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KINETICS OF POLYMERIZATION OF EPOXY ADHESIVES AND COMPOSITES *

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ABSTRACT

The polymerization kinetics of epoxy materials are examined with particular emphasis in assessing (i) the proper use of non-isothermal DTA or DSC data, (ii) the correlation between glass transition temperature and cure degree, (iii) the effect of the filling agent on the phenomenological kinetics of the cure process.

INTRODUCTION

Epoxy resins have been recognized as a technologically important class of polymers and are widely employed as adhesives or composites. The latter consist of an epoxy matrix (the continuous "primary" phase) and a reinforcing or filling agent, discretely dispersed throughout the matrix, which mainly serves to allow the preparation of load-bearing structures. The composition of such polymers is tentatively and empirically planned by the manufacturer; it is extremely complex and remains largely unknown (see HPLC trace in Fig. 1). Therefore, a complete description of the various chemical reactions actually occurring in the cure process does not seem possible at present.

Isothermal and non-isothermal DSC and DMA determinations, however, give a phenomenological interpretation of the kinetic process involved and allow one to suggest some simple models. The experimental data obtained with these techniques are related both to the thermal effect accompanying the cure reaction and to the glass transition temperature.

The following are to be evaluated: (i) the correlation between the amount of heat delivered by the system in the DSC scan and the corresponding cure degree, α; (ii) the correlation between the glass transition temperature, T_g, and either α or the cure temperature, T_{cure}, as T_g gradually increases with α and approaches T_{cure} when α is close to 1 (see Fig. 2); (iii) the effect of the filling agent upon the cure kinetics of composites.

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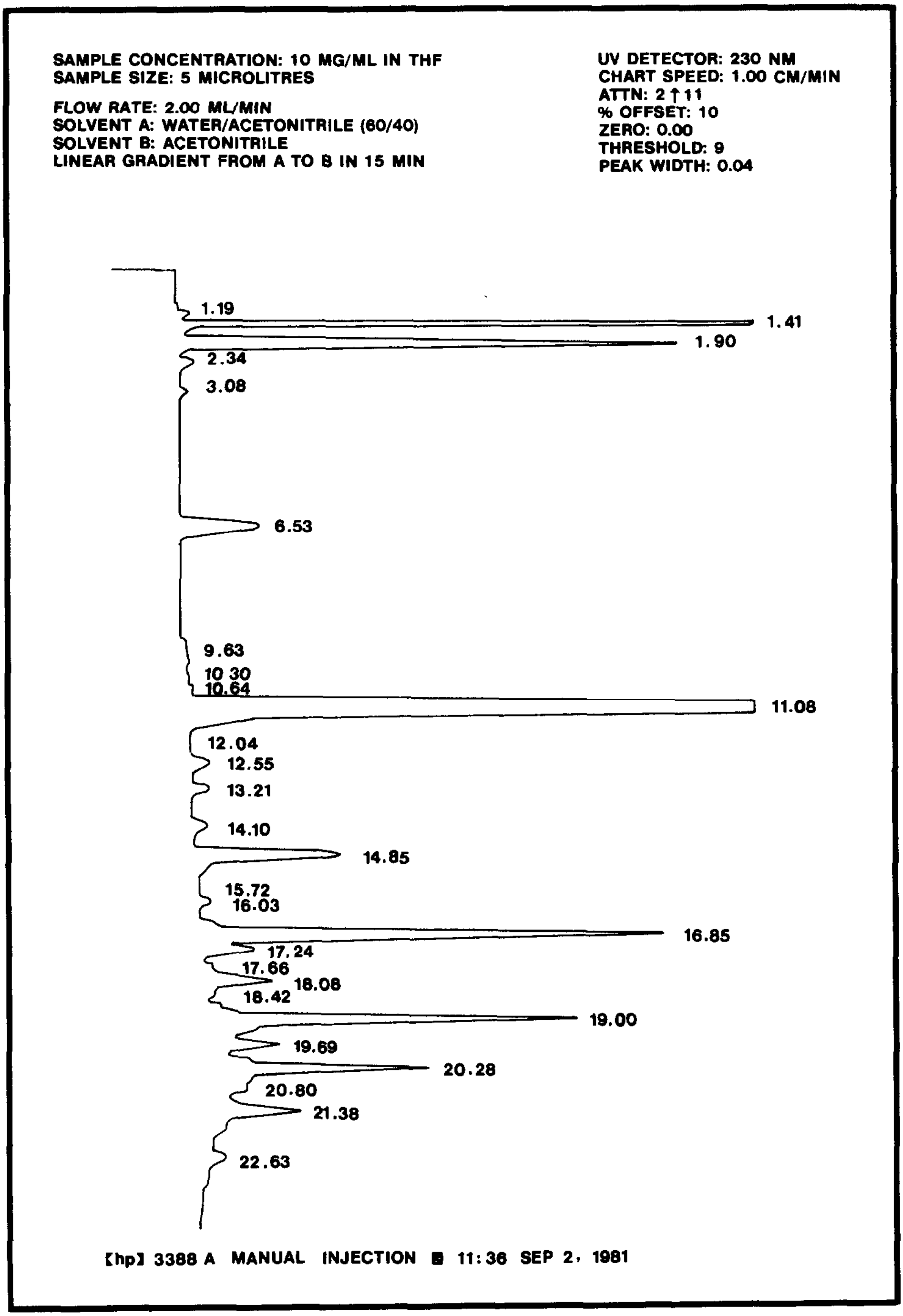

