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# VITRIFICATION AND PHYSICAL AGEING ON ISOTHERMAL CURING OF AN EPOXY RESIN

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Vitrification phenomena and further structural relaxation processes or physical ageing occurring in the isothermal curing reaction of an epoxy resin are studied by Differential Scanning Calorimetry (DSC). The vitrification time, $t_v$, the limiting conversion degree and the limiting glass transition temperature ($T_g$) are evaluated at curing temperatures ($T_c$) between 30 and 100°C. The dependence of limiting $T_g$ with $T_c$ permits the determination of the maximum $T_g$ of the resin (109°C). The physical ageing, which appears as the the last step of curing reaction for curing times above to vitrification, is analyzed through the endothermic peak superposed to the glass transition temperature. The results obtained in partially reticulated resin show the kinetics of the physical ageing to slow down as $T_c$ increases, as a consequence that the segmental mobility is reduced.

## Introduction

The conversion of linear epoxy resins in three dimensional crosslinked or thermosetting materials is performed by curing reaction. The isothermal curing reaction of an epoxy resin is complex as a consequence of the interaction of the chemical kinetics of 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 coresponds to the incipient formation of an infinite network at the first step of curing, causing changes in the macroscopic system properties [3]. Vitrification involves a physical transformation from a supercooled liquid or rubbery state to a glassy solid as a result of the increase of the crosslinking density. This phenomenon occurs occurs when the glass transition temperature, $T_g$, becomes equal to the curing temperature $T_c$. The system is in the glassy state when $T_c$ becomes higher than $T_g$. Vitrification

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affects drastically the progress of curing reaction [3, 4] since the degree of conversion becomes practically quenched.

Additionally, when the system is submitted to a temperature lower than $T_g$ the structural relaxation process or physical ageing appears [5] because the glassy system is not in an equilibrium thermodynamic state and its properties like volume, entropy and enthalpy decrease with time.

This paper studies the conditions of temperature and time of isothermal curing of an epoxy resin in which the vitrification process appears and, also, the further physical ageing process influencing the last steps of curing reaction. Differential Scanning Calorimetry (DSC) technique is used to monitor the curing reaction and to evaluate the thermal properties of the resin during curing.

## Experimental

### *Materials and cure procedures*

The epoxy resin used in this study was the diglycidyl ether of bisphenol-A type (CIBA–GEIGY Araldite CY225) with an epoxy content between 5.0 and 5.3 mol/kg. A hardener derived from phthalic anhydride with accelerator (CIBA-GEIGY HY225) was used to cure the resin. The resin and hardener were mixed at a weight ratio of 10:8. The mixture was stirred at room temperature during 20 min and, then, degasified at vacuum during 15 min. Samples were enclosed in aluminium DSC capsules and cured under nitrogen atmosphere.

### *Differential Scanning Calorimetry analysis*

Isothermal curing was carried out for various periods of curing time, $t_c$, at different curing temperatures between 30 and 130°. Then, the samples of cured resin were analyzed in a Mettler Thermoanalyser 3000, with a Differential Scanning Calorimetry Cellule DSC 30, at a heating rate of 10 deg/min, from –80 to 280°, under nitrogen atmosphere.

The glass transition temperature $T_g$ and the residual enthalpy of curing $\Delta H_R$ were determined in each dynamic DSC curve. $T_g$ was measured as the half way point of $\Delta C_p$, when the polymer passes from the glassy state to the liquid or rubbery state. An apparent degree of conversion of the curing reaction is calculated from the residual enthalpy $\Delta H_R$, measured in the dynamic DSC thermogram of the cured resin during $t_c$, and from the total

enthalpy of reaction $\Delta H_T$ (297.2 J/g) corresponding to one 'as-mixed' sample without curing treatment:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}$$

## Results and discussion

Dependence of the conversion degree and glass transition temperature on curing conditions. The vitrification process.

The conversion degree and the temperature of glass transition increase with the curing time due to the increase of the crosslinking density in the network of the resin. Figures 1 and 2 show these dependences at different curing temperatures. The system vitrifies when $T_g$ equallizes $T_c$ and, then, the chemical reaction becomes practically quenched and prevents full conversion. The reaction times required for reaching $T_g = T_c$ is named vitrification time, $t_v$. At this point, the conversion degree becomes nearly constant and tends to a limiting value $\alpha_\infty$ which depends of $T_c$.

