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# Time-temperature-transformation (TTT) cure diagram for EPY® epoxy system

**Summary** — Curing reactions of the EPY® epoxy system (Epidian 6 + TETA) applied for machine foundation chocks were studied to determine time-temperature-transformation (TTT) isothermal cure diagram for this system. Differential scanning calorimetry (DSC) and rotational viscometry were used to obtain the experimental data. Empirical models based on dependence between conversion degree and glass transition temperature, as well as reckoning of times to gelation and times to vitrification were used and compared to the experimental data. The investigation was made in the temperature range 23—100 °C, which is considered to be optimum for the isothermal curing of the epoxy system studied. The experimental results obtained in this range are in fair agreement with the calculations. The presented curing diagram provides a considerable insight into the thermo-mechanical behavior of the EPY® system during its curing and can be a useful tool for analyzing and designing manufacturing processes of foundation chocks suitable for various practical applications.

**Key words:** epoxy system, curing reaction, conversion, gelation, glass transition, TTT diagram.

## WYKRES SIECIOWANIA CZAS–TEMPERATURA–PRZEMIANA (TTT) DLA UKŁADU EPOKSYDOWEGO EPY®

**Streszczenie** — Badano reakcję sieciowania napełnionego układu epoksydowego EPY® (Epidian 6 + TETA), stosowanego na podkładki fundamentowe maszyn, w celu utworzenia wykresu izotermicznego sieciowania czas-temperatura-przemiana (TTT) dla tego układu. Do sporządzenia takiego wykresu posłużyły dane eksperymentalne uzyskane za pomocą skaningowej kalorymetrii różnicowej (DSC) i wiskozymetrii rotacyjnej oraz wyniki obliczeń z odpowiednio przetworzonych modeli empirycznych zależności między stopniem konwersji, czasem do żelowania i do zeszklenia a temperaturą zeszklenia. Badania eksperymentalne wykonano w optymalnym dla izotermicznego sieciowania tego układu epoksydowego zakresie temperatur 23—100 °C i stwierdzono dobrą zgodność wyników eksperymentalnych z wynikami obliczeń. Sporządzony wykres sieciowania umożliwia pełny wgląd w termomechaniczne zachowanie się tworzywa EPY® podczas jego utwardzania i może być użytecznym narzędziem do analizowania i projektowania technologii wytwarzania podkładek fundamentowych, do różnych praktycznych zastosowań.

**Słowa kluczowe:** układ epoksydowy, reakcja sieciowania, konwersja, żelowanie, przejście szkliste, wykres TTT.

Epoxy systems are some of the most important thermosetting polymeric materials that are widely used as polymer matrices for composite materials, coatings, adhesives and electronic encapsulants. The transformation of linear epoxy resins to three-dimensional crosslinked thermosetting materials is performed by curing reaction with hardeners. The isothermal curing reaction of an epoxy resin is complex as a consequence of the interaction of the chemical curing with other physical processes, such as gelation and vitrification, causing important changes in the macroscopic physical properties of the reacting system [1, 2].

Gelation is a sudden and irreversible transformation of the system from a viscous liquid to an elastic gel. It corresponds to the incipient formation of an infinite network at the first stage of curing, causing changes in the macroscopic properties of a system. Its occurrence depends on the functionality of the epoxy resin and stoichiometry of the components but not on the experimental conditions such as curing temperature [3].

Vitrification involves a physical transformation from a liquid or rubbery state to a glassy state as a result of an increase in the crosslinking density of the material. This phenomenon occurs when the glass transition temperature ($T_g$) becomes equal to the curing temperature ($T_c$). The vitrification point marks a change in the reaction mechanism passing from chemically kinetically-control-

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led to diffusion-controlled one. From that point the reaction becomes slow and finally stops [2, 4, 5].

The time-temperature-transformation (TTT) isothermal cure diagram introduced and developed by Gillham and co-workers [2, 5, 6] for epoxy systems is based on phenomenological changes that take place during cure, such as gelation and vitrification. This diagram can be a very useful tool for analyzing and designing the curing processes of epoxy systems. The schematic diagram is shown in Figure 1, where the time required to reach various states of a material during isothermal cure is plotted as a function of $T_c$. These plots on the diagram include respective states of the cured material: liquid, sol glass, sol/gel rubber, gel rubber, sol/gel glass, gel glass and char. The TTT diagram can be expanded to include other different contours, such as curves of thermal degradation, isoviscosity, and isoconversion or iso-$T_g$ curves, in which full cure or maximum experimental isoconversion is included.

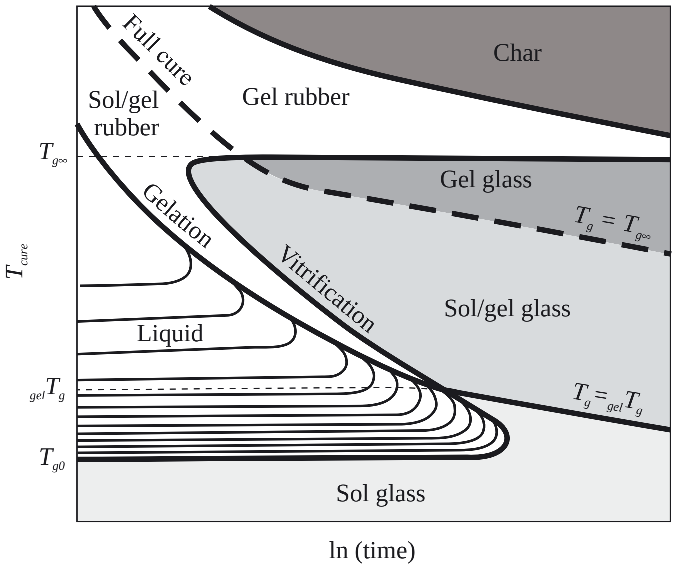

*Fig. 1. Generalized isothermal time-temperature-transformation (TTT) cure diagram for a thermosetting system, showing three critical temperatures ($T_{g0}$, ${}_{gel}T_g$, and $T_{g\infty}$), various stages of the material, and contours characterizing the curing and degradation processes*

