Journal of Thermal Analysis, Vol. 21 (1981) 299—307

QUANTITATIVE DTA OF EPOXY ADHESIVES OF TECHNOLOGICAL INTEREST

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(Received December 6, 1980)

The glass transition temperatures, T_g, and thermal effects of polymerization, ΔH, have been determined for five epoxy adhesives of unknown composition. From the trends ΔH *vs.*/t_{cure} it has been possible to attain a phenomenological kinetic order of the polymerization rate at 100° through an iterative calculation procedure. For most of the investigated adhesives there are reasons (double peak of polymerization and double T_g signal) to assume that they are graft copolymers.

Studies on epoxy materials, prepregs and adhesives have been greatly developed in view of their important technical applications: specially devised investigations have been reported on their elastic properties, thermal expansion, strains associated with the polymerization process, etc. [1, 2].

Qualitative and quantitative chemical analysis is in any case essential in the research into such materials: as a rule it requires an extremely refined instrumentation, allowing the separation and recognition of the individual components within a number of compounds accompanying the main epoxy bulk [3, 4].

As typical investigations, differential thermal analysis (DTA) and/or differential scanning calorimetry (DSC) have been employed either to evaluate the thermal effect accompanying the polymerization or to check the glass transition temperature, T_g [5–10].

In the present work quantitative DTA determinations were carried out for different adhesives behaving as thermosets, in order to establish:

i) the thermal effect accompanying the polymerization,
ii) the phenomenological kinetics of the cure process,
iii) the correlation curve between the degree of polimerization, α, and T_g.

The compositions of these materials are only partially known, but their main ingredients are bisphenol, epichlorhydrine, Novolac, tetraglycidylmethylene dianiline, nitrilerubber, etc., depending on the particular resin.

Experimental

The storage temperature of the prepolymer tapes was about −18°.

From tight rolls of such tapes small soft cylinders of prepolymer (dia. ~3 mm, length ~3 mm) were rapidly cut, weighed (the usual weight was about 50 mg), sealed in silver DTA pans at room temperature and again cooled down to −18°.

Several such samples of each adhesive were isothermally cured in an oven at 100° for different annealing times in order to attain various degrees of polymerization: due to the small heat capacities of the samples as compared with that of the preheated steel block where they were positioned within the oven, the heating up to 100° was assumed to be instantaneous.

DTA curves were obtained with a Du Pont Thermoanalyser mod. 900. The heating rate was 2°/min with 0.2°/inch ΔT sensitivity, and 10°/min with 0.2–2°/inch ΔT sensitivity (depending on the expected order of magnitude) for T_g and the polymerization thermal effect, respectively.

For the determination of T_g the calorimetric furnace was previously shielded with a liquid nitrogen bath in order for signals occurring below and around 0° to be recognized.

Al_2O_3 was employed as reference material: the same DTA pan containing 50 mg Al_2O_3 was employed throughout the present work.

Heats of polymerization were obtained by comparison with the thermal effect accompanying the transition $\beta \leftrightarrow \alpha$-AgI at 147°, *viz.* 4. 18 J/mole: for this purpose, the same three AgI samples, weighing 100, 50 and 22.8 mg, respectively, were repeatedly DTA-checked every day in order to verify the reproducibility of the operating conditions of the instrumentation at the employed ΔT sensitivities.

