

DTA TRACES OF EPOXY RESINS AND COMPOSITES

Effect of fibers on the polymerization kinetics

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Four CIBA epoxy composites, A, B, C and D, have been investigated with the aim of verifying the effects of the respective fibers upon polymerization rate.

For material A a comparison is made between prepreg and fiber-free resin; the remaining three have been directly compared with one another, the epoxy resin being the same for all of them. Although the phenomenological reaction order remains unchanged, always being equal to one, and although no significant difference may be observed for the kinetic constant, relevant effects have been observed for the trend of the polymerization degree vs. the time of cure.

A tentative interpretation, based upon the physico-chemical properties of the fibers, also seems suitable to explain the observed differences in the glass transition temperature.

Epoxy prepreps are of fundamental importance in modern aero space technology, as non-metallic materials for primary structure applications. They are characterized by an epoxy matrix, which is the continuous "primary phase", and by a reinforcing or filling agent, discretely dispersed throughout the matrix, which mainly serves to improve the mechanical properties.

Accordingly, the inert filling agent is generally assumed not to have a significant effect on the polymerization process of the epoxy matrix.

The present study, undertaken to verify this assumption, shows that the filling agent can in fact affect the kinetics of polymerization of the epoxy host.

Four CIBA materials, commonly employed as composites in the aerospace industry and here designated as A, B, C and D, respectively, were investigated by means of non-isothermal DTA, which allows monitoring of the cure process, provided that the experimental results are properly evaluated [1–3].

Experimental

The samples of A were of two kinds: (i) prepreg containing E Glass fibers, and (ii) fiber-free resin, obtained by separation of the insoluble fibers in THF, which

was eventually evaporated. The samples of B, C and D were preregs containing the same epoxy components, but different filling stuffs, viz. Kevlar (Du Pont), E Glass and graphite fibers, respectively.

A previous characterization of the epoxy matrix was carried out by means of IR spectroscopy Pye Unicam SP3-300 spectrophotometer and high-performance liquid chromatography (HPLC). A Pye Unicam LC3 instrument fitted with a gradient elution system with a UV absorbance detector and an HP 3388A peak integrator on line).

Figure 1 shows a typical IR spectrum, whose relevant bands are listed in Table 1 along with the corresponding component of the epoxy matrix.

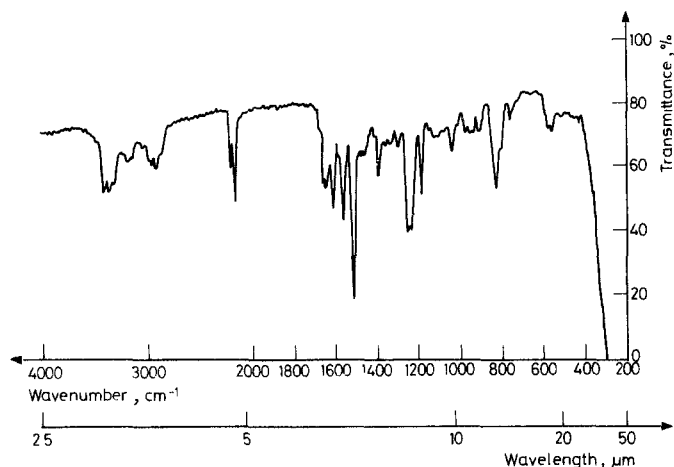


Fig. 1 Typical IR spectrum of the epoxy resin of the composites B, C and D

Table 1 Main functional groups and corresponding component in the epoxy resin of the composites B, C and D, according to the IR spectrum of Fig. 1

Chem. bond	Group	Component	Wave number
N—H	amine	accelerator	3400—3200
O—H	alcohol	epoxy chain	3600—3200
C—H	aromatic	epoxy chain	3030
C—H	aliphatic	epoxy chain	2850
C≡N	nitrile	catalyst	2200
C=C	phenil	epoxy chain	1610
C—C O	epoxide	epoxy chain	1300—1200

The experimental conditions used for the HPLC were a suitable modification of the Dark method [4]. Solutions of the epoxy component of about 1 g/l were obtained by dissolving the prepreg in THF; the injected amount was 10 μ l; the solvents of the mobile phase were a H₂O—CH₃CN mixture (60% H₂O) and CH₃CN; the flow rate

was 2 ml/min; the revelator was set at 230 nm and 0.32 AUFS; the chart speed was 1 cm/min. A typical chromatogram of this investigation is shown in Fig. 2; the components, identified by comparison with standard compounds, are listed in Table 2.

