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Polymers

CALORIMETRIC MEASUREMENT OF THE MAXIMUM GLASS TRANSITION TEMPERATURE IN A THERMOSETTING RESIN

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The measurement of the maximum glass transition $T_{g\infty}$ of a thermosetting resin is usually performed by differential scanning calorimetry in the second scan (T_{g2scan}), after a previous scan by heating up the sample to a temperature where the exothermic curing reaction has been completed. However, this method can eventually produce thermal degradation, decreasing the crosslinking density and the T_g of the sample. Values of T_{g2scan} between 95° and 102°C were found in an epoxy resin based on DGEBA cured with phthalic anhydride. Thermal degradation effects can be avoided if the measurement is performed by isothermal curing and further determination of T_g. A $T_{g\infty}$ value of 109°C is achieved, which is the maximum value of T_g according to the topological limit of conversion.

Keywords: DSC, glass transition temperature thermosetting resin

Introduction

The glass transition temperature T_g of a thermosetting polymer is a property which depends on the conversion degree of the curing reaction. The increase in the crosslinking density reduces the mobility of chain segments, and consequently the T_g increases. When the thermosetting system is fully cured, reaching the topological limit of conversion, the $T_{g\infty}$ becomes a characteristic thermal property of the system which is known as the maximum glass transition temperature. The determination of this property is important to understand the cure process of the thermosetting system [1–4].

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Additionally, the maximum glass transition temperature is a useful property in the construction of the time-temperature-transformation isothermal cure diagram which provides a framework for studying the cure and physical properties of the thermoset in terms of the different material states encountered [2, 4, 5].

The measurment of $T_{g\infty}$ is usually performed by differential scanning calorimetry (DSC) in the second scan, after a previous scan by heating up the sample to a temperature where the exothermic curing reaction has been completed. This second scan gives the glass transition temperature (T_{g2scan}) that is attributed to the fully cured resin. Parallelly, the measurement of $T_{g\infty}$ can be carried out by other thermal analysis techniques. Remarkable are the papers by Gillham and coworkers about torsional braid analysis [2, 4–6]. However, the end temperature reached in the first scan may eventually be high enough to produce thermal degradation [1, 5–7]. This effect may lead to a light decrease in the crosslinking density and, therefore, in the T_g of the cured resin.

An alternative method for measuring $T_{g\infty}$ by DSC is proposed in this paper to avoid thermal degradation effects. The T_g values are determined via isothermal curing at different temperatures and times of reaction. The evolution of T_g with conversion degree at each curing temperature allows to determine the maximum T_g value with negligible thermal degradation effects. Rather different $T_{g\infty}$ values are obtained, which are interpreted in terms of the different curing process of the system.

Experimental

Materials and cure procedure

The epoxy resin was a diglycidyl ether of bisphenol A modified type (CIBA-GEIGY Araldite CY225) with an epoxy equivalent between 188 and 200 g/eq. A hardener derived from phthalic anhydride with accelerator (CIBA-GEIGY HY225) was used to cure the resin. Resin and hardener were mixed at a weight ratio of 10:8. The mixture was stirred at room temperature for 20 min, and then degassed in a vacuum oven at room temperature for 15 min. Samples were enclosed in aluminium DSC pans, introduced in Pyrex tubes under nitrogen atmosphere, and left in a thermostatic bath at the curing temperature T_c for different periods of time (t_c), as described in reference 7.

Differential scanning calorimetry analysis

Calorimetric measurements were performed with a Mettler Thermoanalyser TA 4000 equipped with a low temperature range DSC 30 Differential Scanning

Calorimetry module. The calorimeter was previously calibrated with indium standard. The samples weight were about 10 mg.

After the isothermal curing, the sample was quenched from T_c to room temperature, introduced in the DSC module, and then cooled to –80°C and immediately scanned at a heating rate of 10 deg·min^{-1} to 280°C under nitrogen atmosphere. The first DSC curve (Fig. 1) shows the glass transition region of the partially cured system and its residual enthalpy of curing (curves *b* and *c*), which allows to determine the apparent degree of conversion [7, 8]. The sample was immediately cooled inside the DSC module at a cooling rate ranging 80 and 60 deg·min^{-1}, and a second DSC curve was carried out from 20° to 130°C at the same heating rate. This second scan only shows the glass transition of the resin practically fully cured, and no residual enthalpy was detected (curve *d* of Fig. 1).

