

EPOXY POLYMERS: GLASS TRANSITION/CURE DEGREE CORRELATION

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The correlation between the glass transition temperature, T_g , and the cure degree, α , of epoxy polymers has been analysed on the basis of an extension of the Vogel–Tamman–Fulcher equation for the viscosity of polymers and glasses.

A physical meaning has been given to the coefficients of the series expansion of the function $T_g = T_g(\alpha)$.

This analysis allows one to verify that the experimental (T_g, α) data support the conclusion that, in the case of thermoset polymers, the ideal glass transition temperature, T_0 , appearing in the VTF equation, is larger than T_g .

This conclusion may be supported by the thermodynamic interpretation of T_0 as the temperature at which the excess entropy of the systems tends to vanish: in the case of partially cured thermosets; T_0 would represent the minimum temperature at which the system becomes able to enhance its cure degree.

One of the main parameters allowing the characterization of any polymer is its glass transition temperature, T_g .

In the case of polymers such as epoxy resins, the glass transition temperature depends upon the polymerization degree, α , of the material considered [1]. Accordingly, it is of some relevance to establish the dependence of T_g on α .

As phenomenological evidence, in isothermal cure processes T_g increases up to the cure temperature, T_c , with increasing α , so that, when α approaches unity, $T_g = T_c$. Further, both the T_g vs. α trend and the T_g value at $\alpha = 1$ seem dependent upon T_c . One can thus define a peculiar T_g vs. α trend for each given T_c cure process [1, 2].

The aim of the present work is to interpret the phenomenological correlations between T_g and T_c , and between T_g and α .

General considerations

To attain this goal, it is necessary to define T_g in terms of another suitable property of the material investigated. One possibility is offered by the well-known empirical relationship connecting the viscosity of polymers and glasses with temperature, viz. the Vogel–Tamman–Fulcher (VTF) equation:

$$\eta = A \exp [B/(T - T_0)] \quad (1)$$

where η is the viscosity, T_0 is the “ideal” glass transition temperature, and A and B are constant parameters, characteristic of the material under investigation.

In order to define the glass transition temperature, Eq. 1 can be rewritten as

$$T_g = T_c + \Delta - B/(\log \eta/A) \quad (2)$$

where Δ is the difference ($T_g - T_0$).

For an isothermal ($T = T_c$) progressing cure, one may safely assume that, after a partial cure, viz. $\alpha < 1$, a polymer sample would obey Eqs 1 and 2, provided that $T \leq T_g$, i.e. when the cure may be supposed to be frozen [3]. Accordingly, the expression

$$T_g(\alpha) = T_c + \Delta(\alpha) - B(\alpha)/[\log \eta/A(\alpha)] \quad (3)$$

should adequately represent any intermediate step of an isothermal cure process occurring at T_c .

A more explicit expression describing the T_g vs. α trend requires some assumption about the dependence of η on α .

As the logarithm of η is roughly proportional to the molecular weight of the material investigated [4], it seems reasonably to hazard that $\log \eta$ could parallel the α vs time trend, viz. if

$$\alpha = 1 - \exp(-kt)$$

then

$$\log \eta = \log \eta_0 + \gamma[1 - \exp(-kt)] \quad (4)$$

where $\gamma = \log [\eta(\alpha=1)/\eta_0]$, so that $d\eta = \gamma\eta d\alpha$.

The experimental evidence that T_g attains T_c when $\alpha = 1$ supports the assumption that a function representing the T_g vs. α trend should have a definite value at $\alpha = 1$, viz. T_c .

It then seems reasonable to approach such a function through a series expansion, viz.:

$$T_g = T_g(\alpha = 1) - (1 - \alpha) (dT_g/d\alpha)_{\alpha=1} + \\ + (1 - \alpha)^2/2(d^2T_g/d\alpha^2)_{\alpha=1} + \dots \quad (5)$$

with $T_g(\alpha = 1) = T_c$.