Beside time to gelation and time to vitrification contours there are three characteristic temperatures: $T_{g0}$, ${}_{gel}T_g$ and $T_{g\infty}$ that play important roles in this diagram (Fig. 1). $T_{g0}$ is the temperature below which no significant reaction of the epoxy — hardener mixture occurs. This temperature is considered as the storage temperature for uncured resin mixture. ${}_{gel}T_g$ is the temperature at which gelation and vitrification can simultaneously occur in an ideal system. $T_{g\infty}$ is the glass transition temperature of a fully reacted material at which the conversion degree ($\alpha$) reaches its maximum value (theoretically, $\alpha = 1$). From the experimental point of view, it is impossible to reach $\alpha = 1$ because after vitrification the reaction rate is controlled only by the diffusion of the reacting substrates. For this reason, the curve of maximum isoconversion from TTT diagram is usually considered as the curve of full cure. In the region between $T_{g0}$ and ${}_{gel}T_g$, the liquid resin reacts until its $T_g$, which becomes coincidental with $T_c$ at which vitrification point of the system starts. Between ${}_{gel}T_g$ and $T_{g\infty}$, gelation precedes vitrification. If the cure temperature is above $T_{g\infty}$ the material can not vitrify at $T_c$.

Because of the complexity of the phenomena occurring in cure process, it is difficult to provide an *ad hoc* definition of processing conditions under which the optimal properties of a material, the most suitable for its specific applications, could be achieved. Characteristic information about gelation, vitrification of the system and its extent of conversion, can be determined by means of appropriate thermoanalytical and rheological methods and then can be skilfully gathered and numerically processed in the form of a TTT diagram. All of this information make possible to have full insight into the behavior of an investigated epoxy system during the course of cure process and to choose the optimal processing conditions of a given epoxy material for its specific applications.

The EPY® epoxy system — the object of the investigations presented in this paper — has been produced since 1990. The system is the result of many years of scientific research carried out at the Mechanics and Machine Elements Department of Szczecin University of Technology, in close cooperation with the Polish shipbuilding industry, its research centres as well as service teams specialized in machinery seating [7, 8]. The EPY® material used at first in shipbuilding industry to manufacture foundation chocks in seating of main engines and their drive gear units and later in the installation of many other machines onboard ships, has now found wide and wide applications. Now this chocking material is widely used also in foundation of many various heavy land-based machines in mining, power industry and other fields of heavy industry and building engineering [8]. The material has got many approvals and quality certificates of industrial research institutes as well as approvals of European ship engine producers and classification societies supervising ship building and repairs [8, 9].

The main purpose of the study was to investigate the courses of gelation (by means of rotational viscometry) and vitrification (by DSC method) of EPY® epoxy system in various curing conditions. The investigations were aimed at developing the TTT diagram for the EPY® system and performed by means of empirical and theoretical way without running costly and time consuming experimental measurements [10]. The diagram developed in this manner can give an insight into the thermomechanical behavior of the system during its cure process and creates the basis on which the technology of manufacturing of machine foundation chocks for various practical applications can be analyzed and designed.

## EXPERIMENTAL

### Materials

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

### Sample preparation

The curing and gelation of the system was examined by differential scanning calorimetry (DSC) and rheometric methods (ARES), respectively. In the examinations, a system of samples prepared just before the measurements were used. The samples used for postcuring investigations by DSC method were cast in steel forms in the shape of rectangular bars (50 × 10 × 5 mm) and cured at 23 °C for 12, 24, 48 and 168 h. Besides, several samples cured at 23 °C for 24 h were additionally postcured at 40, 60, 80, 100, 120 and 140 °C for 2 h.

### Methods of testing

#### DSC measurements

The courses of the curing and postcuring reactions of the epoxy system were investigated using a differential scanning calorimeter DuPont DSC 910.

DSC measurements were carried out immediately after mixing of the components of the system using 10 mg samples in 50 μL aluminum pans with covers. The samples were heated in the temperature range from -100 to 250 °C under nitrogen atmosphere at various heating rates: 1, 3, 5 and 10 °C/min and then quenched to -100 °C and reheated to 250 °C at the same rate in order to check if the curing of the system had been completed during the first heating cycle in DSC. An incomplete curing of the system had occurred if an exothermic peak was observed in the last heating.

In the postcuring examinations the measurements were carried out using approximately 20 mg samples cut out from the middle of the bars cured in the way described above. The samples were enclosed in Al-50 μL pans with covers and then subjected to three heating cycles in DSC, at the rate of 10 °C/min from -50 °C (under the nitrogen atmosphere). Because an endothermic peak had appeared in the first heating cycle, the heating of the sample was stopped just beyond this peak, where postcuring was just initiated. Then, the sample was requenched to the initial temperature (-50 °C) and subjected to the second cycle of heating carried out at the same rate up to 250 °C. In the second cycle, the endothermic peak was already relaxed and it did not appear. Instead of that a glass transition occurred at first and then an exothermic peak appeared. After that the sample was quenched again to the initial temperature (-50 °C) and subjected to the third cycle of heating in DSC in order to obtain the glass transition temperature of the fully cured system ($T_{g\infty}$).

#### Viscoelastic measurements

The viscoelastic properties of the epoxy system were investigated using ARES rheometer of Rheometric Scientific, by parallel plate rheometry method. The "as-mixed" sample, 4 g in weight, was subjected to sinusoidal deformations at the amplitude of 3 % and the frequency of 1 Hz. The measurements were performed from the temperature -20 °C to the gel point temperature, at three various heating rates of 1, 3 and 5 °C/min, under nitrogen atmosphere.