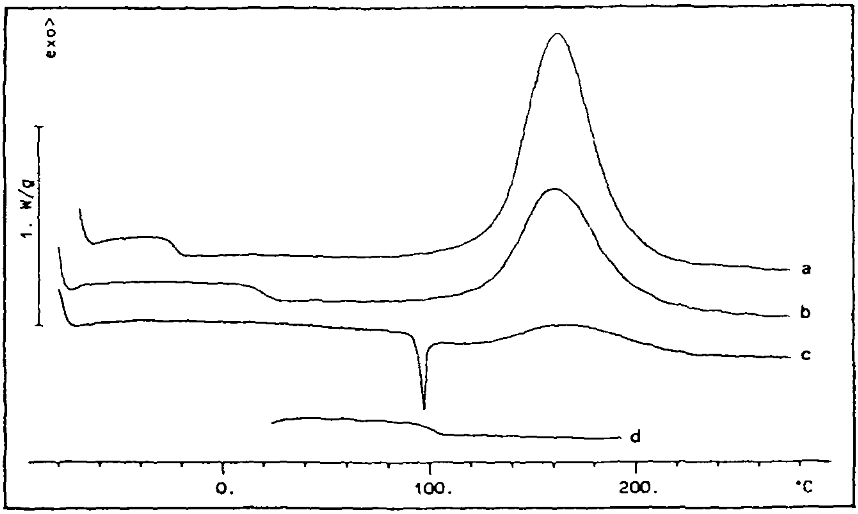


Fig. 1 First DSC curve of the epoxy-anhydride system as received (curve *a*), and cured at 70°C for 9 h (curve *b*) and 262 h (curve *c*). Curve *d* is the second DSC scan after completion of curing reaction

Results and discussion

Calorimetric measurement of T_g in the second scan

The average T_g values obtained in the second scan $T_{g_2\mathrm{scan}}$ are shown in Table 1. After isothermal curing at different T_c for various periods of time, the measured $T_{g_2\mathrm{scan}}$ values are between 98° and 102°C. A light tendence to increase with T_c is observed. On the other hand, when the sample is cured non-isothermally, without the previous isothermal treatment ($t_c = 0$) a$T_{g_2\mathrm{scan}}$ value of about 95°C is obtained.

Table 1 Average glass transition temperatures of the second DSC curve ($T_{g_2\mathrm{scan}}$) and its standard deviation, vitrification time (t_v), conversion degree at vitrification (α_v) and maximum conversion degree (α_∞) at each curing temperature T_c

T_c	$T_{g_2\mathrm{scan}}$	st.dev.	t_v/h$^{(a)}$	$\alpha_v^{(a)}$	$\alpha_\infty^{(a)}$
30	98.4	1.5	340.0	0.50	0.57
40	98.2	2.5	185.0	0.58	0.65
50	98.4	1.6	89.5	0.63	0.74
60	97.3	3.1	48.5	0.69	0.79
70	100.2	1.5	27.0	0.75	0.86
80	100.1	2.2	17.5	0.86	0.93
90	98.1	3.2	11.5	0.92	0.98
100	101.2	4.4	8.5	0.96	0.99
110	101.9	4.3	–		0.99
130	101.3	4.2	–		≈1.00
–	95.5$^{(b)}$	1.7			

$^{(a)}$ Data from Ref. 7; α is the apparent conversion degree determined by the residual enthalpy method (Ref. 7 and 8)

$^{(b)}$ $T_{g_2\mathrm{scan}}$ determined non-isothermally (curing time = 0)

These results show a dependence of $T_{g_2\mathrm{scan}}$ on curing procedure. The end temperature of the first scan is the same in both cases, with or without isothermal curing. This means that the effect of thermal degradation is practically the same in both samples, and that the differences in $T_{g_2\mathrm{scan}}$ are due to changes in the structure of the network. According to Oleinik [1], $T_{g\infty}$ is the maximum glass transition temperature when the curing reaction is completed and the conversion degree reaches the topological limit. Changes in curing conditions may originate different chemical and physical structures leading a conversion lower than its topological value. The physical properties as T_g may change as a consequence of the changes in the structure of the thermosetting system.