SAMPLE CONCENTRATION: 10 MG/ML IN THF
SAMPLE SIZE: 5 MICROLITRES

FLOW RATE: 2.00 ML/MIN
SOLVENT A: WATER/ACETONITRILE (60/40)
SOLVENT B: ACETONITRILE
LINEAR GRADIENT FROM A TO B IN 15 MIN

UV DETECTOR: 230 NM
CHART SPEED: 1.00 CM/MIN
ATTN: 2↑11
% OFFSET: 10
ZERO: 0.00
THRESHOLD: 9
PEAK WIDTH: 0.04

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Fig. 1. Liquid chromatogram of FM 123/2.

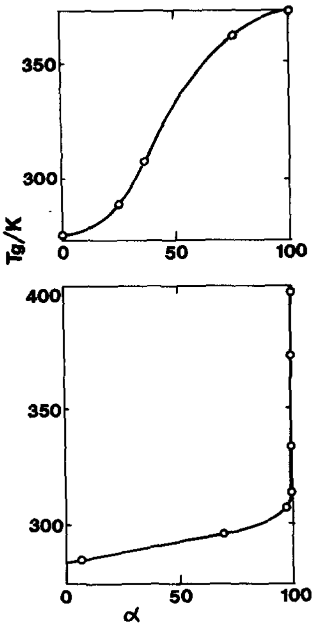

Fig. 2. T_g vs. α of FM 123 cured at 373 K (upper) and at 403 K (lower).

Due to the simpler instrumental setting and to the apparent sparing of time, non-isothermal procedures have become more commonly employed throughout the realm of thermal analysis. In the case of kinetic studies, it has been found expedient to limit the experimental investigation to the analysis of the profile of the DSC exothermic peak corresponding to the evolution of the heat of reaction. This approach is indeed correct [1], whenever the reaction involves initial and final states, the reagents and the products, whose chemical nature is not affected by the reaction conditions. It is not satisfactory for epoxies, however, as they attain completely different structures and physico-chemical properties, according to the cure conditions: this means that, in a cure process of this kind, the final state, i.e., the polymers, is not univocally defined.

It is very easy, for instance, to verify that polymers obtained from the same prepolymeric materials and cured at different T_{cure} temperatures show significantly different T_g values (see Fig. 2), i.e., they have different structural arrangement or, in other words, a different number of cross-links and even a different total number of bonds formed among the monomer molecules.