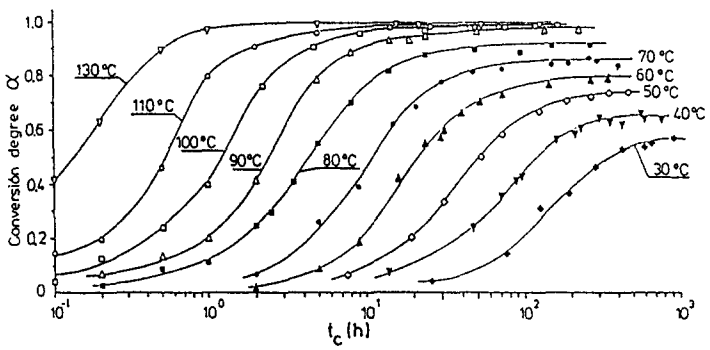


**Fig. 1** Dependence of the conversion degree on curing time at different curing temperatures

Alternatively, above $t_v$, $T_g$ increases slowly with $t_c$, due to the physical ageing process, and approaches asymptotically to a limiting value $T_{glim}$ depending of $T_c$ (Fig. 3). This limiting value increases with $T$ up to 100°, and from this value it remains constant and equal to 109°. This $T_{g\infty}$ is the maximum $T_g$ observed and corresponds to the fully cured resin [2, 3] or to the topological limit of $\alpha$ [4]. The vitrification phenomenon and further physical ageing only appears when $T_c$ is lower than $T_{g\infty}$.

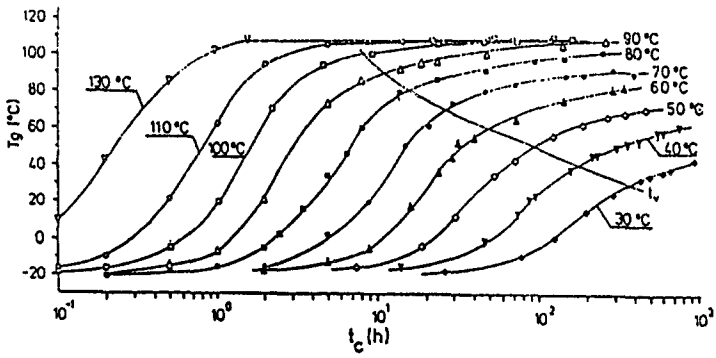


Fig. 2 Dependence of $T_g$ on curing time at different curing temperatures

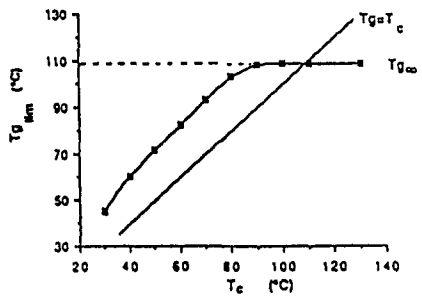


Fig. 3 Dependence of the limiting $T_g$ values on $T_c$

A strong relation is observed between the $T_g$ values (obtained without physical ageing effects when $t_c < t_v$) and $\alpha$ (Fig. 4), showing that $T_g$ is a good index of the curing reaction extent, independently, of the curing temperature [6]. The existence of this unique correspondence between $T_g$ and $\alpha$ makes evident that the same curing mechanisms are existing for temperatures between 30 and 130°.

*Analysis of the physical ageing process*

As indicated before, above the vitrification time, $T_g$, becomes higher that the curing temperature and, as a result, the system is annealed at a $T_c$ below its $T_g$ and a structural relaxation process or physical ageing in the amorphous phase of the material begins [5, 7, 8].

It is well known that the glassy state is not a thermodynamic equilibrium state and, thus, the system tends to evolve to an equilibrium (metastable) state, decreasing its properties such as volume, enthalpy and entropy with

time (see the schematic diagram on Fig. 5*a*). The free volume of the system is reduced and, consequently, the molecular mobility of the chain segments decreases.

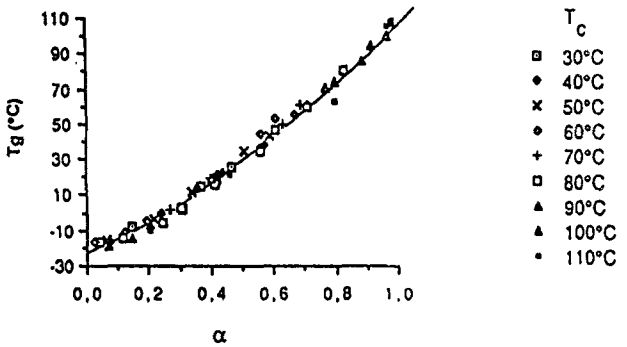


Fig. 4 Relation between $T_g$ and the conversion degree at different curing temperatures $T_c$