T_g of the isothermally cured epoxy resin: maximum glass transition temperature

As mentioned below, an alternative method to determine the maximum T_g is proposed via isothermal curing of the epoxy system. It is well known that the crosslinking density increases during the isothermal curing of the system, and consequently the T_g of the resin also increases [7]. When the isothermal curing is performed at a T_c below $T_{g\infty}$, the system vitrifies when T_g equalizes T_c at a curing time that is called vitrification time t_v. On reaching this point, the reaction rate slows down and becomes practically quenched. The system is in the glassy state and the structural relaxation or physical aging process starts [7, 9]. The slow segmental motions are the only permitted and the reaction becomes controlled by diffusion [1–4, 10]. The consequence is that the conversion degree levels off and becomes practically constant with a limiting value lower than the full conversion [7]. On the other hand, the resin does not vitrify when T_c is above the maximum T_g of the system.

Figure 2 shows the increase of T_g with curing timef or $T_c = 80°C$. When T_g becomes greater than 80°C, an endothermic peak in the glass transition region appears as a consequence of the structural relaxation process. The vitrification time, conversion degre at vitrification, and maximum conversion degree at each T_c are indicated in Table 1.

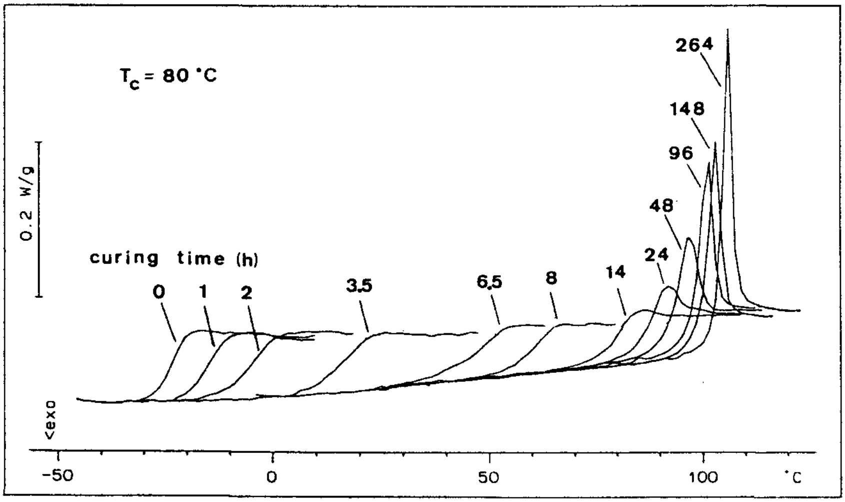
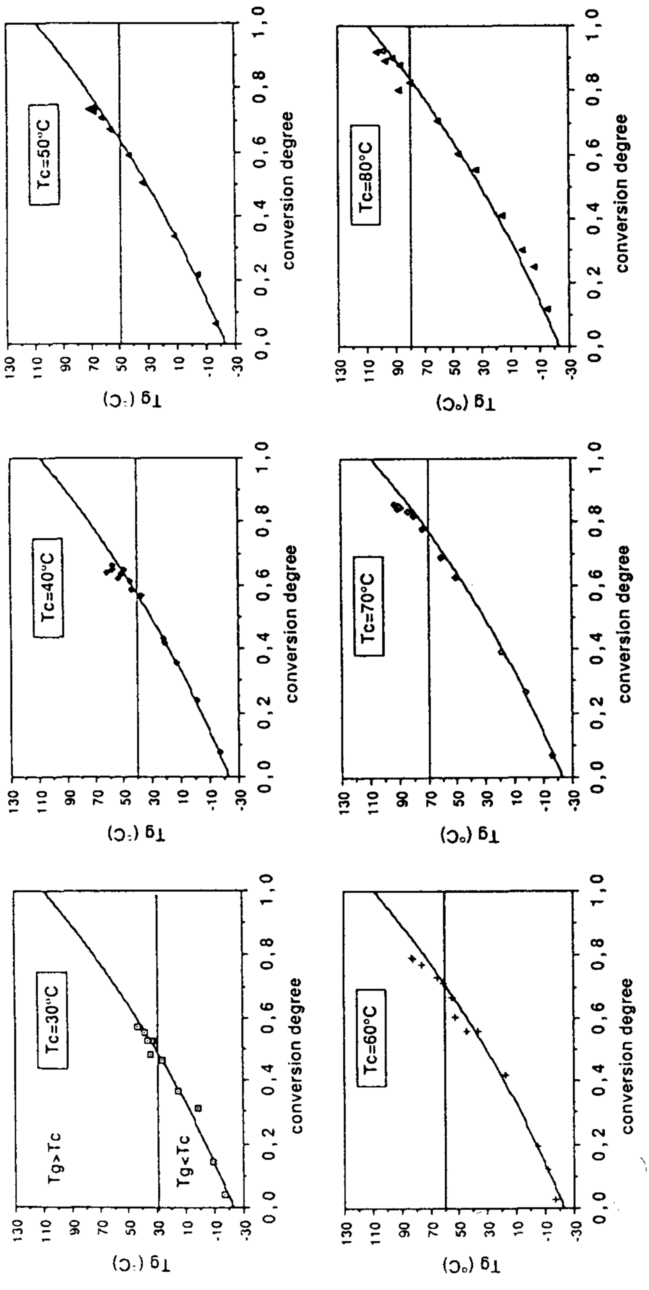