The coefficients of the polynomial expression in Eq. 5 are physically meaningful, inasmuch as they relate to γ and Δ , viz.:

$$(dT_g/d\alpha)_{\alpha=1} = (d\Delta/d\alpha)_{\alpha=1} + \gamma[\Delta^2/B]_{\alpha=1}$$

and

$$(d^2T_g/d\alpha^2)_{\alpha=1} = (d^2\Delta/d\alpha^2)_{\alpha=1} - 2\gamma^2[\Delta^3/B^2]_{\alpha=1}.$$

Experimental

T_g values were determined for four epoxy adhesives, chosen from among those currently employed by the aerospace industries. All of them were isothermally cured at $T_c = 373$ K.

A DuPont differential scanning calorimeter mod. 1090 was employed: a suitable heating rate was found to be 2 deg/min; as a rule, the flexus point of the baseline shift was taken as representative of the glass transition.

A typical sample weight was about $20 \cdot 10^{-3}$ g. When the samples of a given epoxy adhesive showed two or more T_g signals, only the highest ones, i.e. those converging to the corresponding T_c , were taken into account, the remaining signals being attributable to polymer components not involved in the formation process of the final copolymer [1].

Results and discussion

As a rule, the experimental (T_g , α) values can be satisfactorily fitted with second-order polynomials.

When obtained from regression analysis, the latter describe trends with a minimum for some low α value (e.g. rather close to $\alpha=0$), which are therefore physically meaningless.

The incongruity can be overcome, however, by adding the condition $(dT_g/d\alpha)_{\alpha=0} \geq 0$.

If the simplest case, i.e. $(dT_g/d\alpha)_{\alpha=0} = 0$, is assumed, it follows from Eq. 5 that

$$(dT_g/d\alpha)_{\alpha=1} = (d^2T_g/d\alpha^2)_{\alpha=1}$$

and

$$dT_g/d\alpha = \alpha(d^2T_g/d\alpha^2)_{\alpha=1} = d^2T_g/d\alpha^2$$

Under such conditions, it is easy to verify that

$$T_g = T_c - (d^2T_g/d\alpha^2)_{\alpha=1}(1 - \alpha^2)/2$$

$$(d^2T_g/d\alpha^2)_{\alpha=1} = 2[T_c - T_g(\alpha = 0)]$$

and that the "fitting" expression for the T_g vs. α trend reduces to

$$T_g = T_c - [T_c - T_g(\alpha = 0)](1 - \alpha^2) \quad (6)$$

An iterative calculation can therefore be used to single out the best value of $[T_c - T_g(\alpha = 0)]$, which corresponds to the minimum of the sum

$$\Sigma(T_{g,calc} - T_{g,exp})^2$$

Such $[T_c - T_g(\alpha = 0)]$ values are reported in Table 1 for all the epoxies investigated.

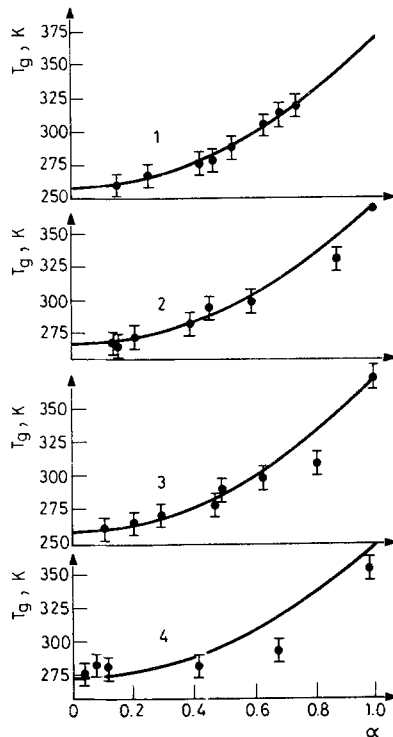


Fig. 1 T_g vs. α experimental data "fitted" with iterative use of Eq. 10. 1) AF 163 WT06; 2) AF 163/2 WT06; 3) FM 53; 4) FM 123/2. All the samples were isothermally cured at 373 K

Table 1

Epoxy	$[T_c - T_g(\alpha = 0), K$
AF 163 WT06	115
AF 163/2 WT06	107
FM 53	117
FM 123/2	101

Figure 1 shows the corresponding "calculated" curves matching the experimental data.

