A STUDY OF THE CURE CHARACTERISTICS OF AN EPOXY RESIN SYSTEM BY
DIFFERENTIAL SCANNING CALORIMETRY AND TORSIONAL BRAID ANALYSIS

J.M. BARTON and W.W. WRIGHT

Materials and Structures Dept., Royal Aircraft Establishment, Farnborough,
Hampshire, UK.

ABSTRACT

The cure of mixtures of tetraglycidyldiaminodiphenylmethane resin with
4,4'-diaminodiphenylsulphone and BF3-ethylamine in various proportions was
studied using DSC to give overall cure rates, and torsional braid analysis to
give isothermal times of gelation and vitrification. The apparent activation
energies for gelation were in fairly good agreement with those for rate of cure
from DSC in the 10–20% conversion range.

EXPERIMENTAL

The resin was CIBA-GEIGY MY720, used with 4,4'-diaminodiphenylsulphone (DDS)

as the curing agent, and BF_3-ethylamine complex (BFE) as an accelerator. DSC

measurements were made with a Dupont 990/910 instrument and the torsional braid

analyser was a modified Chemical Instruments Corporation model.

RESULTS AND DISCUSSION

The compositions of the mixtures studied are given in Table 1. In each case

DSC scans were made at 2,5,10 and 20 K/min, and linear baselines were used under

the exotherms to give heat flow data. The heat flow–temperature profiles showed

a single peak for the compositions containing only resin and DDS, whereas the

addition of BFE produced several overlapping peaks indicating kinetic complexity.

Values obtained for the total heat of cure, Qo, are in Table 1. Each value is

the average of 6 runs, 2 at each heating rate, and no significant effect of

heating rate was found. In the presence of BFE, Qo is seen to decrease with

increasing BFE concentration. BFE is known to initiate cationic hompolymerisat-

ion of epoxide and this appears to involve a lower heat of reaction than amine

or hydroxyl addition.

If the rate of cure is described by the equation $r = d\alpha/dt = kf(\alpha)$ (1)

where α is the fractional conversion and k is of the Arrhenius form the plot

of log r against 1/T should be linear for a given α, with slope E/R, where E is

the apparent activation energy. These plots are given for Mix 4 in Fig 1,

TABLE 1

Resin compositions and heat of cure (Qo)

Mix No	Composition g/100g resin		Qo	
	DDS	BFE	kJ/mole epoxide	Standard deviation
1	53	0	95.5	3.8
2	53	2	88.6	2.4
3	30	0	96.4	2.3
4	30	1	79.9	2.4
5	30	2	74.6	2.4

and they show good linearity in the 10-90% conversion range. The good fit of
the data to the simple kinetic model of Eq. (1) is remarkable in view of the
complex heat flow – temperature profiles obtained for this system. In Eq. (1)
the kinetic function is undefined and is only required to be constant for a
given value of conversion, and this must provide sufficient freedom for the
model to apply as a good approximation. The data for the other compositions
also gave corresponding plots with a high degree of linearity. The slopes of
the plots were determined by linear regression, and the values of apparent
activation energy (E) derived from the slopes are given in Table 2. An increas-
ing trend of E with conversion is observed, except for Mix 4 which shows a
maximum value at 30% conversion. The general upward trend in activation energy
with increasing conversion may be associated with the increasing viscosity and
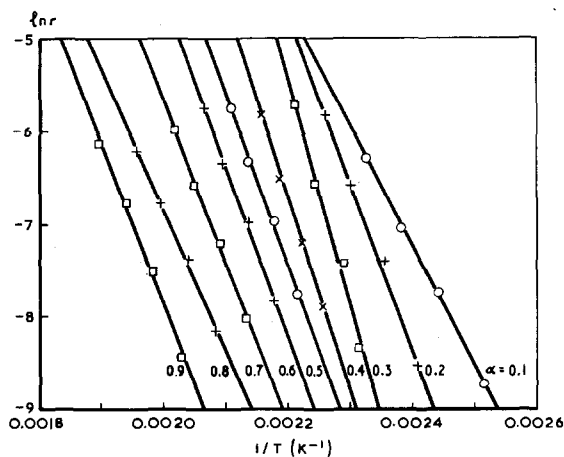higher energy for diffusion as the cure proceeds.