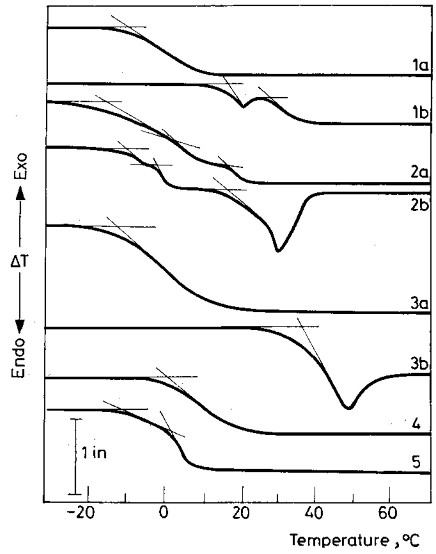

Fig. 1. Some examples of T_g signals encountered in this work: notice cases where an endothermic effect is also present and those where several signals are observed for a given sample (discussion in the text). 1*a* and 1*b*: AF 163 WTO6 uncured and partially cured ($\alpha = 0.47$) samples; 2*a* and 2*b*: AF 163/2 WTO6 uncured and partially cured ($\alpha = 0.59$) samples; 3*a* and 3*b*: FM 53 uncured and partially cured ($\alpha = 0.82$) samples; 4: FM 123 uncured; NARMCO 1113 uncured

T_g values were obtained as intercepts between the extrapolated baseline preceding the endothermic shift and the tangent drawn at the flexus point of the signal: some typical examples are given in Fig. 1.

Results and discussion

The exothermic peaks relating to the uncured samples ($t_{cur} = 0$) and the values of the polymerization heat, $\Delta H(t)$, *vs.* the curing time are reported in Figs 2 and 3, respectively. These data have been worked out in the following way:

i) the cure degree, α, is defined as

$$\alpha(t) = 1 - \Delta H(t)/\Delta H(0) \qquad (1)$$

where $\Delta H(0)$ represents the thermal effect which would characterize the corresponding mixture of monomers and additives; this means that we put

$$\Delta H(0) \neq \Delta H(t_{cur} = 0) \qquad (2)$$

as the so-called prepolymer corresponds to $\alpha \neq 0$;

ii) for a generic "phenomenological" order of the reaction rate, $N \geq 0$ and $N \neq 1$, one has

$$\mathrm{d}\alpha/\mathrm{d}t = K_N(1 - \alpha)^N \qquad (3)$$

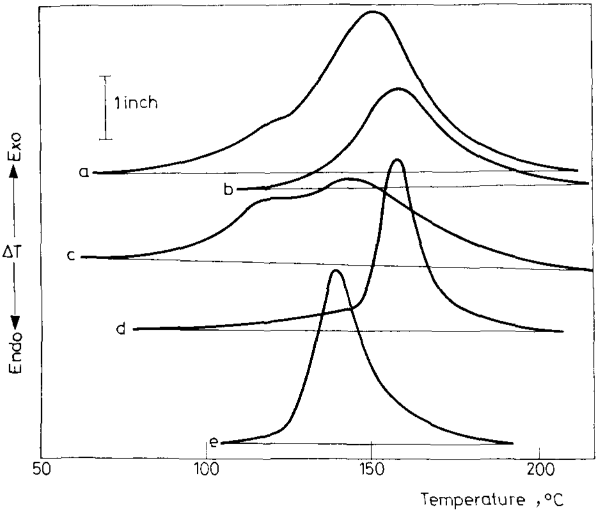

Fig. 2. Exothermic peaks of uncured samples: *a)* AF 163 WTO6, *b)* AF 163/2 WTO6, *c)* FM 53, *d)* FM 123/2, *e)* NARMCO 1113. The multiplicity of *a)* and *c)* is discussed in the text; variations in T_{max} and the shape of the peak of FM 123/2 at higher cure degrees are illustrated in Fig. 4