When one of these polymers, obtained with an isothermal cure at a given T_{cure} for a sufficiently long period, is DSC tested it will not deliver any heat until the scan approaches $T = T_{\mathrm{cure}}$. It will then deliver some "residual" heat corresponding to the formation of bonds requiring a larger "activation energy" for matching active sites. Accordingly, the current method of working out the dQ/dT data, corresponding to the profile of the DSC exothermic peak, is misleading. For the same reasons, one can assume neither a negligible cure degree for the prepolymer material, nor a cure degree for the non-isothermal process occurring in the DSC scan as given by

$$\alpha = 1 - Q(t)/Q(0)$$

where $Q(0)$ and $Q(t)$ correspond to the total area underlying the exothermic peak of the prepolymer DSC trace and to the area swept in the time t after the peak onset, respectively.

Therefore, when the non-isothermal method is employed, a more suitable procedure must be used to draw and work out the experimental data. A suitable method is reported here whereby some phenomenological kinetic parameters of the cure process can be obtained from non-isothermal DTA or DSC traces [2,3]. The underlying model for the cure mechanism is compared with the reticulation process recently described by Seferis and co-workers [4] on the basis of a probability–structure model.

CORRECT APPROACH TO CURE KINETICS

The heat actually delivered by a partially cured sample in a DTA or DSC scan mainly depends upon its polymerization degree previously attained; other important variables are the heating rate, and the mass and shape of the sample.

The previous extent of the polymerization throughout the sample directly affects the number of available reactive sites across the propagation front of the reaction process, since it determines the mutual stereochemical arrangement of the reacting functional groups along the polymeric chains. This may be justified with the following arguments.

The bonds formed in a cure process are primarily those along the chains and those across the chains.

Both bindings can take place in any time and the amount of heat delivered per bond formed is practically the same in either case.

The corresponding rates are similar at the start of the cure, when the two processes are still indistinguishable, then rapidly become different from each other, as the stereochemical arrangement of the reactive groups along the chains, allowing formation of cross-links, requires a much larger activation energy: the longer the chain, the larger the activation energy.

Let us now imagine what the cure process would be if it were possible to give the monomer molecules a suitable mutual orientation, allowing reaction of all the active groups: the final polymer would be characterized by the maximum reticulation and the highest T_g value. Since formed bonds cannot be destroyed, we may also assume that this adjustment would be statistically enhanced by thermal agitation: the higher T_{cure}, the more likely a monomer molecule will orientate its own reactive groups to allow reaction with those of its neighbours. When one active site of a monomer molecule is already engaged in a bond, further adjustment allowing reaction of another site will require some activation energy.

After these two steps, the original monomer molecule is already a part of a polymer chain: if one of the remaining active sites is close and properly orientated with respect to a reactive group of the neighbouring chain, the reaction will progress. If not, the bond will not be formed, unless, for a sufficiently high T_{cure} value, readjustment of the reactive groups can be achieved through whole-chain movements, i.e., via a process involving a very large activation energy.

As a result, the proportion of along- to across-chain bonds will mainly depend upon T_{cure}. Under isothermal conditions, it will rapidly become almost constant during the progress of the cure: the two processes will obey the Wegscheider law for parallel chemical reactions of the same kinetic order. In the case of a non-isothermal cure, such as that taking place in the DSC scan, the curing conditions, viz., T_{cure}, progressively change and eventually allow the formation of cross-links "forbidden" at the beginning of the scan. However, the temperature increase will mainly result in longer chains than more cross-links, since linking is hindered by chain growth.

Let us now suppose that polymerization is quenched within a sample undergoing an isothermal cure at T_{cure} and that this sample is tested with a non-isothermal DSC. The cure process will restart when the T range swept reaches the previous T_{cure} value: just after the onset of the DSC peak, chain lengthening will increasingly impede cross-link formation with increasing T. Cross-link formation will predominate only when lengthening is almost at the end. In other words, whichever the situation attained during the previous isothermal cure, the final polymer at the end of the DSC scan will always have more extended chains and fewer cross-links than that obtainable after the exhaustion of the isothermal cure. Its lower T_g value is also in line with this picture (see Fig. 3).