Figure 1. Plots of log cure rate at fixed conversion against $1/T$ for Mix 4.

TBA experiments were run isothermally in the range 100-170°C.

A typical result is shown for Mix 1 in Fig. 2 as plots of log relative rigidity and log logarithmic decrement against time. Two peaks are observed on the logarithmic decrement plot which have been shown by Gillham [1,2], for various resins, to correspond to the onset of gelation and at a later time to vitrification of the resin. The onset of gelation also coincides with a characteristic increase in relative rigidity. Plots of log gel time against I/T are shown in Fig. 3. Again good linearity is observed in all cases, and values of the apparent activation energy, Eg, derived from the plots are in Table 2. From the Flory theory the onset of gelation is estimated to be about 33% conversion for Mix 1, and the values of Eg and E at 30% conversion are similar. However for the systems containing BFE Eg is significantly lower than E, which may be a consequence of the kinetic complexity of these reactions, and the inadequacy of Eq (1) as a precise kinetic model.
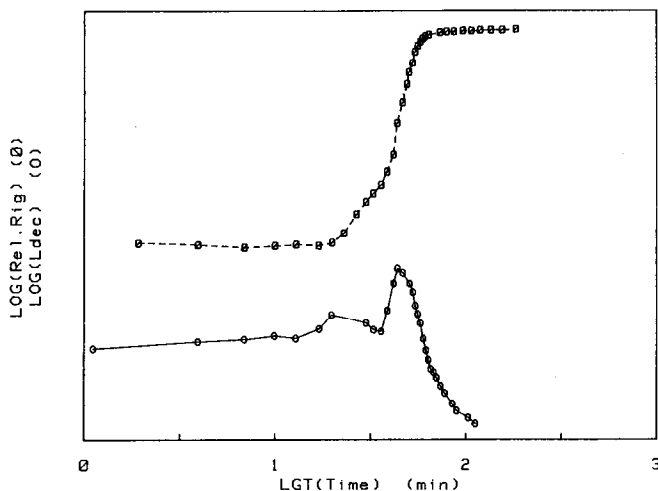

Figure 2. Logarithmic plots of Relative Rigidity and Log Decrement from TBA against time for Resin/DDS (100/53) at 160°C.
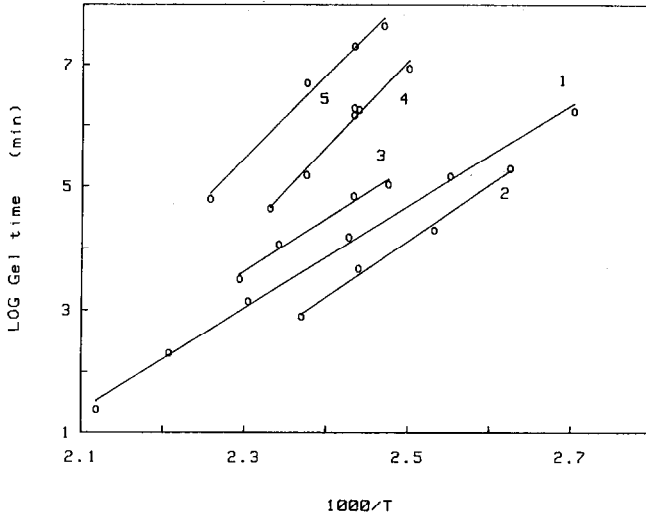
Figure 3.   Log Gel Time from TBA plotted against reciprocal absolute
            temperature.

TABLE 2

Activation energy in kJ/mole from DSC (E) and for gelation from TBA (Eg)

Mix	E					Eg
No	% Conversion					
	10	20	30	50	90	
1	68	69	71	76	154	69
2	86	106	122	147	246	76
3	74	77	82	97	129	70
4	106	149	200	154	143	119
5	89	114	133	183	227	114

REFERENCES

1   J.K. Gillham, Polym. Eng. Sci., 19 (1979) 676.
2   J.B. Enns and J.K. Gillham, J. Appl. Polym. Sci., 28 (1983) 2831.