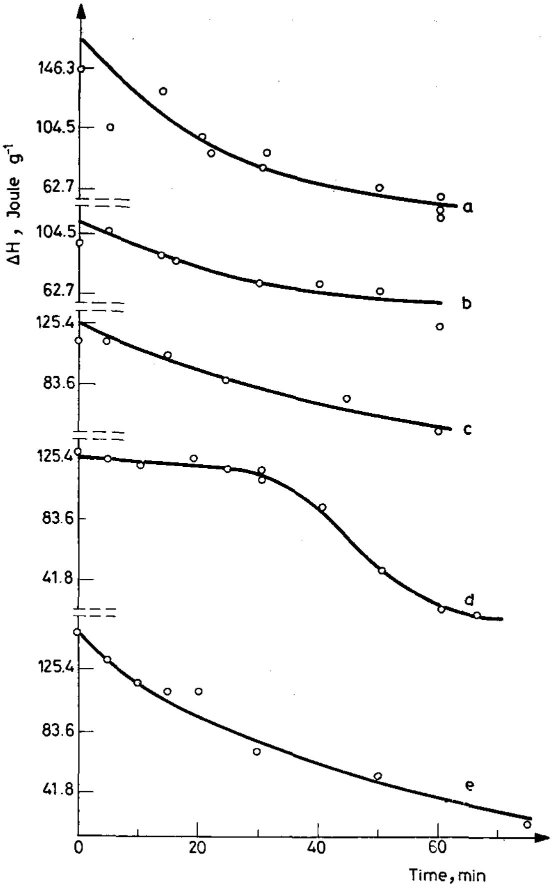

Fig. 3. Polymerization heats $\Delta H(t)$ *vs.* the curing time t at 100°: lettering in the same as in Fig. 2

which through integration gives

$$(1-\alpha)^{-Z} = (1 + ZK_{N}t) = [\Delta H(0)/\Delta H(t)]^{Z} \qquad (4)$$

with $Z = (N - 1)$.

Equation (4) has been numerically solved by employing the following iterative procedure:

– initial input, $\Delta H(0) = \Delta H(t_{\text{cur}} = 0)$ and $N = 0$;

– through 0.1 iteratively increased values of N, find the value of N which gives the minimum of

$$S_{N} = \sum_{i} [\Delta H_{i}(t_{i})_{\text{calc}} - \Delta H_{i}(t_{i})_{\text{exper}}]^{2}$$

the sum being extended to all the results obtained for a given adhesive except for $\Delta Ht_{cur} = 0$);

– by maintaining fixed the best N value, adjust the initial tentative value of $\Delta H(0)$ through 4.18 J/g iterative steps;

– if the best N is very close to one, e.g. 1.01, then fit the data through the linear regression ln $\Delta H(t)$ *vs.* t, coming from the usual first-order equation, $d\alpha/dt = K_1(1 - \alpha)$.

The $\Delta H(0)$'s obtained with the above iterative procedure have been employed to obtain the α values through Eq. (1).

Table 1

Adhesive	Reaction order	$(1-\alpha)$ *vs* t	ΔH(O), J/g	α	T_g,°C	T_{in}, °C	T_{max}, °C
AF163WTO6	2	$(1+0.038t)^{-1}$	170.34	.14	−11	65	125−150
AF163/2WTO6	2	$(1+0.018t)^{-1}$	112.73	.14	−14	90	145
FM 53	1	exp(−0.013t)	129.20	.12	−13	90	146−158
FM 123/2	0	$2.73 \cdot 10^{-3}t$	127.74	.20	− 4	80	159
	1	exp(−0.052t)	674.00				
NARMCO 1113	1	exp(−0.026t)	157.00	.14	−11	110	140

Table 1 summarizes the results found for each investigated material: r.o. is the phenomenological reaction order, t is in min, $\Delta H(0)$ is in J/g, and T_{in} and T_{max} are in °C and refer to the initial drift and to the maximum of the exothermic peak, respectively.

As expected, the so-called prepolymers correspond to a significant cure degree, α, which ranges from 0.12 to 0.20 depending on the material: these results allow the recognition of how crude the usual [6, 10] assumption $\alpha = 0$ for uncured materials would be here.

It must be emphasized that the reaction orders reported in the second column of Table 1 have only a "phenomenological" meaning and should not be directly connected with the actual reaction mechanism.

A special remark is to be made for the material FM 123/2: as already suspected after inspection of the corresponding $\Delta H(t)$ *vs.* t curve in Fig. 3, this material seems to undergo two different processes, viz. with kinetic orders zero and one, respectively, the former at smaller and the latter at larger α values.

Many tentative interpretations may be hazarded to explain such peculiar behaviour, a very simple one being that FM 123/2 has been planned to release small heat amounts during the initial stages of the polymerization, i.e. when the not yet fully cross-linked components are known to be exposed to easy chemical degradation.