### Development of the TTT diagram

An experimental development of TTT diagrams for thermoset resins carried out only on the grounds of experimental results involved costly and time consuming

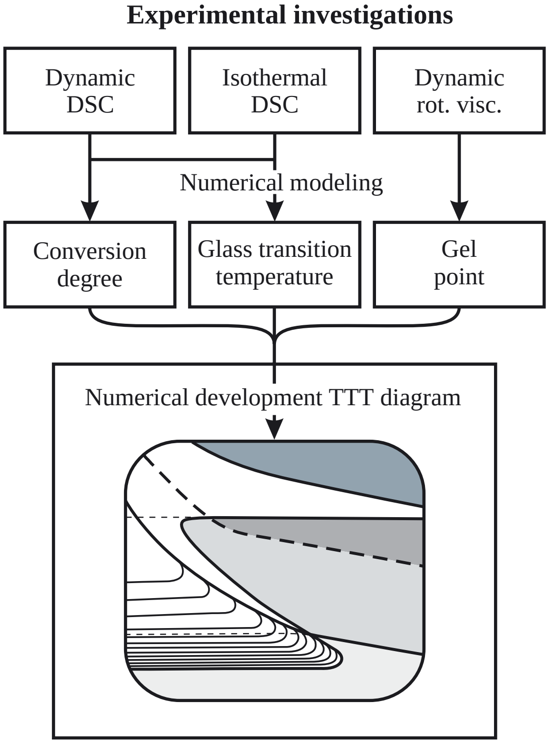

*Fig. 2. Flow chart of the experimental and numerical development of the TTT diagram*

experimental measurements. The number of necessary experimental measurements can be limited to a minimum thanks to implementation of numerical modeling of the diagram [10]. Our experimental investigations included dynamic and isothermal DSC and the determination of the time to gelation with the use of rotational viscometry. Empirical models were derived from the experimental results in order to predict the progression in the cure degree (especially at the gel point), and the glass transition temperature. The results of the measurements and the numerical modeling allow to develop the TTT diagram that is shown schematically in Figure 2. From the practical point of view, the region between the ${}_{gel}T_g$ and $T_{g\infty}$ is the most useful for considering the typical processes.

## RESULTS AND DISCUSSION

### Curing

The chemical structure of the reactants of EPY® epoxy system and the chemical reactions involved in the cure are presented in the previous article [11]. Figure 3 shows some DSC thermograms obtained during the first and the second heating cycles (at the rate of 10 °C/min) which show the course of the system reaction. The total exothermal heat of the reaction ($\Delta H_T$) of the system was 273.8 J/g. When a thermosetting system is crosslinking, its glass transition temperature increases from an initial value $T_{g0}$ = -45.6 °C (glass transition temperature of the uncured monomer) up to a maximum value $T_{g\infty}$ = 111.2 °C which corresponds to the fully cured material. The specific heat values above and below the glass transition temperature for the uncured resin was determined as $\Delta C_{p0}$ = 0.06755 J/(g · °C) and for the fully reacted resin as $\Delta C_{p\infty}$ = 0.02848 J/(g · °C).

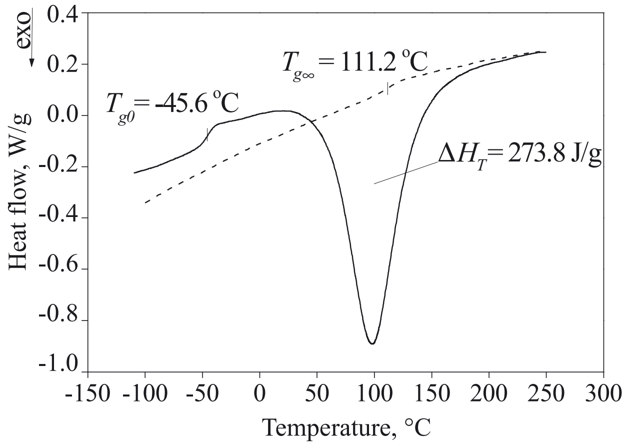

*Fig. 3. DSC thermograms of the EPY® epoxy system, obtained during the first (solid line) and the second heating (dashed line) at rate of 10 °C/min*

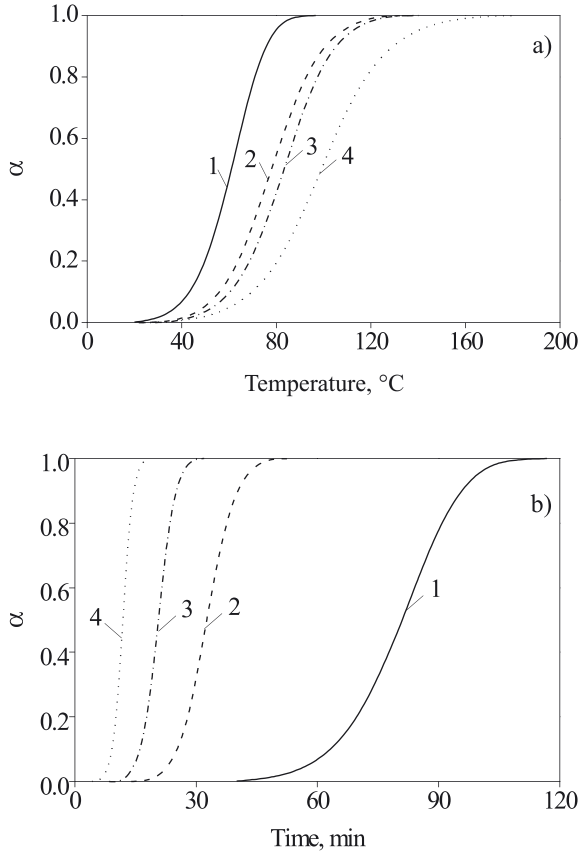

*Fig. 4. Conversion degree (α) as a function of temperature (a) and time (b) for the EPY® epoxy system at various heating rates: 1 — 1 °C/min, 2 — 3 °C/min, 3 — 5 °C/min, 4 — 10 °C/min*

However, the variations of the conversion as a function of the temperature and the time of curing at various heating rates of the investigated system are presented in Fig. 4a and 4b, respectively. These figures show that the curing curves are shifted towards higher temperatures (Fig. 4a) and that the curing times decrease (Fig. 4b) together with an increasing heating rate.

### Gelation and the conversion degree at gel point

Figure 5 presents some results of rheological measurements of the system carried out at the heating rate of 3 °C/min. The intersection point of loss modulus ($G''$) curve and storage modulus ($G'$) curve happens to be at the temperature of 79.7 °C and corresponds to the gel point. The gel point can also be defined by means of equality: tan δ = 1 determining a specific relation between $G''$ and $G'$ [12].

