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Microcalorimetric determination of the cure reaction in some fluorinated polyether rubbers

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Abstract

A microcalorimetric technique is described which enables an entire rubber cure curve to be recorded on a single sample quantitatively. It is non-destructive, operates at moderate temperatures and does not require separate extraction and analysis steps.

The technique is used to record the cure reaction between a variety of isocyanate- and hydroxy-terminated polyfluoroethers. The effect on reaction rate of temperature, degree of cure and type of functional group participating in the crosslinking reaction are studied to provide a general description of the behaviour of mixtures of this type of material during processing.

Keywords: Curing; Kinetics; Microcalorimetry; Polyurethanes; Rubber

1. Introduction

When mixed, hydroxyl and isocyanate end group functionalized fluorinated polyether prepolymers react together to give a crosslinked polyurethane rubber. An understanding of the kinetics of this curing reaction is desirable to enable the selection of suitable storage and processing conditions during manufacture of filled rubbers.

Differential scanning calorimetry has been used to describe the kinetics of the cure reaction in extensively crosslinked systems such as epoxy and polyester resins by monitoring the heat generated during bond formation at elevated temperatures [1, 2]. However, these fluorinated urethane rubbers are relatively lightly crosslinked systems with a correspondingly smaller enthalpy of reaction. The maximum processing temperature that could be employed for the manufacture of filled rubbers was limited to

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around 80°C by the need to use a water jacket for reactor temperature control. DSC was found to be insufficiently sensitive to record the low levels of heat generated at these temperatures particularly during the later stages of the reaction.

Polyurethane cure reaction kinetics have also been studied by wet chemical analysis methods. For example, Yee and Adicoff [3] have described the cure of polybutadiene rubbers by ageing several samples of mixed precursor over a range of temperatures with periodic removal and analysis. The reaction in each subsample was quenched by lowering the temperature; unreacted isocyanate was then extracted with a suitable solvent, reacted with an amine and finally excess amine was determined by titration. The number of separate stages involved makes the procedure labour-intensive, time-consuming and therefore costly. The poor solubility of fluorinated polymers in all common laboratory solvents would create additional problems if this procedure was applied to fluorinated rubbers.

The use of a more sensitive calorimetric method and its application to quantify the effect of various treatments on the cure rate of this type of rubber are described here.

2. Equipment and materials

A Thermometric type 2277 thermal activity monitor [TAM] was used to monitor the cure reaction by recording the associated heat generation. Rubber precursor samples were sealed in 3 cm^3 glass ampoules prior to analysis.

Four polymers were used for this work. Each possessed a similar fluorinated, linear, random copolyether backbone, but were terminated with different functional groups: polymer A was nominally difunctional and terminated with isocyanate groups; polymer B was nominally difunctional and terminated with primary hydroxy groups, adjacent to the fluorinated polymer backbone; polymer C was nominally difunctional and also terminated with hydroxy groups; unlike polymer B, the end groups are separated from the fluorinated main chain by the insertion of short ethoxy blocks; polymer D was nominally tetrafunctional and terminated at each end with one primary and one secondary hydroxy group; Like polymer C the functional groups are isolated from the fluorinated main chain by the insertion of short ethoxy blocks. The same batch of each material was used for all experimental work.

The temperature of the freezer employed for extended storage trials was monitored remotely using a Tinytalk-temp miniature data logger.

Gel times were measured with a Brookfield rotating spindle viscometer.

3. Experimental and results

3.1. General experimental procedure

Rubber precursors were prepared by mixing one or more polyols with polymer A. The proportions were chosen to give mixtures which were stoichiometrically 1:1 in

NCO:OH, based on the equivalent weight values supplied by the manufacturer. In practice, blending will be required to manufacture rubbers with a range of mechanical properties. In order to model these systems, a 3-component blend, consisting of a mixture of polymer D and polymer B cured stoichiometrically with isocyanate-terminated polymer A, was also studied.