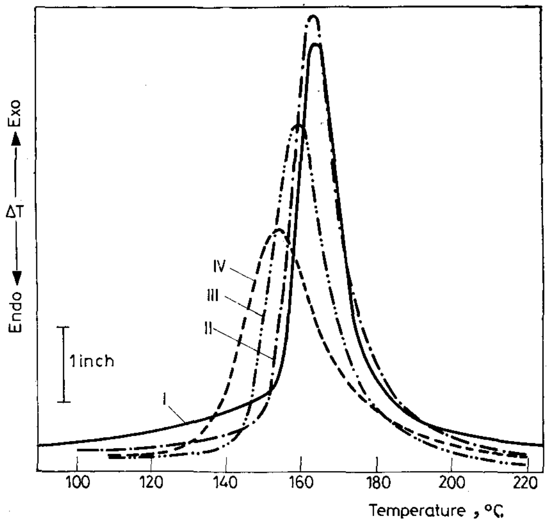

Fig. 4. Variation in the position and shape of the exothermic peak of FM 123/2. Curves concern samples of similar weight (about 40 mg) cured for the following times (min): (I) uncured, (II) 5, (III) 25, (IV) 40

That different processes occur in curing FM 123/2 may also be argued by observing that the features of the corresponding exothermic peak change with increasing α, viz. T_{in} and T_{max} increase and decrease, respectively, with increasing α, the shape of the peak becoming progressively more regular and symmetric (see Fig. 4).

The shape of the exotherm corresponding to the uncured material is quite similar to that of polymers containing nitrilic rubber (which is consistent with our present knowledge about its composition) when no accelerator is present [13].

The α values of the partially cured samples of FM 123/2 have been calculated with $\Delta H(0) = 127.7$ J/g i.e. the value corresponding to $N = 0$.

It has been reported that the glass transition temperature, T_g, is a useful parameter somehow correlated with α [6–11]; it is not our intention to discuss here the theoretical details underlying such a correlation in the case of thermosets: suffice it to say that the present knowledge about this problem is still unsatisfactory.

A clear picture has been established about the necessity of planning thermosets having a sufficiently low T_g, which allows an easier and better processibility by improving flow and reducing brittleness: with this aim, plasticizing agents are added to the main epoxy ingredient.

As a result, in the DTA curves of uncured or partially cured samples one observes T_g shifts at temperatures ranging about 0°.

The T_g value gradually increases with increasing α, eventually approaching the curing temperature [6], as shown in Fig. 5.

It is well known that the observed values of T_g are rather strongly affected by the heating rate employed, due to the complex nature of the process involved:

it is therefore essential to keep in mind that what is to be carefully checked in a DTA curve of any plastic material is the number of T_g signals and their reproducibility under the given operating conditions.