As a further consequence of the above approach, one may easily recognize that the Δ vs. α trend is represented by a function $\Delta(\alpha)$ with derivatives at $\alpha=1$:

$$(d\Delta/d\alpha)_{\alpha=1} = [T_c - T_g(\alpha = 0)] - \gamma(\Delta/B)_{\alpha=1}$$

and

$$(d^2\Delta/d\alpha^2)_{\alpha=1} = [T_c - T_g(\alpha = 0)] + 2\gamma^2(\Delta^3/B^2)_{\alpha=1}$$

From the analysis of the corresponding series expansion for $\Delta(\alpha)$ it follows that

$$\Delta(\alpha = 1) = [T_g(\alpha = 1) - T_0(\alpha = 1)] = [T_c - T_0(\alpha = 1)] = -2B/\gamma < 0$$

which is possible only if

$$\Delta(\alpha) < 0$$

throughout the α range.

Such a conclusion is apparently opposite to the usual observation concerning glasses and non-thermoset polymers [5, 6]. However, it finds simple justification in the fact that the systems investigated here host a progressing chemical reaction, viz. the isothermal extension of a polymer framework.

In fact, T_0 , the ideal glass transition temperature, has been thermodynamically interpreted [7] as the temperature at which the excess configurational entropy of the system vanishes.

In the present case, the progress of the polymerization implies the involvement of further bonds in the polymer network, i.e. a reduction of the "disorder".

Accordingly, the exhaustion of the reaction would correspond to a "no more reactive group situation", i.e. to a completely defined framework [8], whose configurational entropy may be considered zero with respect to the initial mixture of monomers.

Hence, for this kind of polymer, T_0 would represent the minimum temperature at which the system is able to attain (no matter what the time required) the exhaustion of bond formation throughout its own extension.

This also means that a thermoset polymer which is not completely polymerized ($\alpha < 1$) requires to be held at least at $T = T_0 > T_g$ to enhance its α : were the system held at $T = T_g$, it would not be able to support the progressing of the cure.

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Zusammenfassung — Die Korrelation zwischen der Glasumwandlungs-temperatur T_g und dem Aushärtungsgrad α von Epoxidpolymeren wurde analysiert, und zwar basierend auf einer Erweiterung der Vogel-Tamman-Fulcher-Gleichung für die Viskosität von Polymeren und Gläsern. Den bei der Reihenentwicklung der Funktion $T_g = T_g(\alpha)$ auftretenden Koeffizienten wurde eine physikalische Bedeutung zugeschrieben. Diese Analyse ermöglicht nachzuweisen, daß die experimentellen Daten (T_g , α) die Schlußfolgerung stützen, daß im Falle von hitzehärtbaren Polymeren die in der VTF-Gleichung auftretende sogenannte ideale Glasumwandlungstemperatur T_0 höher als T_g ist. Diese Konklusion wird auch durch die thermodynamische Interpretation von T_0 gestützt, nämlich als die Temperatur, bei der die Überschußentropie des Systems gegen Null geht: im Falle von teilweise ausgehärteten hitzehärtbaren Polymeren würde T_0 die minimale Temperatur darstellen, bei der eine Erhöhung des Aushärtungsgrades des Systems einsetzt.

Резюме — Корреляция между температурой расстекловывания T_g и степенью вулканизации (α) эпоксиполимеров анализировалась на основании расширенного уравнения вязкости Вогеля-Таммана-Фулчера для полимеров и стекол. Дано физическое значение коэффициентов широкого ряда функций $T_g = T_g(\alpha)$. Проведенный анализ экспериментальных данных T_g и α подтвердил заключение, что так называемая идеальная температура расстекловывания T_0 , появляющаяся в уравнении Вогеля-Таммана-Фулчера, в случае термореактивных полимеров выше чем T_g . Это заключение подтверждается также термодинамической интерпретацией T_0 , как температуры, при которой избыточная энтропия систем стремится к нулю. В случае частично вулканизированных термореактивных полимеров, T_0 представляет ту минимальную температуру, при которой системы становятся способными к увеличению степени вулканизации.