The components were mixed thoroughly, using a glass rod, and a 0.75 ± 0.25 g aliquot transferred to a TAM sample ampoule, sealed and lowered into the equilibration region of the TAM analytical cylinder. Because the curing reaction of interest commences as soon as the components come into contact, the entire process was performed with minimum delay to reduce errors caused by failure to record the initial stages of the reaction.

After a temperature equilibration period of 5 min, the sample was lowered into the TAM detection region and the power output recorded continuously. Where possible, the signal was monitored until it had dropped to an undetectable level and this was assumed to represent the complete reaction. Because of constraints on time, this was not possible with the less reactive mixtures at the lower end of the temperature range studied and the experiments were terminated when the majority of the reaction was judged to have occurred. In these cases the area under the "tail" was estimated by consideration of the behaviour of identical mixtures when cured at higher temperatures, with the assumption that the total heat generated during the cure reaction was independent of cure temperature.

During the processing and interpretation of the resulting cure curves, the assumption was made that, at any point in the reaction, the cure reaction rate was proportional to the heat generation rate (q) and the degree of advancement of the reaction (α) was equal to the heat evolved at that time as a fraction of the total heat detected during the entire cure.

3.2. *Relative reaction rates of different polymer mixtures*

The cures of 2-component mixtures of each of the three polyols with polymer A were measured at a constant temperature of 80°C. The superimposed cure curves are shown in Fig. 1.

It can be seen that polymer A–B cures far slower than the other two mixtures and the reaction is obviously incomplete after 3 d. The other two mixtures appear to cure much faster by comparison — both decay to very low levels in about a day, the polymer A–C mixture being slightly faster than polymer A–D.

The cure curve of the 3-component blend, polymer A–D–B is shown in Fig. 2.

3.3. *Effect of extent of cure*

Order plots were constructed for each of the four mixtures as follows. Assuming the reaction can be described by a "power law" dependence of rate on concentration and that at any time during the reaction the observed heat generation rate is directly