The results of viscoelastic and DSC measurements were employed to determine both the conversion degree at the gel point (Fig. 6a) and the time to the gel point (Fig. 6b) for the system at various heating rates (1, 3 or 5 °C/min). Leading an ordinate from the gel point (tan δ = 1) to the point where it intersects the curing curve for a given heating rate one can obtain the value of the con-

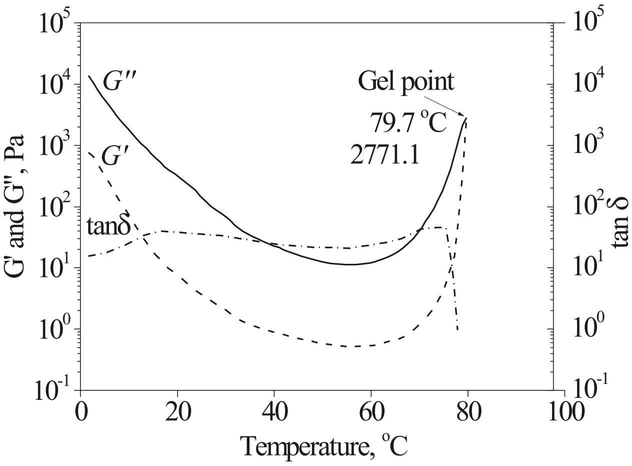

*Fig. 5. Storage modulus (G'), loss modulus (G") and loss factor (tan δ) dependencies on temperature for the EPY® epoxy system at heating rate 3 °C/min; gel point is marked at intersection point of G' and G" curves*

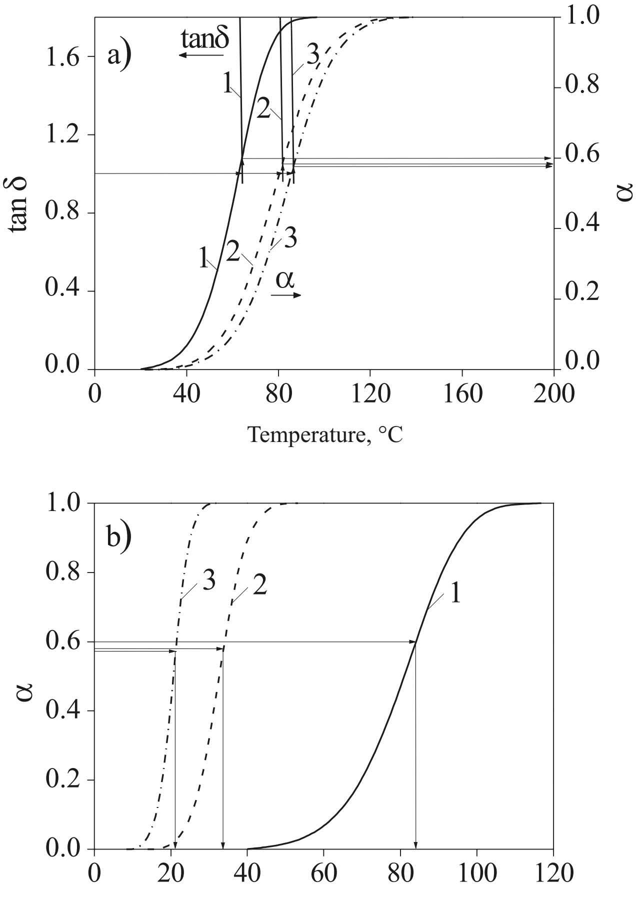

*Fig. 6. Way of determination of conversion degree at gel point (a) and time to gel point (b) for the EPY® epoxy system by means of ARES and DSC measurements at various heating rates: 1 — 1 °C/min, 2 — 3 °C/min, 3 — 5 °C/min*

version degree of the system at the gel point (Fig. 6a). Such a determined conversion degree at the gel point ($\alpha_{gel}$) let find, from Figure 6b, the essential time to reach the gel point ($t_{gel}$) at a given heating rate. The values of the temperature at the gel point as well as the conversion degree and the time to the gel point obtained at various heating rates are collected in Table 1.

**Table 1. Results of rheological (ARES) and thermal (DSC) investigations of the epoxy system's curing process at various heating rates**

| Heating rate °C/min | Gel point | | | |
|---|---|---|---|---|
| | *T*, °C | *G"/G'* | Conversion ($\alpha_{gel}$) | Time to gelation ($t_{gel}$), min |
| 1 | 61.2 | 57 820.4 | 0.60 | 84.0 |
| 3 | 79.7 | 2771.1 | 0.58 | 33.6 |
| 5 | 88.1 | 637.8 | 0.57 | 21.2 |

Gel point is the beginning of a sudden and irreversible transformation from a viscous liquid to an elastic gel. It signifies the first appearance of the infinitive network. Gelation of epoxy system occurs at a specific point in the course of the chemical reaction, usually at conversion degree between 0.55 and 0.80, depending on the functionality, reactivity, and stoichiometry of the reactants [1, 13]. The gelation of the EPY® epoxy system begins at the value of $\alpha_{gel}$ which equals approximately 0.58 (Fig. 6a, Table 1).

The experimentally determined value of the conversion degree of the EPY® system at the gel point $\alpha_{gel}$ = 0.58 corresponds accurately to the theoretical value of conversion for an ideal molecular gelation (0.577) predicted by Flory [1, 3, 6]. This conformity may be interpreted as a manifestation of the universal principle, which says that complex details of a molecular structure of the system are insignificant for its macroscopic description [14].

## Postcuring

### Vitrification observed in DSC thermograms

The vitrification process is observed in the DSC thermograms (Fig. 7) for postcuring temperatures ($T_c$) lower than the glass transition temperature of a fully cured system ($T_{g\infty}$) of which experimentally determined value is 111.2 °C. When glass transition temperature equalizes cure temperature ($T_g$ = $T_c$), the system vitrifies and a peak superposed on $T_g$ appears as a consequence of the physical ageing process (structural relaxation) [15], and residual curing starts just beyond this peak. In order to relax the peak and to determine an accurate $T_g$ value of the system, close behind this peak the sample was quenched (down to -50 °C) and then reheated (up to 250 °C) at the same rate.