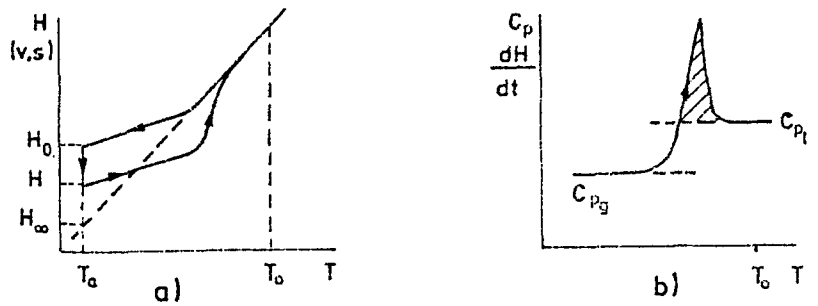


Fig. 5 Schematic digrams of enthalpy-temperature (*a*) and $C_p$ or $dH/dt$- temperature (*b*) illustrating the physical ageing effect

When the material which has been annealed or aged at $T_a<T_g$ is submitted to heating up to a temperature above $T_g$, the system recovers its equilibrium properties in a reduced interval of temperature. In a diagram representing the variation of properties (*H, V, S*) with temperature, an endothermic peak superposed to $T_g$ appears. In the schematic diagram of the Fig. 5*b*, the endothermic peak which appears in DSC curves (heat capacity or heat flow versus temperature) is represented.

These endothermic peaks, in heat capacity-temperature DSC curves, are showed in Fig. 6 for samples of epoxy resin cured at 80° and different total curing times with the condition $t_c>t_v$. The ageing time at $T_a = T_c<T_g$ can be determined by difference between $t_c$ and $t_v$ ($t_a = t_c - t_v$). In these experiments

the vitrification time was kept constant. In thermoplastic polymers [5, 7–10] and fully reticulated resins [11, 12], the intensity, position and area of the endothermic peak depend on the ageing time at $T_a < T_g$.

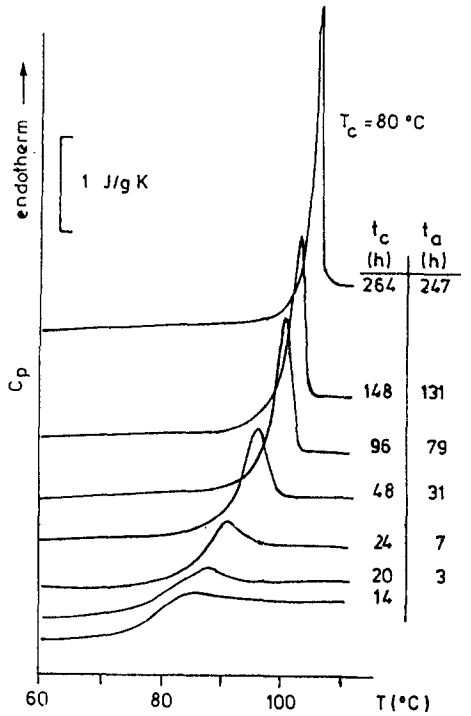


**Fig. 6** Effect of the physical ageing of epoxy resin cured at 80°C: Heat capacity *vs.* temperature for $t_c$ over $t_v$ (17 h); $t_a$ is the ageing time ($t_a = t_c - t_v$)

The area of the relaxation peak ($Q$ ), taking as the base line that of the extrapolated fluid line, is a measure of the recovery of enthalpy [9, 10] and, thus, of the extent of the relaxation process taking place at $T_c < T_g$ in a given time. For each $T_c$, the area of the endothermic peak tends to increase with time, as a consequence of the structural relaxation experimented by the system and the decrease of the properties *v–h–s*. In the partially cured resins, the occurrence of this process also depends of the $T_c$, as it begins when the system vitrifies. For high values of $T_c$, the process begins at low $t_c$ and *vicaversa*, as it is shown in Figs 2 and 7*a*.