When the starting material is a prepolymer, the situation is even more complex, since nothing is usually known about its history, i.e., the "frozen" ratio between the bindings in the prepolymer. If the total number of prepolymer bonds is assumed to be small with respect to that after cure (a low prepolymer T_g could be a proper reference), then a prepolymer sample rapidly heated to a given T_{cure} may be expected to represent a condition slightly shifted from that of a mixture of monomers identically heated and cured at the same temperature for a short time. It is, thus, reasonable to describe the cure process backwards from the state of mixture of the monomers and its "step by step" progress at a given T_{cure} value, i.e., under isothermal conditions and for different lapses of time; the heat amount, Q_0, delivered by the corresponding mixture of monomers would be the conceptually appropriate reference for definition of the cure degree.

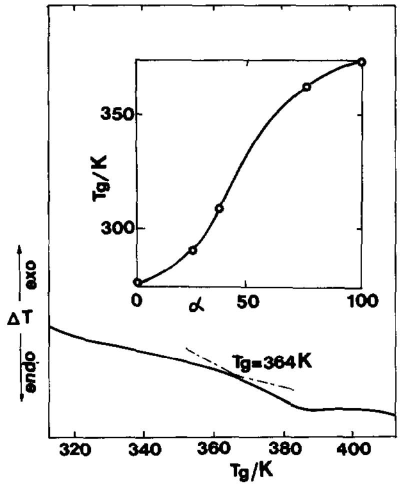

Fig. 3. Comparison between the T_g of samples isothermally cured up to different cure degree ($\alpha = 100\%$; $T_g \approx T_{cure} = 373$ K) and of the polymer obtained after a DSC scan (10 K $\min^{-1}$ heating rate): the latter is lower and suggests a poorer extension of cross-links than for $\alpha = 100\%$.

Let us assume, for the sake of simplicity, that all the N epoxy groups present in a totally uncured sample can form bonds in a non-isothermal DSC scan (this condition could be attained in practice by adjusting the composition of the starting mixture of reagents, as shown below): Q_0 is then related to their reaction. If such a sample is isothermally cured for time t and then scanned, N_i epoxy groups will be engaged in bond formation during the isothermal cure and the remaining $N_{ni} = (N - N_i)$ groups will be responsible for the exhaustion of polymerization during the scan, with a corresponding thermal effect $Q(t)$. Accordingly,

$$\begin{aligned} Q(t)/Q_0 &= N_{ni}/N = 1 - N_i/N \\ &= 1 - \alpha_i \end{aligned} \tag{1}$$

where α_i is the isothermal cure degree and a function of the time spent by the sample under isothermal cure conditions. The practical interest of this expression lies in its correction of the unreliability of the non-isothermal approach to the kinetics of polymerization: it requires samples of the same prepolymer, previously cured at the same T_{cure} for different periods, to be submitted to DSC analysis at the same heating rate.

Since α_i is an isothermal quantity, it is referred to a well-defined chemical process, viz., that starting from N active epoxy groups and ending in a polymer whose along-chain and across-chain bonds are in a definite proportion.

The phenomenological kinetics may thus be written as

$$d\alpha_i/dt = K_n(1 - \alpha_i)^n \tag{2}$$

where K_n and n act as a reaction order and kinetic constant, respectively. Equation (2), however, can only be employed in the integrated form. The experimental data to be fitted are the overall thermal effects, detected by DSC, and the lapses of time spent by the samples in isothermal cure. For $n > 0$ and $n \neq 1$, the integration of eqn. (2) gives

$$[1-\alpha]^{(n-1)} = [1+(n-1)K_n t]^{-1} = [Q(t)/Q_0]^{(n-1)} \tag{3}$$

Equation (3) is solvable through an iterative procedure [2]. This gives the best K_n, n and Q_0 values fitting the experimental data and also allows recognition of the case $n = 1$, i.e., when integration of eqn. (2) corresponds to a linear relationship between log $Q(t)$ and t.

Integers, viz., $n = 1$ and $n = 2$, typically correspond to the best fit. This result might be a consequence of the above model which describes the kinetics of polymerization as a result of several elementary and similar processes, viz., the reaction of single active groups, and differs from that obtained through analysis of the profile of the exothermic peak of the DSC trace, which usually gives non integer n.