Table 2 summarizes the conclusions of this preliminary investigation about the chemical nature of the epoxy resin, which, for the composites B, C and D, is a mixture of bisphenol A diglycidyl ether (DGEBA), dicyandiamide (DICY), urea derivative (Accelerator) and polyvinyl acetalic rubber (Elastomer). An analogous investigation for composite A was given in [5]: tetraglycidyl methylenedianiline (TGMDA) as main component (58%) and no trace of elastomer; the other components were the same as in the above composites, with analogous proportions.

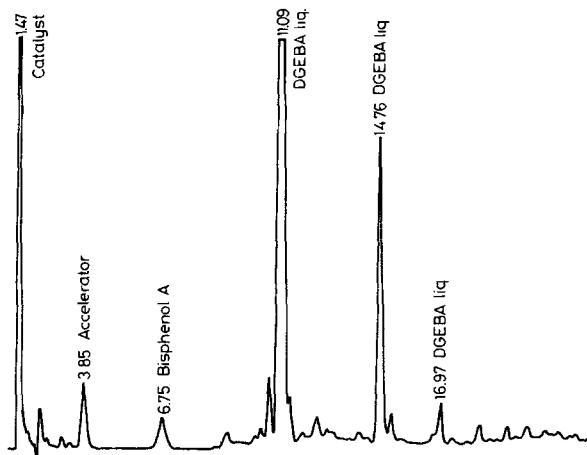


Fig. 2 Typical HPLC trace of the composites B, C and D. Each peak is quoted with the corresponding retention time

Table 2 Main components of the epoxy resin of the composites B, C and D, according to the HPLC trace of Fig. 2

Component	Composite B	Composite C	Composite D
DICY	6.0	5.5	6.0
Accelerator	3.5	3.5	3.5
DGEBA liq.	56.0	55.0	57.0
DGEBA sol.	18.0	18.5	17.0
Elastomer	12.0	11.0	11.0

Table 3 summarizes the main properties of the fibers.

A differential scanning calorimeter (Du Pont mod. 1090) was employed to obtain DTA traces at 10 deg/min heating rate, Al_2O_3 being the reference material. The exothermic effects were evaluated quantitatively.

Samples of about 40 mg were previously cured at 373 K within sealed DTA silver pans before the DTA scan [1-3].

Table 3 Main geometric and physico-chemical properties of the fibers filling the composites investigated

Property	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	—	Organo-silane	Epoxy
Fiber ratio, % volume	48	50	50
Thermal conductivity, W m ⁻¹ K ⁻¹	0.05	1.00	17.50

Results and discussion

Composite A

Figure 3 displays the heat amounts $Q(t)$, delivered by the samples of composite A and of the corresponding fiber-free resin vs. the time of the previous isothermal cure, t_{cure} . The analysis [1] of these data shows that both composite and fiber-free samples undergo a polymerization process with a phenomenological reaction order equal to one. The kinetic constants calculated for $T_{\text{cure}} = 373$ K are:

$$k = 3.16 \cdot 10^{-2} \text{ min}^{-1}$$

$$k = 2.45 \cdot 10^{-2} \text{ min}^{-1}$$

for the composite and for the fiber-free resin, respectively.

The values of Q_0 , i.e. the heat amounts which would be delivered by the corresponding mixture of "monomers" [3], are 566.4 and 215.7 J/g, respectively.

The former, concerning the composite, is referred to the pure epoxy content, viz. 33%, in order to allow direct comparison.

The larger Q_0 value for the composite would suggest that the number of bonds formed in the corresponding prepolymer is larger than in the fiber-free resin.

This could be a direct effect of separating fibers from the epoxy matrix: reactive sites would achieve a better stereochemical arrangement, and polymeric chains, after evaporation of the solvent, would become closer to one another. As a consequence, uncured fiber-free samples should correspond to a larger cure degree than the composite prepolymer.

As the corresponding k values do not differ too much from each other, one might suggest that the discrepancy between the fits of Fig. 3 is fictitious, the lower curve relating to a process whose starting point is actually "shifted" with respect to that of the upper curve.

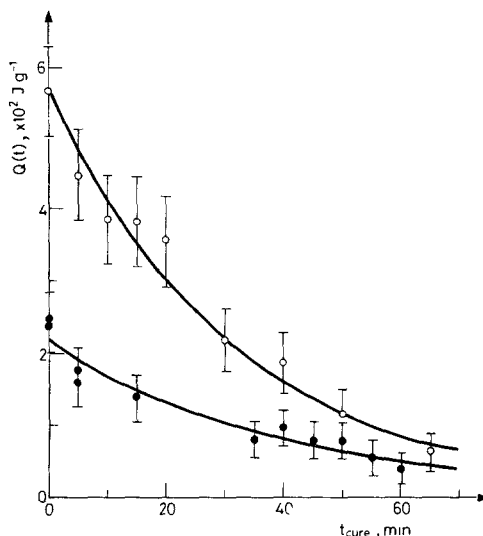


Fig. 3 Composite A: with E Glass fibers (open circles) and fiber-free resin (full circles). $Q(t)$ is the heat delivered in a 10 deg/min DTA scan vs. the time of isothermal cure ($T_{\text{cure}} = 373$ K). $Q(t)$ values of the composite refer to the pure resin content. $k = 3.16 \cdot 10^{-2} \text{ min}^{-1}$