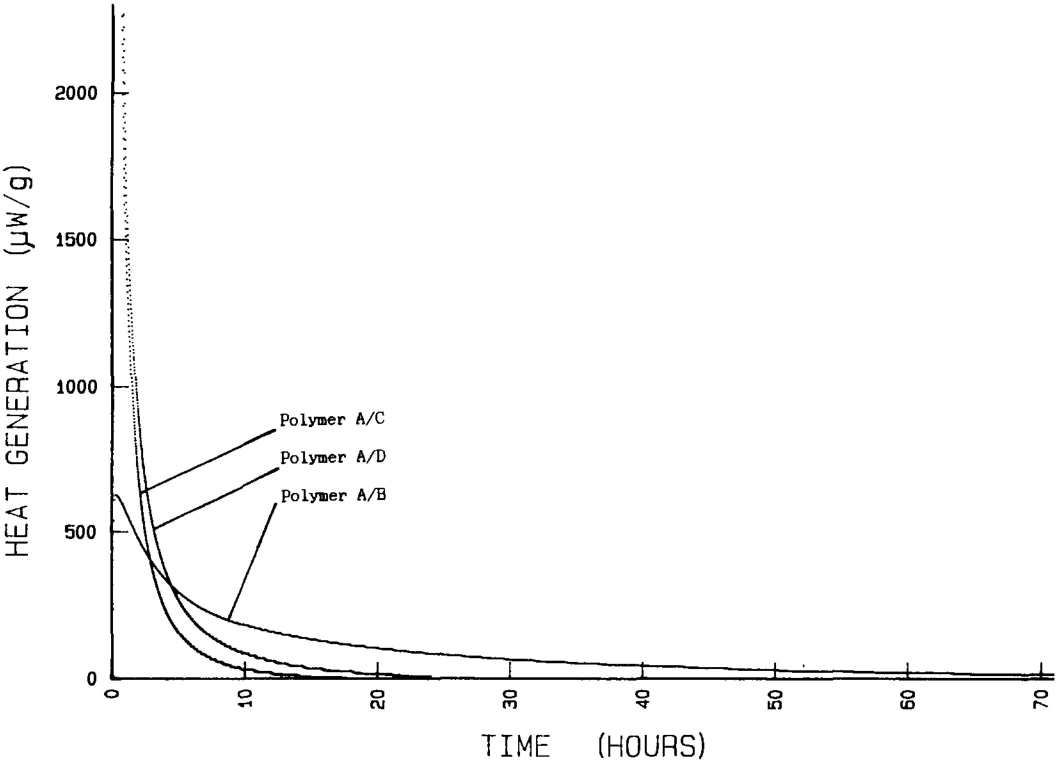


Fig. 1. Cure curves of 2-component polymer mixtures.

proportional to the reaction rate. Then

$$cq = -\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where α is the fraction reacted; q is the heat generation rate, n is the reaction order, t is the time, and c and k are constants.

Eq. (1) can be rearranged to give the equation of a straight line.

$$q = k(1-\alpha)^n \Rightarrow \ln q = \ln k(1-\alpha)^n \Rightarrow \ln q = \ln k + \ln(1-\alpha)^n$$

$$\Rightarrow \ln q = \ln k + n \ln(1-\alpha) \tag{2}$$

From Eq. (2) the order of the reaction will be equal to the gradient of a plot of ln (q) against ln $(1-\alpha)$.

The cure curves for each mixture, recorded at 70°C, were processed in this way. Results are summarized in Table 1 and Fig. 3. All show an approximately second order decay behaviour which may be used to obtain "working estimates" of the time to reach any point in the reaction. However, since each plot is curved, it will not be possible to describe the variation of rate with extent of these cure reactions precisely with any simple "power law" mechanism.

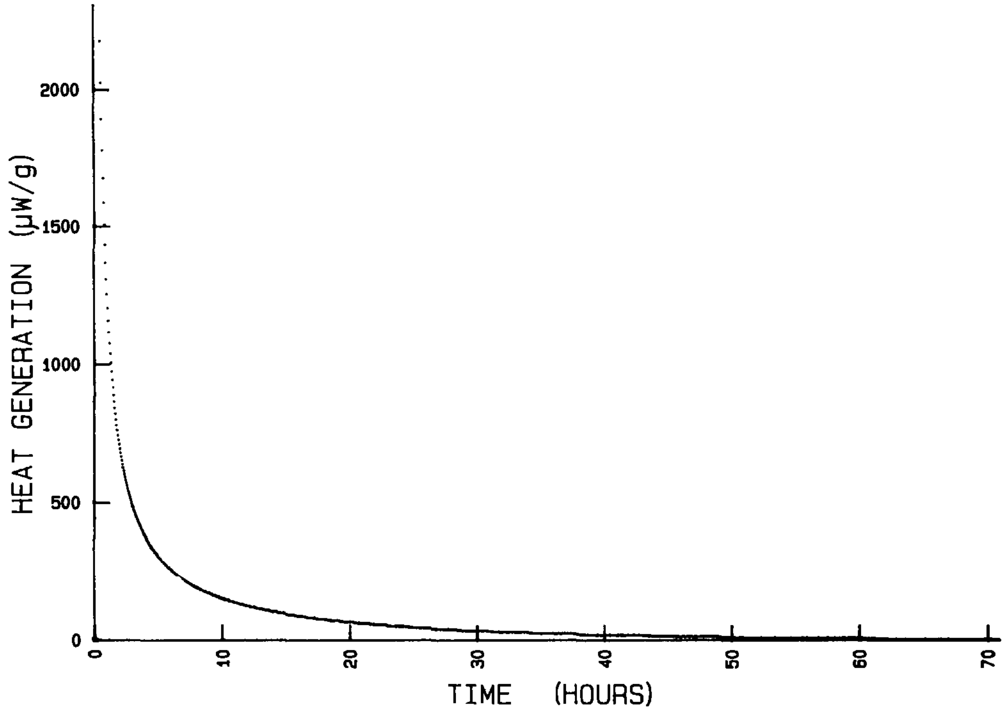


Fig. 2. Cure curve of a 3-component polymer mixture (A–D–B).

