Effect of vitrification on the curing reaction of EPY® epoxy system

(*Rapid Communication*)

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Abstract: The curing reaction of the EPY® epoxy system, applied for machine foundation chocks, has been studied at various temperatures. The values of the glass transition temperature (T_g) and the conversion degree (α) in these curing reactions were determined using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA). DiBenedetto equation was applied for correlation between T_g and α data. These data showed a one-to-one relationship independent of the curing temperature and good conformableness of DiBenedetto equation with the experimental results at every cure temperature was obtained (Fig. 1). The values of T_g obtained using TMA and DMA methods compared to value obtained by DSC method are 2 and 4 °C higher, respectively.

Keywords: epoxy system, glass transition temperature, conversion degree, DiBenedetto equation, differential scanning calorimetry, dynamic mechanical analysis, thermomechanical analysis.

Wpływ zeszklenia na reakcję sieciowania układu epoksydowego EPY®

Streszczenie: Badano reakcję sieciowania układu epoksydowego EPY®, który jest używany do wytwarzania podkładek fundamentowych maszyn i urządzeń. Reakcję prowadzono w temperaturze 23 °C, ale część próbek była dodatkowo utwardzana w 40, 60, 80 lub 100 °C. Wyznaczano wartości temperatury zeszklenia (T_g) i stopnia konwersji (α) za pomocą trzech metod: różnicowej kalorymetrii skaningowej (DSC), dynamicznej analizy mechanicznej (DMA) i analizy termomechanicznej (TMA). Wzajemną zależność między T_g i α określano stosując równanie DiBenedetto. W przypadku wszystkich wartości temperatury utwardzania tworzywa EPY® uzyskano dobrą zgodność opisu wyników badań za pomocą równania DiBenedetto (rys. 1). Wykazano, że wartości T_g uzyskane na podstawie pomiarów TMA i DMA są wyższe, odpowiednio, o ok. 2 i 4 °C od wartości wyznaczonej metodą DSC.

Słowa kluczowe: układ epoksydowy, temperatura zeszklenia, konwersja, równanie DiBenedetto, różnicowa kalorymetria skaningowa, dynamiczna analiza mechaniczna, analiza termomechaniczna.

Epoxide-amine epoxy is a family of thermosetting polymers characterized by complex crosslinked networks. The properties of epoxy systems are significantly determined by these irregular crosslinked networks. The nature of these networks depends on many factors such as the chemistry of resin and hardener, their stoichiometric ratio, and curing conditions. Molecular weight, stiffness of the molecular chain, inter-molecular forces, crosslinking and side branching all have effects on molecular mobility, therefore also on the glass transition temperature. The change in molecular mobility of amorphous materials during the glass transition interval brings unavoidable changes in their mechanical and physical properties.

In order to examine the change of the reaction rate during the vitrification process, the relationship between the glass transition temperature (T_g) and the conversion (α) of the partially cured reacting mixture must be derived.

The relationship between T_g and fractional conversion determines when vitrification occurs during the curing process, for which T_g equals the cure temperature (T_{cure}). At a given T_{cure}, the reaction of a thermosetting material proceeds generally at a rate dictated by chemical kinetics if T_g is less than T_{cure}. However, if T_g is higher than T_{cure}, the reaction rate is controlled by diffusion, because molecular mobility is rapidly reduced.

According to Fox and Loshaek [1], it is assumed that T_g of crosslinked polymer is a function of the crosslink density. Most of theoretical and empirical relations reported in the literature involve exponential dependences [2–5],

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but linear [1, 6] or logarithmic relationships can also be found [7].

The empirical DiBenedetto equation was developed to mathematical description of the relation of T_g and conversion for thermosetting polymers [3, 8]:

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{\left(\dfrac{\varepsilon_\infty}{\varepsilon_0} - \dfrac{F_\infty}{F_0}\right)x}{1 - \left(1 - \dfrac{F_\infty}{F_0}\right)x} \qquad (1)$$

where: T_{g0} – the glass transition temperature of the uncured polymer; x – the crosslink density, defined as the fraction of all segments that are crosslinked; $\varepsilon_\infty/\varepsilon_0$ – the ratio of lattice energy for fully crosslinked and uncrosslinked polymers; F_∞/F_0 – the ratio of segmental mobility for some two polymers.

The modified DiBenedetto equations can be derived from entropic considerations of an idealized system. The system consists of a mixture of a fully cured network and an unreacted monomer phase. Based on thermodynamic considerations it can be derived [9, 10]:

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

where: $T_{g\infty}$ – the glass transition temperature of the fully crosslinked polymer, α – degree of conversion, λ – structure-dependent parameter that is equal to the ratio $\Delta C_{p\infty}/\Delta C_{p0}$ ($\Delta C_{p\infty}$ and ΔC_{p0} are changes in the specific heat capacity at the glass transition of fully crosslinked and uncrosslinked polymers, respectively).