If one computes a cure degree, α , as

$$\alpha = 1 - \frac{Q}{Q_0}$$

and uses for both sets of data $Q_0 = 566.4$ J/g, one can recognize that the Q_0 value obtained for fiber-free samples would correspond to $\alpha = 0.62$, i.e. to $t_{\text{cure}} = 30$ min, with respect to the fit of the prepreg samples.

Accordingly, a proper α vs. t plot, where the $Q(t)$ values obtained for fiber-free samples have been correlated with $t' = (t_{\text{cure}} + 30)$, clearly shows that this set of data may be reasonably fitted by the same cure referring to prepreg samples see Fig. 4.

Composite B, C and D

Figure 5 shows $Q(t)$, referred to the actual epoxy content of each composite, vs. the time of the previous isothermal cure at 373 K: all these trends correspond to a phenomenological reaction order equal to one, and may be represented by the following fitting expressions, which allow one to recognize directly the values of the kinetic constant and of Q_0 :

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

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

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

for composites B, C and D, respectively.

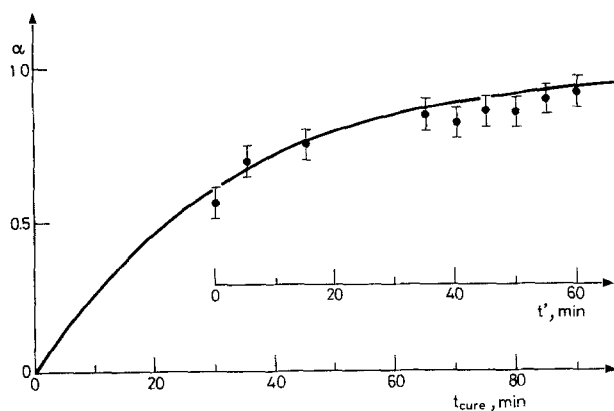


Fig. 4 Composite A: cure degree vs. time of cure. Experimental data refer to the fiber-free resin. The fitting curve is that computed for the corresponding composite. The difference between the series of samples (see Fig. 1) is interpreted as a "shift" of the actual starting point of the cure process.

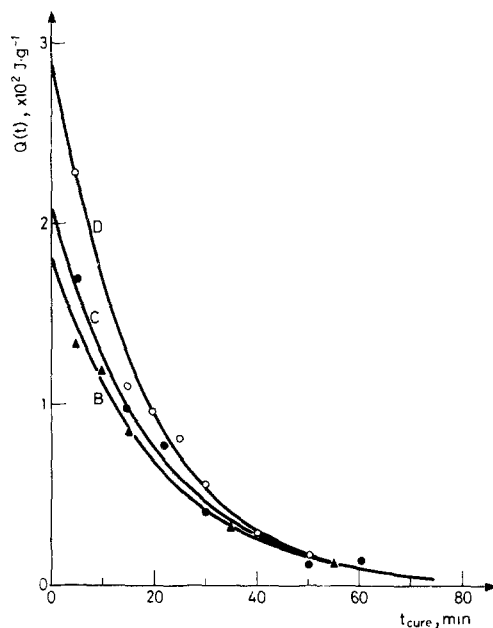


Fig. 5 Composites B (triangles), C (full circles) and D (open circles): $Q(t)$ vs. the time of isothermal cure at 373 K. B: $k = 4.91 \cdot 10^{-2} \text{ min}^{-1}$; C: $k = 5.08 \cdot 10^{-2} \text{ min}^{-1}$; D: $k = 5.68 \cdot 10^{-2} \text{ min}^{-1}$

In this case too, the k values are quite close to each other, while the Q_0 's, i.e. the corresponding pre-exponential factors in the above expressions, are significantly different.

As suggested for composite A, this should be attributed to the different number of bonds formed in the cure process. In this case, however, the reason for such a difference must be found in the physical and chemical properties of the fibers hosted within the epoxy matrix.

It is indeed possible to recognize a correlation between Q_0 and some physical properties of the fibers of each composite.

