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A relationship between the glass transition temperature and the conversion degree in the curing reaction of the EPY® epoxy system

RAPID COMMUNICATION

Summary — There has been studied correlation between the glass transition temperature (T_g) and the conversion degree (α) in the cure reaction of the EPY® epoxy system (applied for machine foundation chocks), following evaluation of both these parameters. Three model correlations of $T_g = f(\alpha)$ developed from DiBenedetto equation by Pascault and Wiliams, by Oleinik and also by Hale were verified. It was proved that the latter model best fits the experimental results T_g *versus* α obtained with the differential scanning calorimetry (DSC) method.

Keywords: epoxy system, glass transition temperature, conversion, modified DiBenedetto equation.

ZALEŻNOŚĆ MIĘDZY TEMPERATURĄ ZESZKLENIA I STOPNIEM KONWERSJI W REAKCJI SIECIOWANIA UKŁADU EPOKSYDOWEGO EPY®

Streszczenie — Badano wzajemną zależność temperatury zeszklenia (T_g) i stopnia konwersji (α) podczas reakcji sieciowania systemu epoksydowego EPY® stosowanego do produkcji podkładek fundamentowych maszyn. Dokonano weryfikacji wyprowadzonych z równania DiBenedetto trzech modelowych zależności $T_g = f(\alpha)$ zaproponowanych przez Pascaulta i Williamsa oraz Oleinika, a także Hale'a. Wykazano, że równanie zaproponowane przez Hale'a najlepiej opisuje wyniki eksperymentalne T_g i α (rys. 1) uzyskane metodą różnicowej kalorymetrii skaningowej (DSC).

Słowa kluczowe: układ epoksydowy, temperatura zeszklenia, konwersja, zmodyfikowane równanie DiBenedetto.

Epoxy resins are one of the most important class of thermosetting polymers, widely applied as surface coatings, structural adhesives and matrices for fiber-based composites [1—4]. In recent years there has been increased interest in ordered polymeric networks as potential materials for electronics packing and also for advanced composites including machine elements [5, 6]. Among many desirable properties of epoxy materials are high compressive strength and good performance at elevated temperatures. The effect of temperature and conversion on glassy-state properties of these materials is a matter of importance for their performance.

The glass transition temperature (T_g) is one of the most important parameters of a polymeric system. T_g determines the temperature boundary of significant changes in the enthalpic, viscoelastic, dilatometric *etc.* properties of all glass-forming materials. The relationship between T_g and conversion degree in the curing reaction (α) of thermosetting materials is a central concept in analyzing cure phenomena. The relevance of T_g to processing and properties of material is based on the following:

— the processing of a reactive material must be performed at temperatures above the value of T_g of uncured material (T_{g0}) so that the material can be conveniently applied in a state of low viscosity;

— the value of T_g at full conversion of a thermoset ($T_{g\infty}$) is related to the upper temperature limit of the glass-converted material.

The relationship between T_g and α determines when vitrification occurs during cure, for which T_g

equals the cure temperature (T_c). At a given T_c, the reaction of a thermosetting material proceeds generally at a rate dictated by chemical kinetics if T_g is less than T_c. However, if T_g is higher than T_c, the reaction rate is controlled by diffusion.

T_g of a thermosetting polymers is a property which depends on the α value [7, 8]. An increase in the crosslinking density reduces mobility of chain segments and consequently T_g increases. Among numerous theoretical and empirical relations between T_g and crosslinking density (thus conversion therein) reported in the literature involve mostly linear dependences [9, 10], but exponential [11, 12] or logarithmic relationships can also be found [13]. To predict T_g *versus* α a relationship of thermosetting systems DiBenedetto equation [14] is usually applied in widely known Nielsen's form [12]. Some other equations developed from it, *e.g.* Pascault and Williams [15] or Hale [16] equations can also give good fit to the experimental results.

The cure process of thermosetting systems is conveniently presented both in an isothermal time-temperature-transformation (TTT) cure diagram [17, 18] and in a conversion-temperature-transformation (CTT) one [19]. The former displays phenomenological changes that took place (gelation and vitrification) during the cure and the latter shows the relationship between the α value in the system and T_g developed. Such diagrams plotted for the EPY® epoxy system, using amongst other DiBenedetto equation $T_g = f(\alpha)$, were presented in previous articles [20, 21]. Besides other thermal diagram of T_g-temperature-property (T_gTP) [22, 23] is very useful to consider the relationship between physical properties of the material after curing (*e.g.* loss modulus, density, physical ageing rate) and α at different temperatures. For example, a relation of loss modulus and α for the EPY® system was described by means of a diagram showed in the previous article [24].