Table 1
Variation of reaction rate with the extent of cure-reaction curves recorded at 70°C

Time/h	Rate/(μW g^{-1})	ln(Rate/(μW g^{-1}))	α^a	$1-\alpha$	$\ln(1-\alpha)$
Polymer A–C					
0.25	5122.6	8.541	0.195	0.805	−0.2175
0.5	3148.3	8.054	0.336	0.664	−0.4098
1	1725.8	7.453	0.499	0.501	−0.6929
2	828.4	6.719	0.669	0.331	−1.1062
3	495.0	6.204	0.760	0.230	−1.4292
4	329.1	5.796	0.818	0.182	−1.7043
5	233.4	5.452	0.857	0.143	−1.9491
6	171.7	5.145	0.886	0.114	−2.1744
Order of reaction indicated by slope of linear regression line of data plotted in Fig. 3 = 1.70.					
Polymer A–D					
0.25	5706.0	8.649	0.159	0.841	−0.1741
0.5	3712.5	8.219	0.291	0.709	−0.3446
1	1960.2	7.580	0.443	0.557	−0.5866
2	972.0	6.879	0.599	0.401	−0.9153
3	621.1	6.431	0.688	0.312	−1.1669

Table 1 (*Continued*)

Time/h	Rate/(μW g^{-1})	ln(Rate/(μW g^{-1}))	α[a]	$1-\alpha$	$\ln(1-\alpha)$
Polymer A–C					
4	441.7	6.090	0.748	0.252	−1.3815
5	332.4	5.806	0.792	0.208	−1.5741
6	258.7	5.555	0.826	0.174	−1.7521
Order of reaction indicated by slope of linear regression line of data plotted in Fig. 3 = 1.96.					
Polymer A–B					
1	575.4	6.355	0.051	0.949	−0.0523
3	397.9	5.986	0.180	0.820	−0.1984
5	294.4	5.685	0.272	0.728	−0.3174
10	180.8	5.197	0.425	0.575	−0.5534
15	132.6	4.887	0.529	0.471	−0.7529
20	105.8	4.661	0.609	0.391	−0.9390
25	80.9	4.393	0.671	0.329	−1.1117
30	64.4	4.165	0.720	0.280	−1.2730
35	53.5	3.980	0.760	0.240	−1.4271
40	44.3	3.791	0.794	0.206	−1.5799
45	37.1	3.614	0.821	0.179	−1.7204
Order of reaction indicated by slope of linear regression line of data plotted in Fig. 3 = 1.591.					
Polymer A–D–B					
0.25	3249.3	8.086	0.100	0.900	−0.1054
0.5	2098.2	7.649	0.176	0.824	−0.1936
0.75	1545.7	7.343	0.231	0.769	−0.2626
1	1228.0	7.113	0.272	0.728	−0.3175
3	482.0	6.178	0.452	0.548	−0.6015
5	303.7	5.716	0.545	0.455	−0.7875
10	152.2	5.025	0.676	0.324	−1.1270
15	94.6	4.550	0.750	0.250	−1.3863
20	66.5	4.197	0.799	0.201	−1.6045
25	45.3	3.813	0.833	0.167	−1.7898
30	34.4	3.538	0.857	0.143	−1.9449
35	24.1	3.182	0.875	0.125	−2.0794
40	18.3	2.906	0.889	0.111	−2.1982
Order of reaction indicated by slope of linear regression line of data plotted in Fig. 1 = 2.317.					

[a] Where α is the integral of the cure curve up to that time, as a fraction of the integral of the entire reaction curve.

3.4. *Effect of temperature*

A series of isothermal cure curves were recorded on samples of each of the four mixtures, over the temperature range 40–80°C. The curves for the polymer A–B mixtures are illustrated in Fig. 4 — curves from the other three mixtures resembled these and are not shown.