When the postcuring temperature $T_c$ is higher than $T_{g\infty}$, the cure reaction occurs in the rubbery state. Under these conditions, as shown in the DSC thermograms

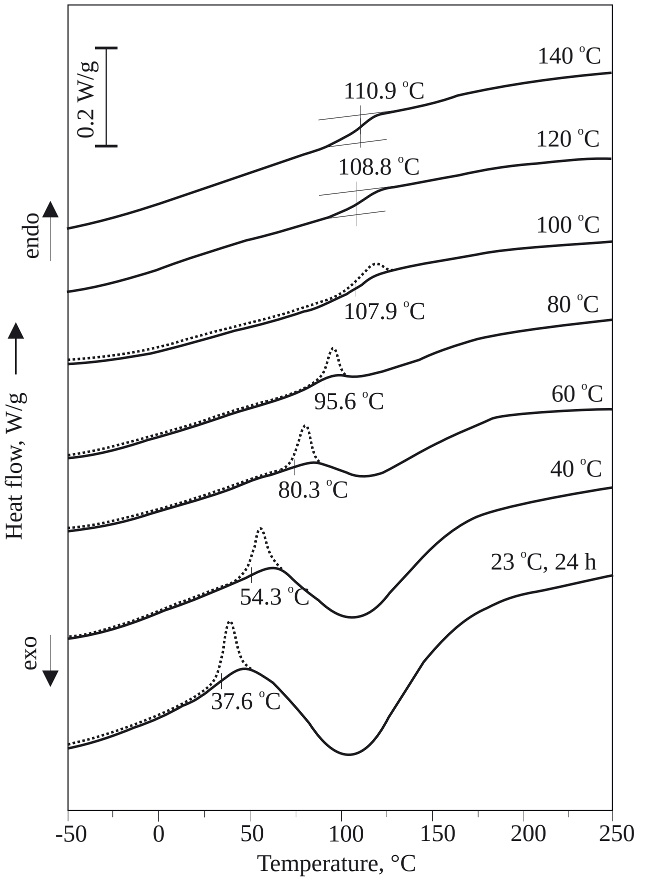

*Fig. 7. DSC thermograms of the EPY® material cured and postcured at various temperatures, obtained during the first (dotted line) and the second heating (solid line) at rate of 10 °C/min*

(Fig. 7) obtained at $T_c$ = 120 and 140 °C for 2 h, no effects of physical ageing appear any longer.

### Dependence of the conversion degree on curing time

The dependence of the conversion degree (α) of the system on the natural logarithm of curing time ($t_c$) at the isothermal curing temperature of 23 °C (presupposed temperature of casting and curing of machine foundation chocks) is shown in Figure 8. For a given curing temperature the sigmoid shape of the approximated curve α = f (ln $t_c$) indicates that the conversion degree increases more and more intensively (the dashed line in Fig. 8) as it approaches the gel point (Z). Starting from this point subsequent increments in the α values are smaller and smaller and the curve (solid line in Fig. 8) approaches asymptotically the limiting value of $\alpha_\infty$, attainable at this curing temperature.

The conversion degree of the curing reaction is calculated from the residual enthalpy $\Delta H_{res}$ of the partially cured resin and from the total enthalpy of reaction $\Delta H_T$ (273.8 J/g) corresponding to one "as-mixed" sample without curing treatment [16]:

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

When $T_c < T_{g\infty}$, the isothermal curing progresses through two different curing stages [15, 17]. The first one is controlled by the chemical reactivity of the functional groups; the curing reaction develops in liquid state, and $T_g$ of the system is lower than $T_c$. The reaction progresses at a rate depending on $T_c$ until $T_g$ equals to $T_c$. When this point is reached, the second stage of curing starts. The system vitrifies, and the reaction rate decreases considerably until the reaction becomes practically inhibited by a restricted reacting groups mobility, which prevents the full conversion. The reaction time required for reaching $T_g = T_c$ is called vitrification time ($t_v$). Its values for the EPY® system cured at temperature $T_c$ = 23 °C is $t_v$ = 8 h 40 min. The way to determine the value of the vitrification time by means of the approximated curve $T_g$ = f (ln $t_c$) obtained from the experimental data (solid line) is shown in Figure 9. When the system reaches the glass state, the chemical reaction becomes controlled by diffusion [17, 18], and the conversion degree tends to attain a limiting value $\alpha_\infty$, dependent on $T_c$, thus reaching of

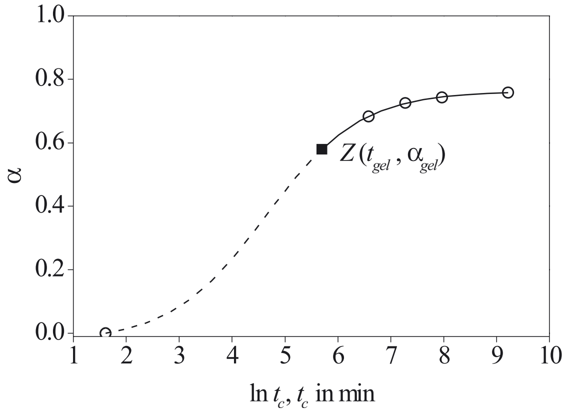

*Fig. 8. Dependence of conversion degree (α) on natural logarithm of curing time at temperature of 23 °C for the EPY® material*

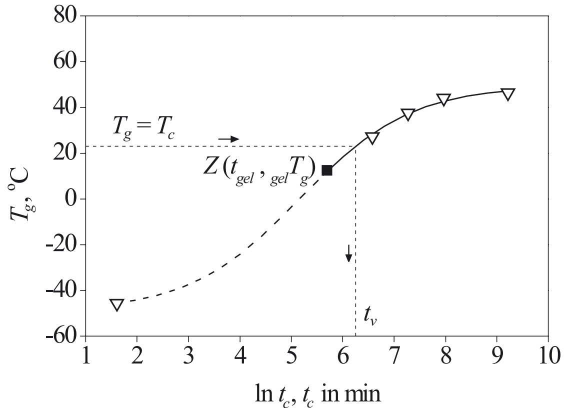

*Fig. 9. Dependence of glass transition temperature ($T_g$) on natural logarithm of curing time at temperature of 23 °C for the EPY® material*