It must be borne in mind that the Q_0, n and K_n values allowing the fit of the experimental data only refer to the process occurring at the T_{cure} fixed for the prior isothermal cure; it would be misleading to evaluate, for instance, an "activation energy" from K_n values obtained for different T_{cure} values, as they would correspond to the formation of completely different polymers. Some examples for epoxy adhesives are given in Table 1, and some typical $Q(t)$ vs. t curves are reported in Fig. 4.

Seferis and co-workers [4] presented a probabilistic formulation of the cure process in a mixture of tetraglycidyl diamino diphenyl methane (TGDDM; four epoxy groups per molecule) and diamino diphenyl sulphone (DDS; two NH_2 groups per molecule). The network structure is predicted from a calculation of the probability of reaction between the epoxy groups and an amino hydrogen, assuming that the secondary amino hydrogen would

TABLE 1

Examples of epoxy materials commercially available and employed as adhesives (upper group) and composites (lower group) in aerospace industries. RO is the reaction order; Q_0 is in J g^{-1} and, for the composites, is referred to the pure epoxy content

Epoxy polymer	RO	K_n	Q_0
AF 163WT06	2	0.038	170
AF 163/2WT06	2	0.018	113
FM 53	1	0.013	129
FM 123/2	1	0.052	128
NARMCO 1113	1	0.026	157
NARMCO 5216	1	0.036	382
F 920	1	0.049	334

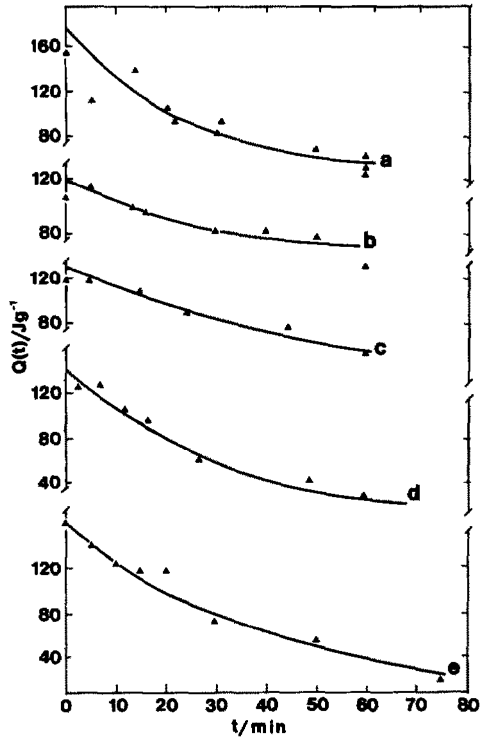

Fig. 4. Exothermic effects of polymerization detected by means of DSC from partially and isothermally cured samples ($T_{\text{cure}} = 100°C$) of various epoxy adhesives: (a) AF 163, (b) AF 163/2, (c) FM 53, (d) FM 123/2, (e) NARMCO 1113.

only react after exhaustion of the primary amino hydrogens. A cross-link is formed whenever at least three epoxy groups of a TGDDM molecule or a secondary amino hydrogen of a DDS molecule have reacted. The number of cross-links at the end of the first step (reaction of the primary amino hydrogen) is thus proportional to $[{}^3P + 2{}^4P]$, where ${}^3P$ and ${}^4P$ are the probabilities that three and four TGDDM epoxy groups, respectively, will react with a primary amino hydrogen. These P values depend on the composition of the TGDDM + DDS mixture. However, the ratio between the number of bonds across and along chains is unequivocally defined for a given proportion between TGDDM and DDS. The final number of cross-links depends on the fraction of secondary amino hydrogen reacted: this, in turn, depends on the composition. Once again, the number of TGDDM molecules with three or four groups reacted is definite for any given composition.

This means that when bond formation, either along or across chains, is limited solely by the availability of neighbouring active sites, the two processes behave like parallel reactions. What has been added to the model reported at the beginning of this chapter is that this availability depends on the stereochemical arrangement of the reacting molecules. This, in turn, mainly depends on T_{cure}.

CORRELATION BETWEEN T_g AND T_{cure}

This approach to the correlation between the DSC thermal effect, detected in a non-isothermal scan, and the cure degree of an epoxy polymer, provides a qualitative explanation of the T_g vs. T_{cure} correlation, viz., the higher T_{cure}, the more cross-links and the higher T_g.