Fig. 2 Glass transition temperature for epoxy resin samples cured at 80°C at the indicated curing times. First DSC curve at a heating rate of 10 deg·min^{-1}

In Fig. 3 the T_g of the resin determined in the first DSC curve, after the isothermal curing period, is plotted *vs.* the degree of conversion. The T_g values reported in Fig. 3 correspond to the temperature of the midpoint between the liquid and the glassy lines from the heating curves. In terms of the dependence of enthalpy on temperature, the glass transition temperature may be defined as the intersection point of the extrapolation of enthalpy lines for both the glassy and liquid states obtained from a cooling experiment. However, it is not always possible to obtain precise values of C_p from DSC measurements obtained by cooling


Tc=30°C
Tg>Tc
Tg<Tc
Tc=40°C
Tc=50°C
Tc=60°C
Tc=70°C
Tc=80°C
Tg (°C)
130
110
90
70
50
30
10
-10
-30
conversion degree
0,0
0,2
0,4
0,6
0,8
1,0

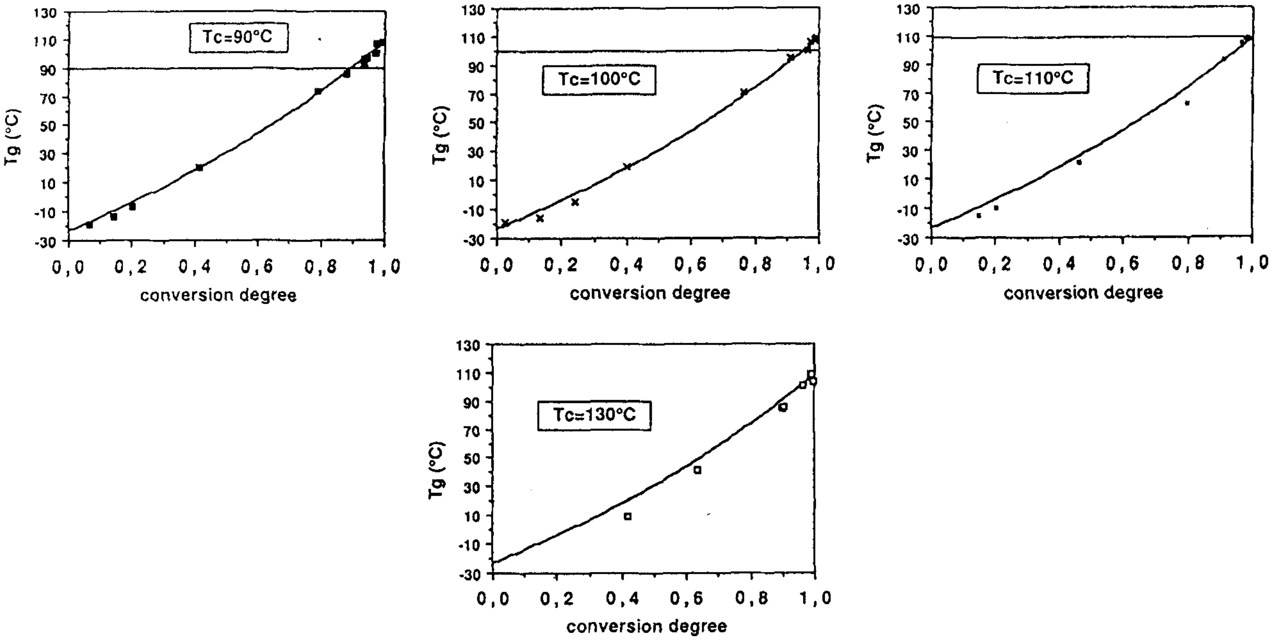


Fig. 3 Glass transition temperature *vs.* apparent conversion degree at different curing temperatures. The horizontal line marks the vitrification phenomenon at $T_g = T_C$. The curve corresponds to the plot of DiBenedetto modified equation [1] obtained with all the T_g values below the vitrification point, and $\lambda = 0.69$