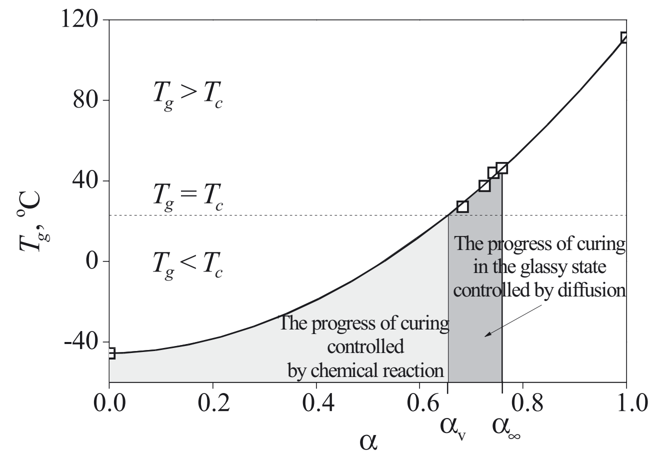

*Fig. 10. Dependence of glass transition temperature ($T_g$) on conversion degree (α) for the EPY® material at curing temperature of 23 °C; occurrence of vitrification ($T_g$ = $T_c$) is marked by dotted line*

the full conversion of the chemical reaction is practically impossible. These two stages of curing of the epoxy system EPY® at 23 °C are shown in the diagram of $T_g$ versus α (Fig. 10). The conversion degree at vitrification time ($\alpha_v$) determines the progress of curing controlled by chemical reaction. The difference between $\alpha_\infty$ and $\alpha_v$ shows the progress of the curing reaction in the glassy state controlled by diffusion. When vitrification happens ($T_g = T_c$) in the EPY® system isothermally cured at the temperature $T_c$ = 23 °C, its conversion degree ($\alpha_v$) equals to 0.65. This value was graphically obtained from Fig. 10 using the relationship between the glass transition temperature and the conversion degree. The highest value of conversion obtained experimentally in the EPY® system cured at 23 °C for 168 h was assumed as limiting value of conversion degree ($\alpha_\infty$ = 0.76) for this system.

When $T_c > T_{g\infty}$, the curing reaction is controlled by chemical reactivity only [15].

### Dependence of the glass transition temperature on curing time

During the isothermal curing at a given temperature ($T_c$ = 23 °C) $T_g$ of the system increases along with $t_c$ as a consequence of the growth in the crosslinking density of the network. For samples cured at $T_c < T_{g\infty}$, deceleration has been observed to happen near $T_g = T_c$ as a consequence of the system vitrification (Fig. 9). Beyond $t_v$, $T_g$ becomes higher than $T_c$, and under such conditions ($T_g > T_c$) a physical ageing process begins [15]. The effects of this process are observed in the DSC thermograms (Fig. 7) as endothermic peaks coincidence $T_g$. In the ageing conditions ($T_g > T_c$) increase in $T_g$ proceeds slowly along with the curing time and approaches asymptotically to the limiting value, ($T_{g\,lim}$) depending on $T_c$. The value of $T_{g\,lim}$ is different for each cure temperature due to diffusion control of reaction kinetics, which becomes significant after the vitrification point reached. However, when the energy supplied to the curing system is lower, the reaction is hindered because of structural limitations, which become more pronounced at low cure temperatures [19]. The highest value of $T_g$ = 46.4 °C obtained experimentally in this system cured at 23 °C for 168 h was assumed as the limiting value of $T_{g\,lim}$ for the EPY® system.

The profiles of $T_g$ versus ln $t_c$ curves have similar shapes before and beyond the gel point just like α versus ln $t_c$ curves (Figs. 8 and 9), indicating a high correlation between these two properties.

The lack of a distinct increase in the α value and thereby no improvement of the mechanical properties of the material indicates that the curing time prolongation (from 12 to 168 h) at the temperature 23 °C (Fig. 8) is useless if the cost of machine foundation is concerned. Further increase in α value is possible only by postcuring of the material at a higher temperature. The experiments carried out with the EPY® material were continued using samples cured at 23 °C for 24 h and then additionally postcured at various temperatures ranging from 40 to 140 °C (at every 20 °C) for 2 h.

### Dependence of the conversion degree and the glass transition temperature on curing temperature

Both $\Delta H_{res}$ and $T_g$ change with increasing postcuring temperature ($T_c$) of the system; $\Delta H_{res}$ decreases until the reactants are fully consumed while $T_g$ increases asymptotically close to the value of $T_{g\infty}$ = 111.2 °C (Fig. 11) due to the growth of crosslinking density of the network of the system. Both effects can be observed in the DSC thermograms in Figure 7.

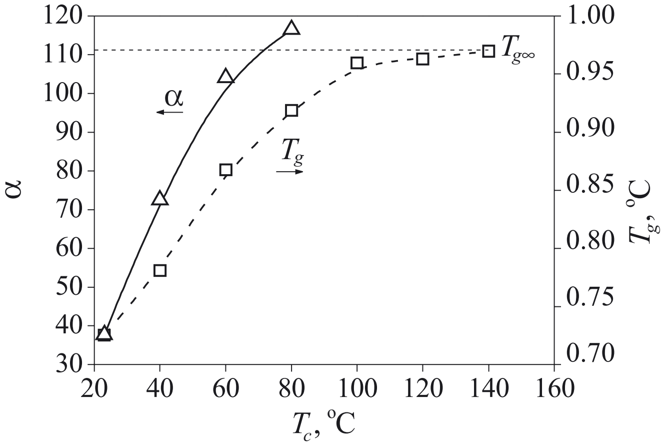

*Fig. 11. Dependences of conversion degree (α) and glass transition temperature ($T_g$) on postcuring temperature ($T_c$) for the EPY® material*

A comparison of how α and $T_g$ increase with the growth of $T_c$ of the system is presented in Figure 11. The figure clearly shows that $T_g$ can be used as a direct and reliable measure of conversion. This is a significant advantage from the practical point of view since $T_g$ can be measured more easily and with better accuracy than the conversion, especially in high conversions at which $T_g$ increases although the calorimeter does not show any changes in the residual heat.