From a phenomenological point of view, it is evident that in a isothermal cure process T_g increases up to T_{cure} with increasing α, so that when α approaches unity, $T_g = T_{\text{cure}}$.

It is also clear that both the T_g vs. α trend and the T_g value at $\alpha = 1$ depend upon T_{cure}: i.e., for each T_{cure}, the glass transition temperature can be seen as a function of the degree of polymerization [2]. It would thus be useful to find a formal relationship for the dependence of T_g on α. This requires definition of T_g in terms of another suitable property of the material investigated. One possibility is offered by the well-known empirical relationship between the viscosity of polymers and glasses and temperature viz., the Vogel–Tamman–Fulcher (VTF) equation

$$\eta = A \exp[B/(T - T_0)] \tag{4}$$

where η is the viscosity, T_0 is the ideal glass transition temperature, and A and B are constants for the material in question. Equation (4) may be rewritten as

$$T_g = T_{\text{cure}} + \Delta - B/(\log \eta/A) \tag{5}$$

where Δ is the difference $(T_g - T_0)$. Equations (4) and (5) apply to an epoxy sample after a partial isothermal $(T = T_{\text{cure}})$ cure, viz., $\alpha < 1$. The expression

$$T_g(\alpha) = T_{\text{cure}} + \Delta(\alpha) - B(\alpha)/[\log \eta/A(\alpha)] \tag{6}$$

can thus represent any intermediate step of an isothermal cure process occurring at T_{cure}.

Since $\log \eta$ is roughly proportional to the molecular weight of the material investigated, it may be supposed to parallel the α vs. time trend; for example, in first-order kinetics

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

then

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

where

$$\gamma = \log[\eta(\alpha = 1)/\eta_0]$$

i.e.

$$\mathrm{d}\eta = \gamma\eta\,\mathrm{d}\alpha \tag{7}$$

Since the experimental evidence shows that $T_g \approx T_{\mathrm{cure}}$ when $\alpha = 1$, a function representing the T_g vs. α trend can be checked through a series expansion, viz.

$$T_g = T_g(\alpha = 1) - (1-\alpha)(\mathrm{d}T_g/\mathrm{d}\alpha)_{\alpha=1} + (1-\alpha)^2/2\left(\mathrm{d}^2T_g/\mathrm{d}\alpha^2\right)_{\alpha=1} + \dots \tag{8}$$

with $T_g(\alpha = 1) = T_{\mathrm{cure}}$. As a rule, the trend of the experimental data supports the assumption that $(\mathrm{d}T_g/\mathrm{d}\alpha)_{\alpha=0} = 0$, which, due to eqn. (8) means that

$$\left(\mathrm{d}T_g/\mathrm{d}\alpha\right)_{\alpha=1} = \left(\mathrm{d}^2T_g/\mathrm{d}\alpha^2\right)_{\alpha=1}$$

and

$$\mathrm{d}T_g/\mathrm{d}\alpha = \alpha\left(\mathrm{d}^2T_g/\mathrm{d}\alpha^2\right)_{\alpha=1} = \mathrm{d}^2T_g/\mathrm{d}\alpha^2$$

Under such conditions, it is easy to show that the "fitting" expression for the T_g vs. α trend reduces to

$$T_g = T_{\mathrm{cure}} - \left[T_{\mathrm{cure}} - T_g(\alpha = 0)\right](1-\alpha^2) \tag{9}$$

The best value of the difference $[T_{\mathrm{cure}} - T_g(\alpha = 0)]$, corresponding to the minimum of the sum

$$\sum\left(T_{g,\mathrm{calc}} - T_{g,\mathrm{exp}}\right)^2$$

may be easily found through an iterative calculation. Figure 5 shows these "calculated" T_g vs. α trends. They fit the experimental data satisfactorily.

Some further consequences of this analysis are discussed elsewhere [5]; one only need be mentioned, namely that $T_g < T_0$ throughout the α range. This conclusion runs counter to the usual finding for glasses and non-thermosetting polymers, but is quite reasonable for systems hosting a progressing chemical reaction, viz., the isothermal extension of a polymer framework.

