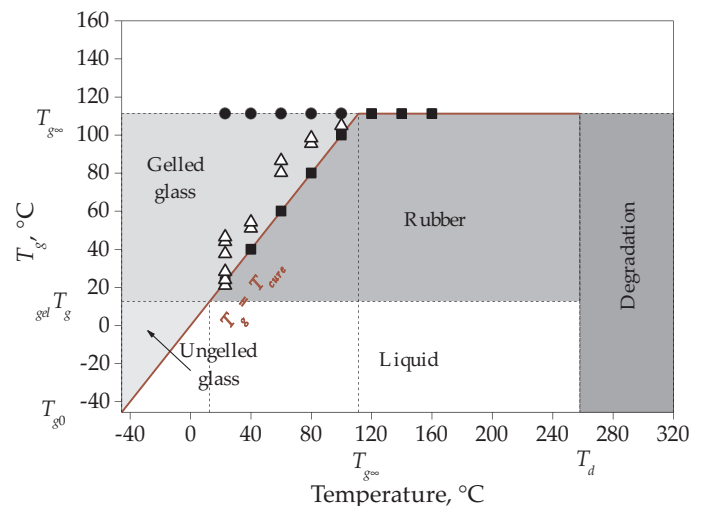
Fig. 6. Glass transition temperature-temperature-transformation (T_gTT) cure diagram for the EPY® material

gree is $\alpha = 0$ (no reaction occurs), whereas $_{gel}T_g = 12.5$ °C is the temperature at which the system gels and vitrifies simultaneously. The system cured at temperatures between T_{g0} and $_{gel}T_g$ reacts until its increasing T_g becomes equal with T_{cure} at which vitrification starts and the reaction becomes diffusion-controlled and gelation may not be achieved. Reactive material below $_{gel}T_g$ is converted to a vitrified solid (ungelled glass state) of low molecular weight, which has an infinite shelf-life and can be later liquefied by heat and processed.

Below $_{gel}T_g$, the temperature at which the t_{gel} is the same as t_{vit} and the rate of the curing reaction in the liquid state fits the Arrhenius relationship defining E_A and both can be calculated using eqs (4) and (5).

Temperatures well below $_{gel}T_g$ are needed if a reactive thermosetting system is to be stored so as to avoid gelation and provide a long shelf-life. The possibility of arresting the chemical reaction in the above mentioned temperature range may be employed for other practical purposes. For example, it may be used to prepare pre-reacted thermosets in the form of ungelled glasses that become liquid and continue the cure when heated (*i.e.*, in a mold to obtain the final shape). Also, large structural parts that must undergo a uniform curing to avoid residual stresses may be crosslinked starting at T close to T_{g0} to attain the vitrification curve, and then by increasing the temperature in small steps. As the thermoset remains always very close to the vitrification curve, the curing kinetics are extremely slow, allowing the dissipation of the reaction heat. The curing cycle is very slow but finally leads to a part with a unique conversion *versus* temperature history at every position [32].

Region of $_{gel}T_g < T_{cure} < T_{g\infty}$

Between $_{gel}T_g$ and $T_{g\infty}$, *i.e.*, between 12.5 °C and 111.2 °C for the EPY®, gelation occurs before vitrification in the epoxy system. After gelation sol fraction is replaced by gel fraction in the cured material. The gel initially formed is weak and can be easily disrupted. After the gel point is reached (conversion at that point for the EPY® equals $\alpha_{gel} = 0.58$ [21]), the gel fraction increases at the cost of the sol fraction because more and more molecules are connected to the three-dimensional network. Finally, the sol fraction totally decays and the maximum extent of conversion for the material is achieved. As concerns the rates of the isothermal reaction, they are presumably the same before gelation (in the liquid state) and up to the time of vitrification (in the rubbery state). On vitrification, when T_g rises to the level of T_{cure}, the molecular and submolecular mobilities become quenched and chemical reactions are brought to a standstill leaving a significant number of unreacted functional groups in the system. Therefore, the extent of reaction close to total conversion ($\alpha = 1$) can be achieved only after postcuring at a temperature above $T_{g\infty}$ in order to improve the material properties. This possibility is shown in Fig. 6 distinctly as the anticipated relation between the temperature of isothermal cure (T_{cure}) and the resultant T_g. It is also shown that $T_{g\infty}$ can be obtained most easily after curing above this value.

The region between $_{gel}T_g$ and $T_{g\infty}$, in which the material becomes converted from liquid into the sol/gel glass state is the most important and useful for typical cure processes applied in practice of thermoset manufacturing.

Region of $T_{cure} > T_{g\infty}$

In the region above $T_{g\infty}$ (111.2 °C for the EPY® system), the cure reaction proceeds with the rate as for $T_{cure} < T_{g\infty}$, presumably (according to Arrhenius relationship) and the material is gelled but vitrification does not occur. Moreover, a high cure temperature can lead to thermal degradation (degradation temperature $T_d = 258$ °C for the EPY® material) causing irreversible loss of useful material properties.

The nature of the curing reaction is determined not only by the inherent reactivity of functional groups, but also by the geometry and polarity of the growing chain segments that determine the transition temperatures ($_{gel}T_g$, T_g, $T_{g\infty}$) of the reactive systems [27]. All of these affect the behavior of the epoxy system in relation to the isothermal curing temperature.

CONCLUSIONS

The generalized phase diagram and T_gTT cure diagram developed for the EPY® epoxy material presented in the article can be an important supplement to three other cure diagrams: TTT cure diagram, CTT cure diagram and T_gTP diagram, which were presented earlier [21, 22, 25] for this epoxy material known in the wide world in many applications [28].

All of these five cure diagrams are a useful framework for understanding and analyzing the behavior of the epoxy systems during the isothermal cure process. The cure diagrams are useful tools for the better comprehension of relationships between the reactants, cure path, structures, physical transitions and states, as well as final properties of the cured material.

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