### Glass transition temperature vs. conversion degree relationship

The empirical DiBenedetto equation, modified by Nielsen as reported in [20], has been used to introduce one-to-one relationship between $T_g$ and α:

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

where: $T_{g0}$ — *the glass transition temperature of the uncured monomer,* λ — *a structure-dependent parameter between 0 and 1.*

Pascault and Williams [20] show that λ is theoretically equated to:

$$\lambda = \frac{\Delta C_{p\infty}}{\Delta C_{p0}} \tag{3}$$

where: $\Delta C_{p\infty}$ *and* $\Delta C_{p0}$ — *differences in heat capacity between the glassy and rubbery (or liquid) states at* $T_g$ *for the fully cured network and monomer, respectively.*

Both the experimentally determined values of characteristic glass transition temperatures $T_{g0}$ and $T_{g\infty}$ and the value of parameter λ = 0.426 calculated from eq. (3) and then substituted into DiBenedetto's eq. (2) allow to present the relationship between $T_g$ and α for the EPY® system in the following form:

$$T_g = -45.6 + \frac{(111.2 + 45.6)\,0.426\,\alpha}{1-(1-0.426)\alpha} \tag{4}$$

Formula (4) is an (empirically determined) mathematical model which characterizes the dependence of $T_g$ on α for the EPY® system. This relationship is presented in Figure 12 where the experimental values and the gel point (Z) are also marked.

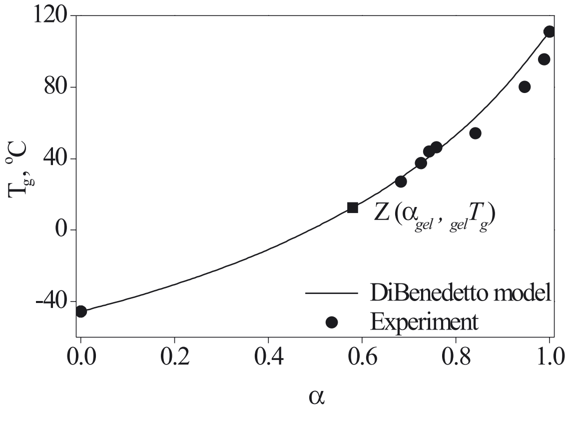

*Fig. 12. Findings of* $T_g$ *versus conversion degree (α) for the EPY® material: calculated with DiBenedetto model [solid line, eq. (4)] and obtained experimentally (symbols)*

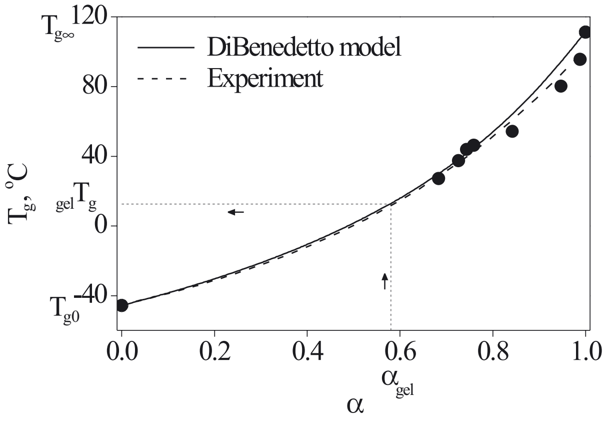

*Fig. 13. Comparison of dependence of glass transition temperature* ($T_g$) *on conversion degree (α) obtained experimentally (dashed line) with the other calculated using DiBenedetto equation (solid line); way of determination of* $_{gel}T_g$ *value for the EPY® material is marked in the figure*

The experimentally conducted revision of the assumed model [eq. (4)] in the region above the gel point of the system (0.58 < α < 1) for the samples cured at 23 °C for 12, 24, 48 and 168 h as well as the samples postcured at 40, 60 and 80 °C for 2 h showed it well fits the results obtained experimentally, which can be seen in Figure 13. The fitting of the model (solid line) with the experimental data (dotted line) at high conversions is so good that it allow to convert α values into $T_g$ values and vice versa. The little scatter of the $T_g$ data at high conversions is attributed to a lower sensitivity of the DSC in measuring of the conversion level comparison with that of $T_g$ measurement [19, 21]. The relationship between the glass transition temperature and the conversion degree that was found for the EPY® system was independent on the cure temperature. This relationship for different epoxy systems was also observed by some other authors [21, 22, 23].

The value of parameter λ calculated using Pascault and Williams' equation (3) and the value of the conversion degree at the gel point $\alpha_{gel}$ = 0.58 determined experimentally allow to calculate the temperature at which gelation and vitrification occur simultaneously, $_{gel}T_g$ = 12.5 °C (Fig. 13). The correlation between $\alpha_{gel}$ and $_{gel}T_g$ marked in Fig. 13 clearly shows that at small degrees of cure, the increase in $T_g$ is due to an increasing molecular weight of the epoxy resin, whereas, at high conversion, an increasing $T_g$ results from higher crosslinking densities [23].

### TTT diagram

The TTT diagram of isothermal curing of the EPY® epoxy system is given in Figure 14. To plot a TTT diagram it is necessary to know three characteristic temperatures: $T_{g0}$, $_{gel}T_g$, $T_{g\infty}$. For the system studied here $T_{g0}$ = -45.6 °C and $T_{g\infty}$ = 111.2 °C were experimentally deter-

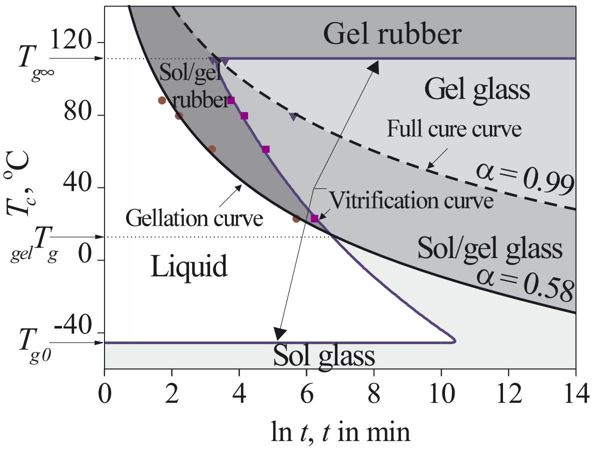

*Fig. 14. Calculated TTT isothermal cure diagram developed for the EPY® material*

mined by means of DSC while $_{gel}T_g$ = 12.5 °C was calculated using the DiBenedetto's eq. (4). The value of conversion degree at gelation $\alpha_{gel}$ = 0.58 was determined experimentally by ARES and DSC methods.