The present article is aimed at verification of experimental data with theoretical values of function T_g *versus* α obtained from three equations derived by Pascault—Williams [15], Oleinik [25] and Hale [16] from DiBenedetto equation [12, 14] for the EPY® epoxy system applied as a material for the foundation chocks in seating of ship machinery and installations and also for many various heavy land-based machines [26]. Differential scanning calorimetry (DSC) was employed for monitoring the curing reaction and determining thermal properties of the system during its cure progress.

EXPERIMENTAL

Materials

The main components of the investigated material, which trade name is 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 curing agent to resin ratio is constant and equals 14 weight parts of the curing agent per 100 parts of the resin. The epoxy system is completed with additives giving appropriate technological properties and utility of the material. Chemical structures of the reacting materials are shown in the previous article [27].

Sample preparation

The system samples were cast in steel forms in the shape of rectangular bars (50 × 10 × 5 mm) and cured at 23 °C for 4, 8, 12, 24, 48 and 168 h. Also, several samples cured at 23 °C for 24 h were additionally postcured at 30, 40, 50, 60, 70, 80 and 100 °C for 1, 2 or 4 h. The preparation of the samples used in the investigations of curing and postcuring processes was given in the previous article [20].

The method of testing

Differential scanning calorimeter (Du Pont DSC 910) was used to measure the glass transition temperature (T_g) and the change in specific heat capacity at the glass transition temperature (ΔC_p) of the different samples at 10 °C/min heating rate under the nitrogen atmosphere. The following values were determined with DSC thermograms:

— T_g as the temperature corresponding to the point of half heigh of specific heat capacity change (ΔC_p), when the polymer passes from the glassy state to the rubbery state;

— ΔC_{p0} — change of the isobaric specific heat capacity at the glass transition of uncured resin;

— $\Delta C_{p\infty}$ — change of the isobaric specific heat capacity at the glass transition of fully reacted resin;

— 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 [20]) corresponding to one "as-mixed" sample without curing treatment:

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

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

The method applied was the same as defined in the previous article [20]. The DSC technique has been also described in detail in [28—30].

RESULTS AND DISCUSSION

Having taken one after the other relations between T_g and α given by different equations we can verify which of them could better fit the experimental results obtained for the EPY® system.

Pascault—Williams model

The empirical DiBenedetto equation [14] gives one-to-one relationship between T_g and α for a wide variety of thermosets in the form introduced by Nielsen [12]:

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

where: T_{g0} — *the glass transition temperature of the uncured resin* (α = 0), $T_{g\infty}$ — *the glass transition temperature of the fully reacted resin* (α = 1), λ — *a structure-dependent parameter with value between 0 and 1*.

From an extension of the Couchman equation [31], Pascault and Williams [15] showed that λ is equal to the ratio $\Delta C_{p\infty}/\Delta C_{p0}$.

Equation (2) is defined between α = 0 and α = 1. In general it is supposed that the epoxy/amine system can reach α = 1 after postcuring. Thus, the thermal values for the EPY® system *i.e.* the maximal value of glass transition temperature $T_{gmax} = T_{g\infty}$ = 111.2 °C, T_{g0} = -45.6 °C, $\Delta C_{p\infty}$ = 0.02848 J/(g · °C) and ΔC_{p0} = 0.06755 J/(g · °C) [20] were determined with the DSC method. The DiBenedetto curve $\alpha = f(T_g)$ [according to eq. (2)] in the form proposed by Pascault and Wiliams for the investigated system is shown in Figure 1 (solid line).

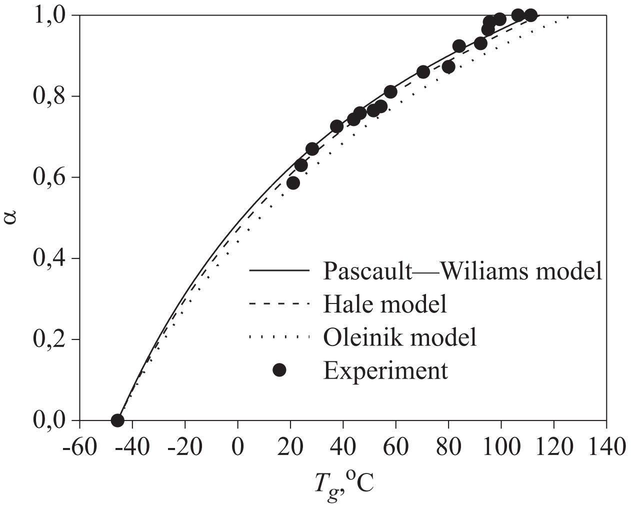

Fig. 1. Conversion degree (α) as a function of the glass transition temperature (T_g) for the EPY® epoxy system