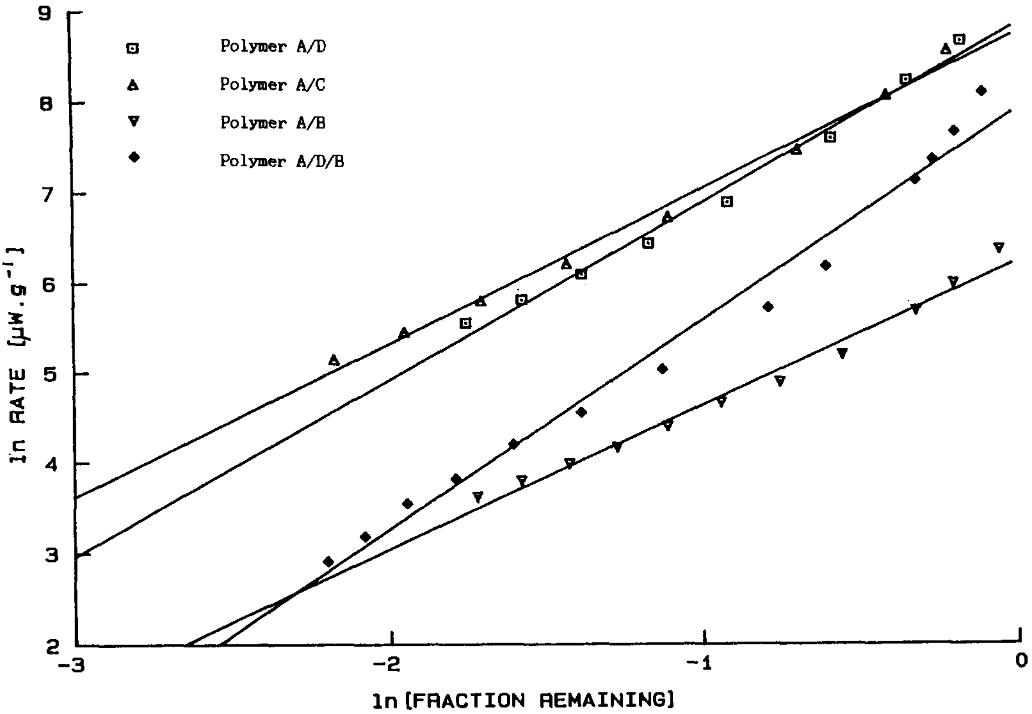


Fig. 3. Reaction order plots.

In the case of a calorimetry experiment where the heat generation rate was effectively constant throughout the duration of the test (kinetically zero order), it would be possible to obtain the activation energy by applying the Arrhenius equation:

$$q = Ae^{-E/RT} \tag{3}$$

where A is the Arrhenius factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

This implies a constant value of q for constant values of E and T—a condition which is clearly not met with these cure reactions, so Eq. (3) cannot be used. However, it has been proposed by Van Geel [4] that if the degree of reaction (as denoted by the quantity of heat evolved up to that point, Q) is taken into account then a modified form of the equation:

$$q = F(Q)e^{-E/RT} \tag{4}$$

where $F(Q)$ is a function of Q, can give a value of E which is independent of the degree of reaction. Eq. (4) may be expressed as:

$$\ln q = -\frac{E}{RT} + \ln F(Q) \tag{5}$$

and a plot of $\ln(q)$ vs $1/T$ should be linear, with a gradient equal to $-E/R$.