[9]. Moreover, this measurement requires the sample to be heated about 50°C above T_g, which in the case of resins could modify the network. In the case of partially crosslinked resin, residual curing may starts just beyond the glass transition region as curve *c* of Fig. 1 shows, increasing the crosslinking density of the resin, and modifying the T_g to be measured. For this reason, it is better to determine the T_g of an epoxy resin from heating experiments. This T_g is expected to be close to the T_g obtained by cooling if heating follows immediately after cooling. The T_g can be measured from the intersection of both extrapolated *H–T* lines for glassy and liquid states [11, 12] or, if there is not physical aging effects, can be determined directly from the DSC curve as the temperature of midpoint of ΔC_p. This temperature will be called $T_{g1/2}$. Differences lower than 1°C between the two methods have been found in the determination of the T_g of the fully cured epoxy resin. According to Richardson *et al.* [12] greater differences can be found if endothermic relaxation peaks in C_p occur.

The horizontal line in the diagrams T_g–α of Fig. 3 marks the vitrification phenomenon ($T_g = T_c$). For T_g values below the horizontal line, the curing reaction has been performed in a liquid or gelled rubber. In these conditions, the reaction was controlled by the chemical kinetics of the reactive groups. In the schematic enthalpy-temperature (*H–T*) diagram of Fig. 4a is represented the evolution of the enthalpy in the isothermal curing at T_c (path AB), quenching from T_c to room temperature (path BC) and further heating through the glass transition region (path CB). The glass transition measured from the intersection of extrapolated *H–T* lines is very close to the $T_{g1/2}$ determined in the DSC curve shown in Fig. 4b.

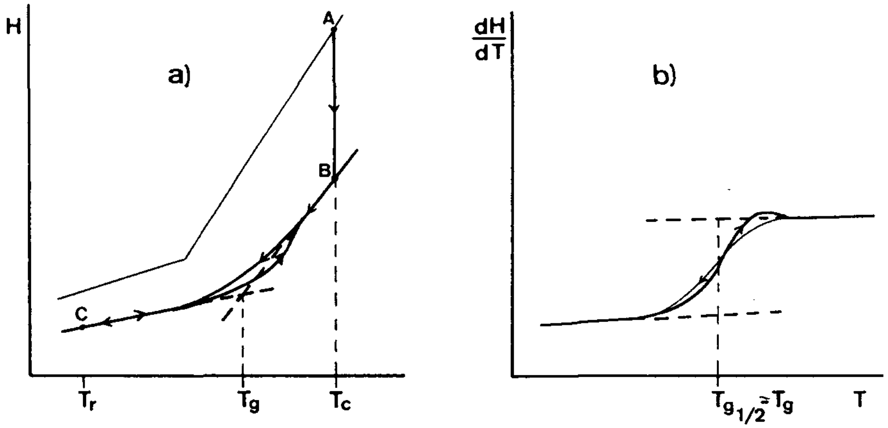


Fig. 4 Epoxy resin cured at $T_g < T_c$: a) schematic enthalpy-temperature diagram showing the isothermal curing at T_c and the determination of T_g; b) First DSC curve of the partially cured sample showing the $T_{g1/2}$ determination ($T_{g1/2} \approx T_g$)

For T_g values above the horizontal line of Fig. 3, the system is in the glassy state and, consequently, structural relaxation process occurs. In the schematic H–T diagram of Fig. 5a, the evolution of the enthalpy during curing from a liquid or gelled rubber to an ungelled or gelled glass respectively (path AB) is represented. Later, the glass is cooled to room temperature (path BC) and then heated through the glass transition region (path CBD) producing the well known recovery of enthalpy called 'T_g–overshoot'. This recovery generates the endothermic peak which appears in the DSC curve shown in Fig. 5b. A subsequent cooling to room temperature (path DE) will let the determination of the T_g of the system. However, in the epoxy resin used in this work, as the exothermic reaction of residual curing begins just after the glass transition has not been possible the measurement of T_g. In the schematic H–T diagram (Fig. 5a) and DSC curve (Fig. 5b) the T_g and $T_{g1/2}$ are indicated as well as other characteristic temperatures of the structural relaxation process such as endothermic peak temperature (T_m) and fictive temperature (T_f) defined by Tool [13] as the hypothetical temperature at which the structure of the glass would be at equilibrium.