Theoretical considerations on the T_g and α relationship for thermosetting polymers can be found in research of Pascault-Williams [11], Hale [12], and Venditti and Gillham [13]. The relationship between T_g and α in the curing reaction of the EPY® epoxy system based on Pascault-Williams model, Oleinik model, and Hale model was shown in the previous article [14].

Venditti and Gillham [13, 15] proposed a relatively simple equation to describe the T_g and α relationship for thermosetting systems, which was based on thermodynamic considerations put forth by Couchman [16, 17] to predict the dependence of T_g on the mole fraction of constituents of a linear copolymer:

$$\ln(T_g) = \frac{(1 - \alpha) \cdot \ln(T_{g0}) + \dfrac{\Delta C_{p\infty}}{\Delta C_{p0}}\alpha \cdot \ln(T_{g\infty})}{(1 - \alpha) + \dfrac{\Delta C_{p\infty}}{\Delta C_{p0}}\alpha} \qquad (3)$$

To date, the equation in various modifications has been proposed to fit the T_g and α values data of epoxy systems with relatively uncomplicated curing reactions. These systems include epoxy-amine [13, 15, 18–20], epoxy-hexahydro-4-methylphthalic anhydride [21], novolac [22], dicyanate ester [23] in which the T_g increases rapidly in the later stages of cure.

The generality of eqs. (2) and (3) may be contrasted with other T_g versus α relationships for thermosetting systems, which are derived by explicitly accounting for the effects of changes in molecular architecture on the value of T_g [18, 19, 22, 24]. For example, Aronhime and Gillham [15] determined a T_g versus α relationship by separating the contributions of the sol and gel fractions to the overall T_g of thermosetting systems:

$$T_g = \omega_s T_{gs} + \omega_g T_{gg} \qquad (4)$$

where: ω_s and ω_g – the sol and gel weight fractions, respectively, T_{gs}, T_{gg} – the values of glass transition temperatures of the sol and gel fractions, respectively.

It is of interest to note that the relationship between T_g and α in eqs. (2) and (3) was derived using general thermodynamic arguments, e.g., by equating the entropy of the liquid with the entropy of the glass at the glass transition. Information on structural features of the molecular architecture versus α is not necessary to utilize eqs. (2) and (3). For example, the molecular weight and the conversion at gelation are not used in the equation.

The investigations presented in this and earlier paper [14] concern the EPY® epoxy system as a material for the foundation chocks in seating of a ship machinery and installations and also for many various heavy land-based machines in mining, power industry, and other fields of heavy industry and building engineering [25].

The aim of this work was to show that the T_g versus conversion behavior for the EPY® epoxy system can be predicted using the adapted DiBenedetto equation and differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) measurements on the uncured or the non-fully or fully cured materials.

EXPERIMENTAL PART

Materials

The main components of the investigated material, whose trade name is EPY® (from Marine Service Jaroszewicz, Szczecin, Poland), are: epoxy resin Epidian 6 (characterized by epoxy number of 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 was completed with additives giving appropriate technological properties and utility of the material.

Sample preparation

The system samples were cast in steel forms in the shape of rectangular bars (50 x 10 x 5 mm) for DSC and DMA investigations as well as in the shape of cylinders (ϕ = 10 x 50 mm) for TMA testing and then cured at 23 °C for various periods of time (4, 8, 12, 24, 48 or 168 h). Some samples cured at 23 °C for 24 h were post-cured additionally at 40, 60, 80 or 100 °C for 1, 2 or 4 h.

Method of testing

DSC measurements

The course of the curing and post-curing reaction of the material was investigated using a differential scanning calorimeter DSC Q100 (TA Instruments). The samples (approx. 20 mg) were subjected to two heating cycles in DSC, at the rate of 10 °C/min from -50 °C (under 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 post-curing 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 order to determine an accurate value of T_g. This value was determined from DSC thermograms as the temperature corresponding to half height of ΔC_p, when the polymer passes from the glassy state to the rubbery state.

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 one "as-mixed" sample without curing treatment there was calculated the degree of "chemical" conversion (α_{DSC}) of the curing reaction:

$$\alpha_{DSC} = 1 - \frac{\Delta H_r}{\Delta H_T} \qquad (5)$$

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

TMA measurements

Thermal linear expansion of the investigated material was measured on the stand whose design project was based on the recommendations of the ASTM D 696 standard. This stand, measuring system and procedure were described in the previous work [25]. Measurements of sample length were executed in the temperature range of 23–135 °C at the heating rate of 1.5 °C/min. The T_g was determined in the inflexion point of curve for relative increase of sample length ($\Delta L/L_0$) dependent on temperature.

The degree of "mechanical" conversion in TMA (α_{TMA}) is calculated as [26]:

$$\alpha_{TMA} = \frac{L_t - L_0}{L_\infty - L_0} \qquad (6)$$

where: L_t, L_0, L_∞ – lengths of the sample at a time t, at the onset (uncured sample) and upon completion of the reactive process when the material is fully cured, respectively.