The representation of $Q$ *vs.* the logarithm of the total curing time is used to analyze the process at various curing temperatures (Fig. 7*a* ). The slope of these lines shows the overall rate of increase of relaxation process with

$\log t_c$ for each $T_c$ (Fig. 7*b*). This slope, called 'pseudo-relaxation rate', decreases with the annealing temperature,, contrarily to the behaviour of thermoplastic polymers [9, 10] and fully reticulated resins [11, 12]. When $T_c$ increases, the 'pseudo-relaxation rate' decreases because the segmental mobility of the partially crosslinked system becomes more restricted, due

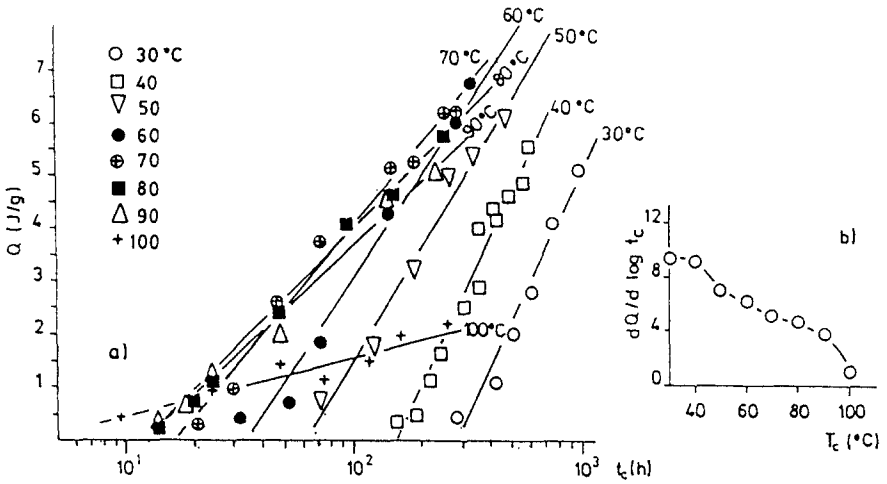


**Fig. 7** Representations of enthalpy recovery $Q$ *vs.* total curing time (*a*) and 'pseudo-relaxation rate' *vs.* curing temperature (*b*)

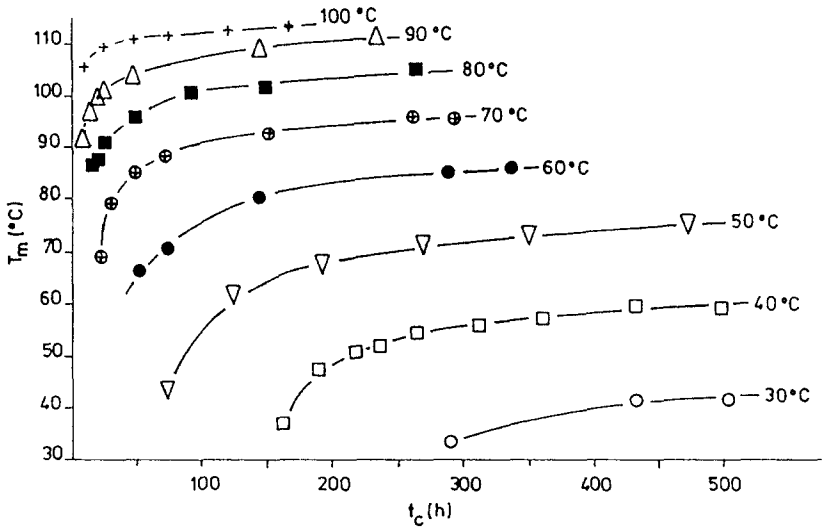


**Fig. 8** Dependence of the maximum of the endothermic peak, $T_m$, on the total curing time at different $T_c$

to the increase, of the crosslinking density (higher values of $\alpha_\infty$ are reached). In the case of high $T_c$, the limit conversion degree is high and is reached for low $t_c$ and, for the same $t_c$, the segmental motions are more restricted than curing at lower $T_c$.

Similarly, the position of the relaxation peak $T_m$ tends to increase with the total curing time for each $T_c$ as a consequence of the progress of the relaxation process and tends to a limiting value depending on $T_c$ (Fig. 8).

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**Zusammenfassung** – Vitrifikationphänomeme und strukturelle Relaxations-respektive Alterungsvorgänge von Epoxiden wurden mitells isothermer DSC Messungen untersucht. Die Vitrifikationszeit, der Grenzwert des Unwandlungsgrades und die Grenztemperatur der Glasumwandlung wurden in Bereich von 30 bis 100°C ermittelt. Werden Epoxide für Temperaturen unterhalb der Glasumwandlungstemperatur einer thermischen Behandlung ausgesetzt, so bilden sich Spannungszustände aus, die bei der Erwärmung unmittelbar über der Glasumwandlungstemperatur mit einem endothermen Vorgang relaxieren.