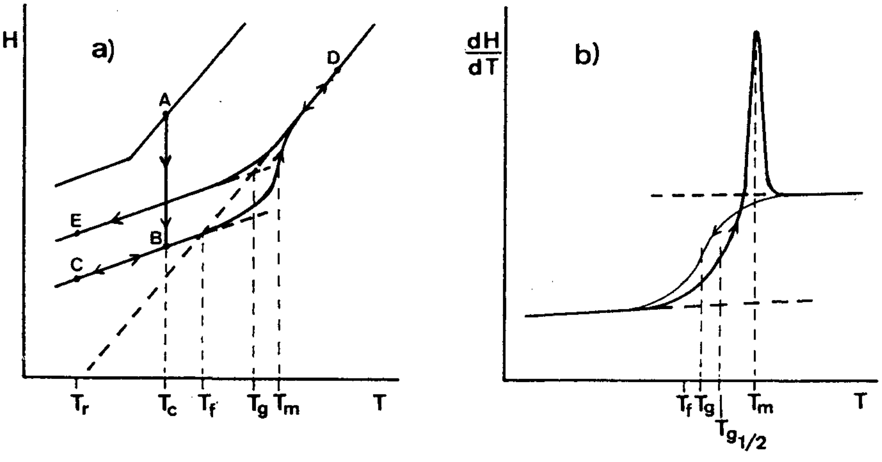


Fig. 5 Epoxy resin cured at $T_g > T_c$: a) schematic enthalpy-temperature diagram showing the isothermal curing at T_c with structural relaxation process, heating through glass transition region with the T_g overshoot, and further determination of the T_g of the system; b) First DSC curve of the partially cured and aged sample. Characteristic temperatures of glass transition region ($T_{g1/2}$, T_g, T_m and T_f) are represented in both diagrams (See text for a more detailed description of the plots)

Thus when $T_g > T_c$, the T_g of the system is not coincident with $T_{g1/2}$ and neither is the temperature of the endothermic peak of relaxation. Figure 3 shows the $T_{g1/2}$ values. These values practically are those of T_g only when the system has not vitrified ($T_g < T_c$). Consequently, in the study about the relationship between T_g and the conversion degree (α) only the T_g values before the vitrification phenomenon will be taken into account. A similar conclusion has been achieved by Pascault *et al.* [14] who recommend the use of T_g values only up to vitrification time.

The maximum glass transition temperature T_{g_∞} achieved by isothermal curing is about 109°C as indicated by the curves $T_g - \alpha$ for $T_c = 110°$ and 130°C of Fig. 3. This value of T_{g_∞}, contrarily to the achieved by $T_{g_{2scan}}$, has not got practically any thermal degradation as this begins between 250° and 300°C [7]. Therefore, this value of T_{g_∞} can be considered the maximum glass transition temperature of the system in accordance with the topological limit of conversion.

The theoretical equation proposed by DiBenedetto [15] modified by Pascault *et al.* [14] has been applied to our experimental T_g and conversion degree:

$$\frac{T_g - T_{g_0}}{T_{g_\infty} - T_{g_0}} = \frac{\lambda\alpha}{1-(1-\lambda)\,\alpha} \qquad (1)$$

where λ is an adjustable parameter between 0 and 1, which represents the ratio of segmental mobilities for crosslinked and uncrosslinked polymer (F_x/F_m), T_{g_0} is the glass transition temperature of the reactants (–23.2°C) and $T_{g_\infty} = 109$°C. Considering the T_g values for $t_c < t_v$, the best fit for experimental data was found for $\lambda = 0.69$. A good correspondence between the curve plotted and experimental data is observed in Fig. 3.

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Zusammenfassung — Der maximale Glasumwandlungspunkt $T_{g\infty}$ on hitzehärtbaren Harzen wird immer mittels DSC im zweiten Scan (T_{g2scan}) gemessen, nachdem in einem ersten Scan die Probe auf jene Temperatur erhitzt wird, bei der die exotherme Härtungsreaktion abgeschlossen wurde. Diese Methode kann jedoch thermischen Abbau verursachen, welcher die Vernetzungsdichte und T_g der Probe herabsetzt. Für ein Epoxidharz auf DGEBA-Basis, verhärtet mit Phthalsäureanhydrid wurden für T_{g2scan} Werte zwischen 95° und 102°C gefunden. Thermische Abbaueffekte können vermieden werden, wenn die Messung mittels isothermer Härtung und anschließender Bestimmung von T_g erfolgt. Es wird ein $T_{g\infty}$ Wert von 109°C erreicht, was der höchste Wert für T_g ist und dem topologischen Grenzkonversion entspricht.