DMA measurements

The dynamic mechanical properties in flexion of the investigated material were determined with the DMA MK-II dynamic thermal analyzer of Polymer Laborato-

ries. The testing was carried out on three-point bending mode with an oscillating frequency of 1 Hz at temperatures ranging from -100 to 250 °C and at the heating rate of 3 °C/min under nitrogen atmosphere. The T_g was determined by maximum peak of loss modulus (E'').

The degree of "mechanical" conversion in DMA (α_{DMA}) is calculated as [27]:

$$\alpha_{DMA} = \frac{E_t' - E_o'}{E_\infty' - E_o'} \qquad (7)$$

where: E_t', E_o', E_∞' – the storage moduli at a time t, at the onset (uncured sample) and upon completion of the reactive process (fully cured sample), respectively.

RESULTS AND DISCUSSION

The experimental dependence of T_g *versus* α obtained by means of three methods (DSC, TMA and DMA) for EPY® epoxy system cured at different temperatures are shown in Fig. 1. In this figure a fit of T_g *versus* α relation using DiBenedetto equation [eq. (2)] are also presented. Structure-dependent parameter for EPY® system amounted to λ = 0.426 [14]. Additionally, α value in which gelation occurs (α_{gel}) is marked with an arrow. Value of α_{gel} = 0.58 was determined experimentally using ARES (Advanced Rheometric Expansion System) and DSC methods [14].
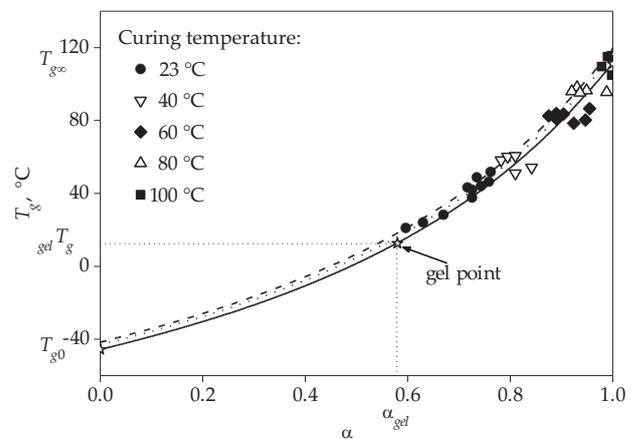

Fig. 1. Relationship between T_g and conversion degree (α) for EPY® material at various cure temperatures [solid line – the relationship determined using eq. (2) for DSC data, dashed line – the relationship determined using eq. (2) for TMA data, dotted line – the relationship determined using eq. (2) for DMA data]

Verification of the DiBenedetto's equation over gelation point of the EPY® system ($0.58 < \alpha \leq 1$) conducted on the material samples both cured and post-cured for different temperatures and periods show good correlation with the experimental results obtained with DMA, TMA as well as DSC methods at every cure temperatures, which can be seen in Fig. 1. The resulting regression analysis performed using eq. (2) to the experimental data presented in Fig. 1 gave a high degree of correlation, judging from the obtained values of the squared coefficient of correlation (R^2) of 0.992; 0.994 and 0.972 for DMA, TMA and DSC measurements, respec-

tively. The T_g values obtained for the investigated material adequately by means of different experimental techniques are different of course. The values obtained with TMA and DMA methods are by 1–3 °C and by 2–5 °C higher, respectively, than those obtained by means of DSC method. It results from the fact that TMA and DMA methods include the effect of distortion force and its frequency on glass transition process which is omitted in the calorimetric method of DSC.

As far as small degrees of cure ($\alpha < 0.58$) are concerned, the increase in T_g occurs due to an increasing molecular weight of the epoxy resin, whereas, at high conversion degree, a T_g increase results from higher crosslink densities [23]. Obtained results show a two-stage progressive increase in the T_g values. At the first stage ($T_{cure} > T_g$), the T_g increase took place rapidly, but as the T_g approached T_{cure}, the rate of increase dropped significantly. The point separating these two stages is named the vitrification point. The cure reaction prior to vitrification is distinctly dominated by the rate of the chemical reaction of cure. As the crosslink density increases with the progress of the chemical reaction, the difference between the transient T_g value and the cure temperature decreases. The increase in the crosslink density in turn results in a state which seriously hinders the physical movement of the molecules. At this time the reaction becomes dominated by a diffusion type control and relative lack of mobility of the reactive groups conduces to decrease of the overall crosslink conversion rate by several orders of magnitude.

CONCLUSIONS

Performed tests enable us to establish the relationship between the degree of "chemical" conversion and the degree of "mechanical" conversion, and the relationship between the T_g determined by DSC and TMA and DMA.

The one-to-one relation between T_g and α obtained for the EPY® material by means of three different experimental methods allows one to convert α values into T_g values or *vice versa* at any stage of the curing process. The T_g values obtained with TMA and DMA methods compared to DSC method are higher by about 2 and 4 °C, respectively.

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