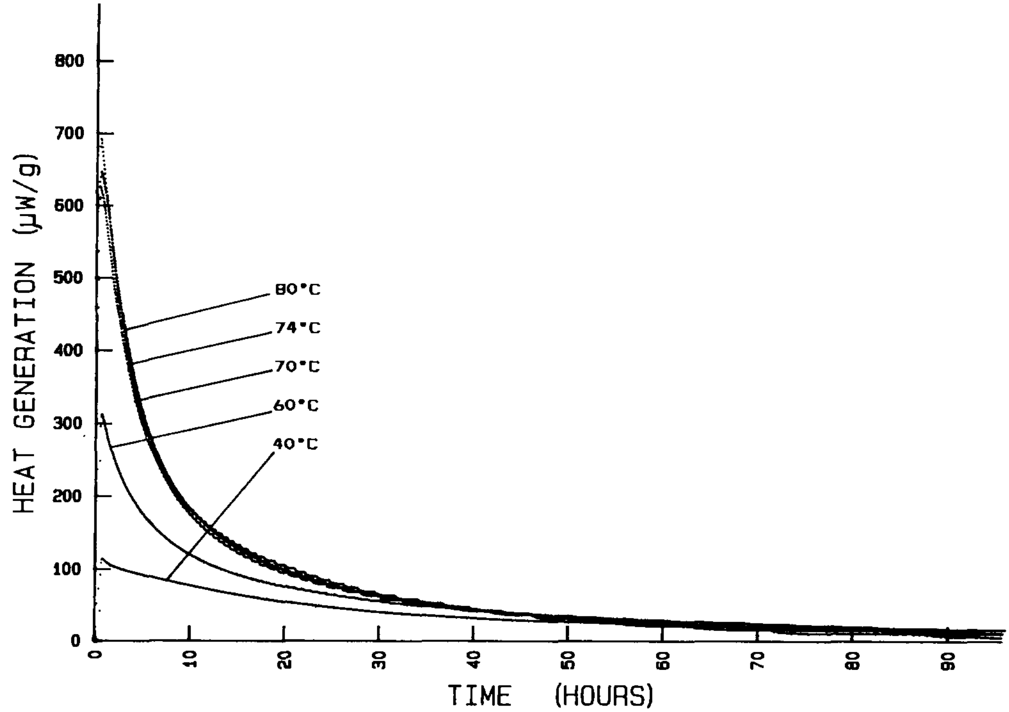


Fig. 4. Cure curves for polymer A–B mixtures at different temperatures.

In practice, this requires an accumulative integration of the rate vs time plot output from the TAM. Corresponding rates of heat generation at the points of identical total heat generation can then be selected from the tabulated data from several different isothermal experiments carried out over a range of temperatures. Results are summarized in Table 2 and Fig. 5.

3.5. *Storage life of polymer mixtures*

The temperature of a storage deep-freezer was monitored for several days and found to maintain a temperature of $-32 \pm 0.5°C$. An estimate of the expected half-lives of each of the four mixtures under consideration was made, using the descriptions of temperature-dependence obtained in the previous section. In the case of the less reactive mixtures (A–B and A–D–B), these times were too long to enable them to be conveniently tested by experiment and expected half-lives at 23°C were estimated instead.

Given that the reaction half-life is proportional to the reciprocal of the initial rate. i.e.

$$r = \frac{k}{t_{0.5}} \tag{6}$$

where r is the initial rate, $t_{0.5}$ is the reaction half-life, and k is a constant.

Table 2
Temperature-dependence of reaction rate

Temperature/°C	1/Temperature/K^{-1}	Heat generation rate (μW g^{-1}) when $\alpha = 0.5$	ln(Rate/(μW g^{-1}))
Polymer A–C			
80	0.0028316	3291	8.0989
74	0.0028806	2545	7.8418
70	0.0029142	1955	7.5781
60	0.0030016	1927	7.5637
40	0.0031933	538.5	6.2887
From plot of ln(Rate) vs 1/K (Fig. 5), activation energy = 39.75 kJ mol^{-1}.			
Polymer A–D			
80	0.0028316	2667	7.8887
74	0.0028806	2500	7.8240
70	0.0029142	1856.5	7.5264
60	0.0030016	1662	7.4157
40	0.0031933	512.5	6.2393
From plot of ln(Rate) vs 1/K (Fig. 5), activation energy = 38.19 kJ mol^{-1}			
Polymer A–B			
80	0.0028316	188.2	5.2375
74	0.0028806	128.0	4.8520
70	0.0029142	151.0	5.0173
60	0.0030016	45.6	3.8199
40	0.0031933	14.45	2.6707
From plot of ln(Rate) vs 1/K (Fig. 5), activation energy = 61.37 kJ mol^{-1}			
Polymer A–D–B			
80	0.0028316	554.7	6.3184
74	0.0028806	438.7	6.0838
70	0.0029142	374.8	5.9264
60	0.0030016	110.0	4.7005
40	0.0031933	47.4	3.8586
From plot of ln(Rate) vs 1/K (Fig. 5), activation energy = 60.03 kJ mol^{-1}			