According to a thermodynamic interpretation [6], T_0 is the temperature at which the excess configurational entropy of the system vanishes. In the case of epoxy polymers, the progressing cure may be referred to the building of a network, i.e., to a reduction of the "disorder" with respect to the initial mixture of monomers. T_0 would therefore represent the lowest temperature at which the system is able to complete the polymeric network, however long this may take. This also means that after a partial cure ($\alpha < 1$) a thermosetting polymer requires to be held at least at $T = T_0 > T_g$ to enhance its α value, since at $T = T_g$ the system could not support the progress of the cure.

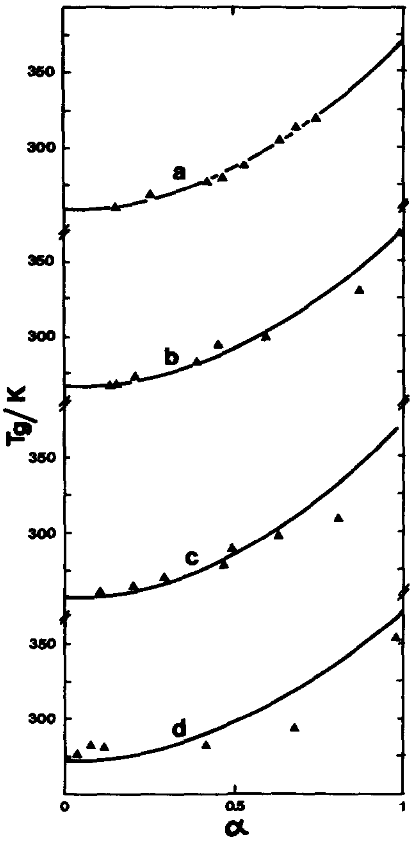

Fig. 5. T_g vs. α experimental data "fitted" with eqn. (8): (a) AF 163 WT06, (b) AF 163/2 WT06, (c) FM 53, (d) FM 123/2.

EFFECT OF THE FILLING AGENT IN THE CURE OF COMPOSITES

As reported earlier in the introduction, filling agents in composite materials mainly serve to confer some mechanical properties on the final polymer. They are usually glass or graphite fibres glued together by the epoxy matrix (see Fig. 6) and are supposed not to affect the polymerization. Systematic evalution of the cure process kinetics in epoxy composites, however, reveals some significant differences among materials prepared with the same epoxy component and different filling agents.

The first comparison is between the free epoxy component and one of the corresponding composites: Fig. 7 reports an example for what is here called composite A. The corresponding fitting equations are

(A) $Q(t) = 566.4 \exp(-3.16 \times 10^{-2} t)$

(A, fibre-free) $Q(t) = 215.7 \exp(-2.45 \times 10^{-2} t)$

For both materials $n = 1$, but the corresponding Q_0 values are quite differ-

Fig. 6. Bunch of glass fibres within an epoxy matrix acting as a glue.

ent from each other. Since the K values are very close to each other, it has been suggested [7] that the polymerization process occurring in each material is the same, but for the actual starting point. In other words, the process in the fibre-free material would appear to start from a state characterized by more advanced prepolymerization. Figure 8 shows how α_i data on the fibre-free polymer can be fitted with the equation for those of the composite, provided its time scale is shifted 30 min forward.

The second step is to compare the polymerization processes in composites with the same epoxy matrix, but different filling agents. Three composites with the same epoxy and aramidic (composite B), E-glass (composite C) and graphite (composite D) fibres gave $Q(t)$ values fitted vs. the time of the isothermal cure ($T_{\text{cure}} = 393$ K) by the following expressions