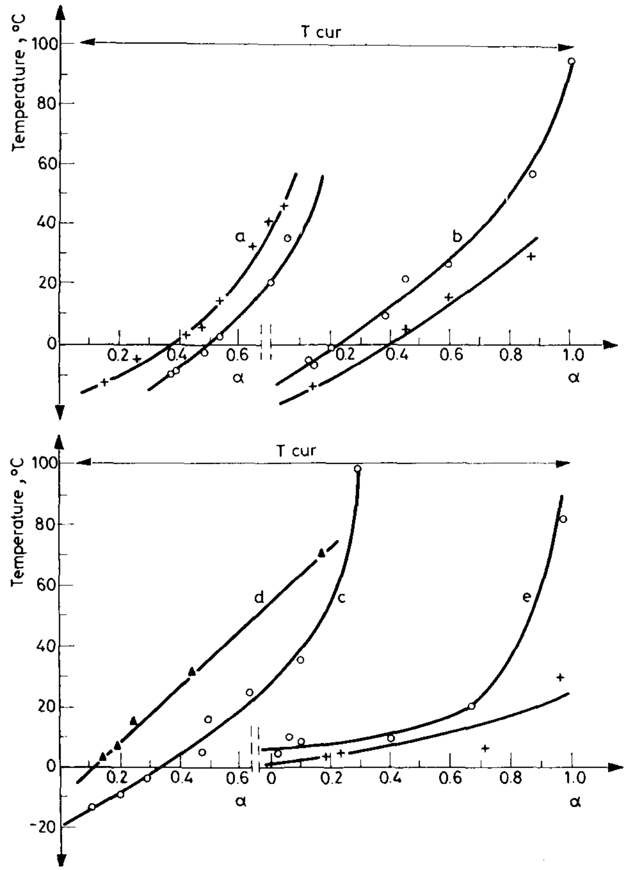

Fig. 5. T_g *vs.* α: *a)* AF 163 WTO6, *b)* AF 163/2 WTO6, *c)* FM 53, *d* NARMCO 1113, *e)* FM 123/2

In the present case many curves of partially cured samples show several endothermic shifts of the baseline before the exothermic peak of polymerization (see Fig. 1).

The temperatures at which the T_g signals are observed for a given material show different trends with increasing α (see Fig. 5*a*, *b*, *e*).

Since this finding is systematic and satisfactorily reproducible, it may be excluded that these endothermic shifts of the baseline are due to bulk stresses or other thermomechanical effects [6].

As a naive interpretation it might be suggested that each observed T_g signal corresponds to a particular component of the resin, so that the overall picture for these curves should be compared with that for graft copolymers [9].

The finding is more or less evident, depending on the particular adhesive, and is consistent with the presence of a double peak of polymerization, which varies in observability (see Fig. 2): in the case of AF 163 WT 06 this signal consists of a "shoulder" preceding the maximum, whereas for FM 53 two partially overlapped peaks appear in the DTA curve of the uncured sample.

Again as a simple tentative interpretation, it might be suggested that such double peaks correspond to the formation of two different polymers coexisting in the thermoset, e.g., according to our present knowledge about the composition of these materials, that arising from bisphenol + epichlorhydrin and that arising form Novolac.

It is also possible that cases where this double exothermic signal is not observed, as in AF 163/2 WT 06, correspond to improved materials where the mixture of ingredients has been planned to avoid inhomogenity in the behaviour of releasing the heat of polymerization however, in this case too the multiplicity of the T_g signals suggests that a number of polymerization processes take place during the curing of the prepolymer.

Further work has been planned to yield a better insight into the composition of these epoxy adhesives, as well as the corresponding materials containing glass fibers or other excipients.

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Résumé — On a déterminé, pour cinq adhésifs époxy de composition inconnue, les températures de transition vitreuse T_g et les effets thermiques de polymérisation ΔH.

A partir de la variation de ΔH en fonction du temps de recuit et par une méthode de calcul itératif, un ordre cinétique phénoménologique de la vitesse de polymérisation à 100° a pu être obtenu.

Pour la plupart des adhésifs étudiés l'existence d'un pic double de polymérisation et d'une double transition vitreuse T_g permet de supposer qu'il s'agit de copolymères greffés.

ZUSAMMENFASSUNG — Die Glas-Übergangstemperaturen (T_g) und die ΔH thermische Effekte der Polymerisation wurden für fünf Epoxy-Klebstoffe unbekannter Zusammensetzung bestimmt.

Aus den Trends ΔH gegenüber t_{cure} war es möglich eine phenomenologische kinetische Ordnung der Polymerisationsgeschwindigkeit bei 100° durch ein iteratives Berechnungsverfahren zu ermitteln.

Für die meisten untersuchten Klebstoffe besteht der Grund — Doppelpeak der Polymerisation und doppeltes T_g-Signal — sie als Pfropfcopolymere zu betrachten.

Резюме — Для пяти эпоксидных клеев неизвестного состава определены температуры стеклообразования T_g и термические эффекты полимеризации ΔH. Из наклона графических кривых в координатах ΔH—$t_{\text{отвержд.}}$ представилось возможным достичь необычного порядка кинетики реакции полимеризации при 100° через повторяющийся метод вычисления. Наличие для большинства исследованных клеев двойных пиков полимеризации и двойных сигналов T_g привело к выводу, что эти клеи должны быть графт-кополимерами.