The TTT diagram (Fig. 14) was calculated from the contours of the time to gelation and to vitrification as functions of the reaction temperature, taking into account the fact that the gelation curve and vitrification curve intersect at the curing time, corresponding to $_{gel}T_g$. The experimental and calculated data were employed to plot both the curves. The isoconversion curves corresponding to α = 0.58 and 0.99 are also plotted in the diagram.

The contour of the vitrification curve as the locus of cure times at which $T_g = T_c$, was calculated by transformation of conversion degree values into $T_g$ values through DiBenedetto eq. (4) derived for the EPY® system. The gelation curve was calculated using the value $\alpha_{gel}$ = 0.58 experimentally determined by rheometric and DSC methods for the system studied here and considering that gelation and vitrification curves intersect at a cure time corresponding to the value of $_{gel}T_g$ calculated using eq. (4). The experimental value of $\alpha_{gel}$ = 0.58 and the ideal molecular gelation value of 0.577 predicted by Flory's theory are in good agreement. It was found, at the experimental gelation points, that conversion had almost been constant and independent on temperature and heating rate. The experimental values and the values calculated from gelation and vitrification curves are in good agreement.

The isoconversion plot α = 0.99 corresponds to the maximum achievable experimental values of the conversion degree and is taken as the full cure curve in the TTT diagram.

The vitrification curve plotted in the TTT diagram is S-shaped. The times to vitrification pass through a maximum at a cure temperature just above $T_{g0}$ because of the competing effects of increasing reactivity and decreasing viscosity with increasing temperature. In contrast, the times of vitrification pass through a minimum at a temperature of cure just below $T_{g\infty}$ because of the competing effects of the increasing constant of the reaction rate and the increasing extent of the reaction at vitrification with increasing temperature [24].

The curves and lines in the TTT diagram (Fig. 14) segregate the following states: liquid, sol glass, sol/gel rubber, gel rubber, sol/gel glass and gel glass which epoxy system can pass under given cure conditions.

According to the TTT cure diagram, as an epoxy material cures, its $T_g$ increases with the conversion degree. When $T_g$ reaches the value of the isothermal $T_c$, the material vitrifies. In the vicinity of vitrification, the segmental mobility decreases, and the overall rate of the reaction may become controlled by the limiting diffusion of the reacting species.

$T_{g0}$ = -45.6 °C corresponds to the glass transition temperature of the EPY® system with the conversion degree α = 0. Below $T_{g0}$ the system does not react, and is a glassy solid soluble in suitable solvents.

$_{gel}T_g$ = 12.5 °C is the temperature at which the EPY® system gelates and vitrifies simultaneously.

Between $T_{g0}$ and $_{gel}T_g$ (-45.6 °C < $T_c$ < 12.5 °C) the system will react until its continuously rising glass transition temperature becomes coincidental with the cure temperature ($T_g = T_c$) at which vitrification stage will begin and reaction will become diffusion-controlled, so gelation may not be achieved. For vitrification below $_{gel}T_g$ the resulting material will have a low molecular weight and it will be passing from liquid to sol glass state and flowing during heating.

Between $_{gel}T_g$ and $T_{g\infty}$ (12.5 °C < $T_c$ < 111.2 °C) gelation precedes vitrification in the system. After gelation, the cured material contains sol as well as gel fractions. The gel initially formed is weak and can be easily disrupted.

After the gel point (conversion at gelation point $\alpha_{gel}$ = 0.58) more and more molecules are connected to the three-dimensional network. Gel fraction increases at the cost of sol fraction until the latter will reach zero and the material will reach the maximum extent of conversion. At vitrification ($T_g = T_c$), the molecular and submolecular mobilities decrease and chemical reactions become inhibited leaving still a significant number of unreacted functional groups in the system. Therefore, the system can reach on extent of reaction close to the total conversion (α = 1) only after postcuring at temperature above $T_{g\infty}$.

For practical considerations, the region between $_{gel}T_g$ and $T_{g\infty}$, in which the material is passing from liquid into sol/gel glass state is the most useful for typical cure processes.

If the cure reaction of the EPY® system proceeds above $T_{g\infty}$ (111.2 °C), the material is gelated but vitrification does not occur. High cure temperature can lead to the thermal degradation of a material causing loss of its useful properties.

## CONCLUSIONS

The time-temperature-transformation (TTT) isothermal cure diagram for the EPY® epoxy system developed by empirical and theoretical ways can be a useful tool for analyzing and designing of the curing processes of this material. Since the diagram implies that the times required to gelation and to vitrification are functions of isothermal cure temperature and indicates characteristic temperatures of the system ($T_{g0}$, $_{gel}T_g$, $T_{g\infty}$), all of the phenomenological changes that take place during the cure reaction converting a viscous liquid into a solid can be presented here.

To consider the processing of the epoxy system, many important data can be obtained from the TTT diagram. For instance, on the grounds of the gelation curve dependent on the cure temperature one can determine an adequate time within epoxy resin remains in liquid state and fits for processing, whereas on the grounds of the vitrification curve the moment of resin solidification can be determined. The diagram can be expanded to include other different contours such as isoconversion plots which allow to get information on cure degree of the system and to determine the final mechanical and thermal properties of the material. The isoconversion plot of $\alpha$ = 0.99 in the presented diagram corresponds to the maximum value of conversion degree achieved in the experiments.

Therefore, the TTT cure diagram for the EPY® epoxy material let choose an optimal path of time-cure temperature so that gelation and vitrification will occur in a controlled manner and result in a system showing useful properties needed for a specific application of the material.

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