(B) $Q(t) = 180.25 \exp(-4.91 \times 10^{-2}t)$

(C) $Q(t) = 209.11 \exp(-5.08 \times 10^{-2}t)$

(D) $Q(t) = 295.05 \exp(-5.68 \times 10^{-2}t)$

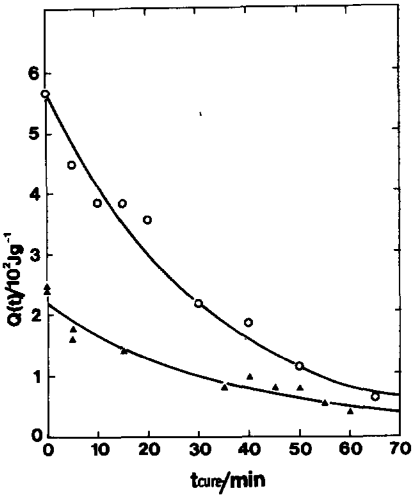

Fig. 7. F 913, here indicated as composite A, with glass fibres (○) and fibre-free epoxy (▲). Heat delivered in a 10 K min^{-1} DSC scan vs. the time of isothermal cure (T_{cure} = 393 K). $Q(t)$ values of the composite refer to the pure epoxy content.

The highest and the lowest Q_0 values concern composite D and composite C, respectively (see Fig. 9). In this case, properties of the fibres were known (see Table 2) and reasons for the differences in the cure kinetics could be suggested.

The same decreasing order is found for the thermal conductivities and the fibre–epoxy interfacial area, either of which may affect the delivery of heat from the sample and, hence, the homogeneous distribution of temperature within it. When the temperature is practically the same throughout the sample, the cure conditions at the surface and the core will be the same; when the thermal conductivity of the sample is poorer, the surface will be

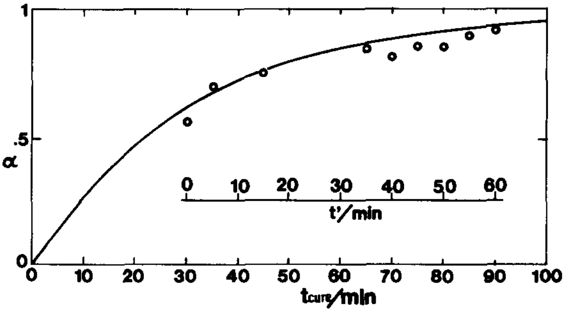

Fig. 8. Composite A cure degree vs. time of cure. Experimental data refer to the fibre-free epoxy. The fitting curve has been computed from the corresponding composite. The difference between the series of samples (see Fig. 7) is interpreted as "shift" of the actual starting point of the cure process.

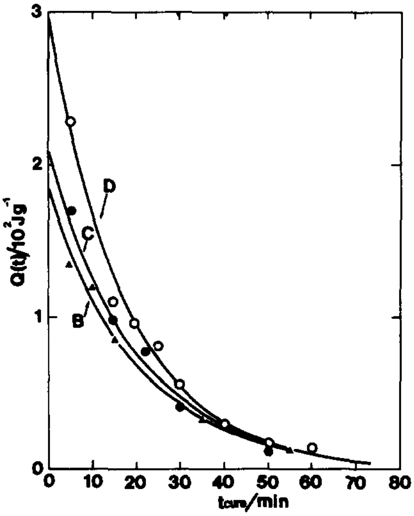

Fig. 9. Composites B, C and D: $Q(t)$ vs. time of isothermal cure at 373 K.

superheated with respect to the bulk of the sample, which is the major reacting mass.

Accordingly, for a given T_{cure}, a composite with better thermal conductivity and a larger fibre–epoxy interfacial area may be expected to undergo more exhaustive polymerization. The final polymer will have a higher T_g value. A TMA check, in fact, gave $T_g = 363$, 380 and 390 K, for B, C and D, respectively.

Composite D fibres are finished with an epoxy covering, those of B are bare, those of C are finished with an organo-silane coating. More rapid and more exhaustive polymerization would thus be expected in D than in C, than in B: and this was indeed the case.

TABLE 2

Properties of the filling agent of three composites with the same epoxy matrix.

Composite	B	C	D
Fibre kind	Kevlar	E-glass	Graphite
Density (g cm^{-3})	1.44	2.60	1.86
Filament diam. (10^{-6} m)	11.9	10.0	7.8
Cross-section	round	round	round
Surface finish	none	organosilane	epoxy
Fibre ratio (% volume)	48	50	50
Therm. conductivity (W m^{-1} K^{-1})	0.05	1.00	17.50

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