The highest Q_0 is that of composite D containing graphite fibers; the lowest is that of composite B containing Kevlar fibers. The same decreasing order occurs for the respective thermal conductivity and for the fiber-epoxy interfacial area see Table 3. Both these parameters directly effect the amount of heat which can be spread throughout the composite and eventually delivered to the external ambient. In other words, the higher these parameters, the more homogeneous the temperature throughout the sample, i.e. the smaller the superheating of the external regions with respect to the core. A lower temperature of the core would significantly modify the actual cure conditions, i.e. the number of bonds which can actually be formed.

As mentioned in previous papers [3, 5], a higher T_{cure} always implies a higher T_g , i.e. a larger number of bonds formed in the cure process, because of a better mutual orientation among the reactive groups, either of monomer molecules or of polymeric chains in the starting material. Accordingly, when the temperature is practically the same within the sample, the cure process will occur under the same conditions at the surface as in the core. Thus, for a given T_{cure} , the number of bonds formed will be larger for a material with a better thermal conductivity.

One may add a further consideration based upon the chemical surface finishing of the fibers. Composite D, i.e. that with the highest Q_0 , contains graphite fibers finished with epoxy material, whereas composites B and C contain bare and organosilane-finished fibers, respectively. Accordingly, one would expect polymerization to occur more rapidly and more exhaustively in D than in C, than in B: which is indeed what actually happens. If the highest Q_0 is chosen as reference to compute a comparative polymerization degree for the three composites considered, viz.

$$\alpha' = \alpha * \frac{Q(t)}{Q_{0D}}$$

the trends reported in Fig. 6 are obtained. This figure allows one to visualize the actual difference in the polymerization of the three composites better than from the values of the rate constants given by the direct fit of the experimental data shown in Fig. 5.

Composite D will form a polymer with a more extended cross-linking network and, accordingly, after exhaustive cure, it will show a higher T_g ; this is indeed in agreement with the experimental evidence, viz. $T_g = 363$ K, 380 K and 390 K for composites B, C and D, respectively, as obtained with TMA on samples exhaustively polymerized.

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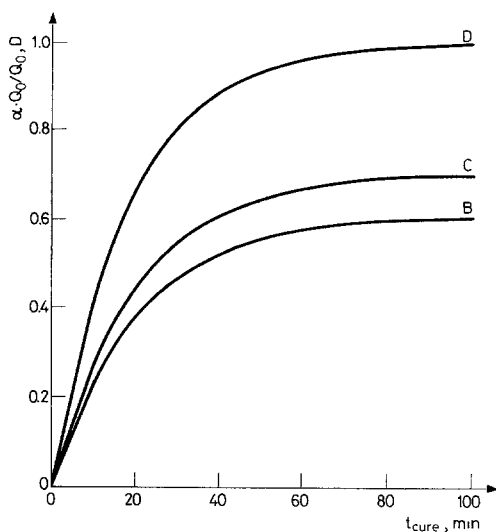


Fig. 6 Comparative polymerization degree for the composites B, C and D. The highest Q_0 , viz., that of the composite D, has been used for reference

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Zusammenfassung – Vier CIBA-Epoxykomponenten A, B, C und D wurden mit dem Ziel untersucht, die Wirkungen der entsprechenden Fasern auf die Polymerisationsgeschwindigkeit festzustellen. Für Material A wurde ein Vergleich zwischen "prepreg" und faserfreiem Harz angestellt; die anderen drei wurden direkt miteinander verglichen, wobei stets das gleiche Epoxyharz verwendet wurde. Obwohl sich die phänomenologische Reaktionsordnung nicht ändert und immer gleich 1 ist, und obwohl für die kinetischen Konstanten keine signifikanten Unterschiede zu beobachten sind, wurden doch erhebliche Effekte hinsichtlich des Trends des Polymerisationsgrades in Abhängigkeit von der Zeit der Aushärtung gefunden. Eine auf den physikalisch-chemischen Eigenschaften der Fasern beruhende tentative Interpretation scheint auch zur Erklärung der beobachteten Unterschiede in den Glasübergangstemperaturen geeignet zu sein.

Резюме — Четыре эпокси композитных материала (А, В, С и D) фирмы ЦИБА были исследованы с целью подтверждения влияния соответствующих волокон на скорость полимеризации. Для материала А сравнение было проведено между безволокнутой и импрегнированной волокном смолами. Остальные три материала были прямо сопоставлены друг с другом, поскольку эпокси смола для них была одна и та же. Хотя фактически порядок реакции оставался неизменно равным единице и не наблюдалось значительного различия в константах скорости реакций, соответствующие эффекты проявлялись на зависимости степени полимеризации от времени консервации. Предварительная интерпретация, основанная на физико-химических свойствах этих волокон, оказалась приемлемой для объяснения наблюдаемых различий в температурах стеклообразования.