Pascault—Wiliams model verified in the region above the gel point of the EPY® system *i.e.* above α_{gel} = 0.58 (the conversion degree at the gel point) [20] with the samples cured at 23 °C for different time intervals (from 4 to 168 h) and postcured at different temperatures (from 30 to 100 °C) for various time intervals (from 1 to 4 h) appears to be in rather good accord with the experimental results (symbols) which can be seen in Figure 1. The temperature at which gelation and vitrification occur simultaneously $_{gel}T_g$ = 15.1 °C given by Pascault—Wiliams curve at the Flory's theoretical gel point α_{gel} = 0.577 [32] and experimental value of $_{gel}T_g$ = 12.5 °C differ a little. Nevertheless the theoretical curve fits well enough the experimental α up to its value of 0.9. One can note that a small increase in α leads to a significant increase in T_g due to the slope of Pascault—Wiliams curve in the high T_g region. Thanks to that the DSC method is able to detect a small increment in α as soon as the T_g measurement is precise in this region, while other methods fail at the end of the curing reaction.

Oleinik model

It is convenient to assume that the postcured networks reached a T_{gmax}, which is equal to $T_{g\infty}$. However, such networks can reach only a T_{gmax} corresponding to a conversion degree of α_{max}, which is unknown. Oleinik's research [25] on epoxy/amine system suggested that α_{max} conversion degree should be equal to 0.95—0.96 because topological limitations produce an effect of non-equal reactivity at high α value. The unreacted epoxy or amine groups are spatially separated from each other and cannot meet and react due to the high network connectivity at the end of reaction [25]. Taking into account the latter value of α_{max} reached at the experimental value of T_{gmax} = 111.2 °C, one can see that the theoretical curve $\alpha = f(T_g)$ plotted for the EPY® system (dotted line in Figure 1) gives the values of $_{gel}T_g$ = 20.8 °C and $T_{g\infty}$ = 127.5 °C none of which fits well enough the experimental results. It stands to reason that one should not take this curve into account.

Hale model

Hale *et al.* [16] found, for their epoxy/novolac system, an optimum α value of 0.85. They explained this low value by more severe topological limitations because their system had a much higher functionality than an amine/epoxy system.

To estimate $T_{g\infty}$, Hale *et al.* [16] suggested to restate DiBenedetto equation (2) as:

$$\frac{T_g - T_{g0}}{T_{gM} - T_{g0}} = \frac{\lambda'\alpha'}{1-(1-\lambda')\alpha'} \tag{3}$$

where: T_{gM} — *the glass transition temperature of a network whose conversion degree is perfectly known and close to 1*, α' — *the* α/α_M *ratio, where* α_M *is the conversion degree of the network showing* $T_g = T_{gM}$ *and* $\lambda' = \Delta C_{pM}/\Delta C_{p0}$, ΔC_{pM} — *the changes in heat capacity trough the glass transition of the* T_{gM} *network (index M denotes the highest value used)*.

To apply eq. (3) to the EPY® system, the experimental data: T_{gM} = 92.2 °C, α_M = 0.93, ΔC_{pM} = 0.0325 J/(g · °C) were taken. This new theoretical curve (dashed line in Figure 1) gave the theoretical values $_{gel}T_g$ = 15.5 °C and $T_{g\infty}$ = 114.6 °C. We can see here that this new curve (dashed line) up to value α ≈ 0.96 fits the experimental results (correlation coefficient R^2 = 0.988) better than the curve plotted for the Pascault—Wiliams model (solid line).

CONCLUSIONS

This one-to-one correspondence between the T_g and α that was found for the EPY® system is independent of the cure temperature and is just what we need to convert α values into T_g values and inversely when it is necessary. Similar relationships for different epoxy systems were also reported by other authors [33, 34].

The correlation between α and T_g marked in Figure 1 clearly shows that at a small conversion region, an increase in T_g proceeds due to a growing molecular weight of the epoxy resin, whereas in high conversion, an increasing T_g results from growth in crosslinking densities [35].

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