Assuming the reaction obeys an Arrhenius temperature-dependence law, then

$$\ln(r) = \ln\frac{k}{t_{0.5}} = C - \frac{E}{RT} \tag{7}$$

where C is a constant.
On rearrangement, a straight line relationship is obtained.

$$\ln t_{0.5} = \frac{E}{RT} - B \tag{8}$$

where B is a constant (the sum of C and $\ln k$)

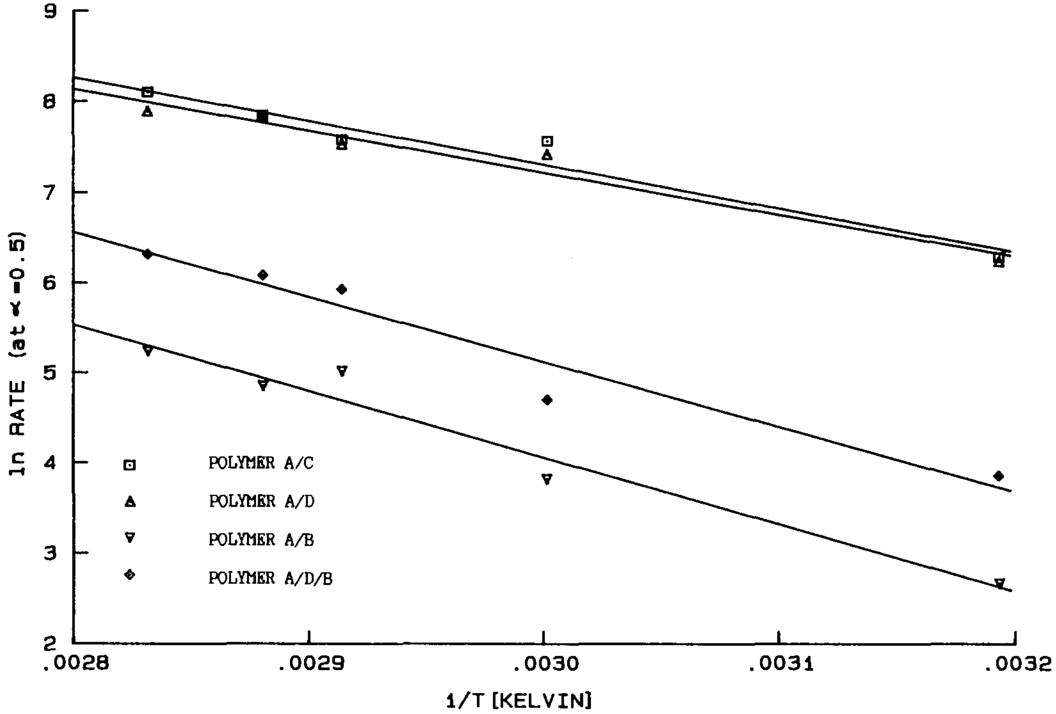


Fig. 5. Temperature-dependence of cure rate.

The value of the constant B must first be determined by substitution of an experimentally determined half-life and the temperature at which it was measured into Eq. (8). Half-lives at any other temperature can then be estimated by applying the same equation.

Curable mixtures were prepared, sealed in TAM ampoules and transferred either to the freezer, or a 23°C water bath without delay. After the predicted half life had elapsed, each sample was moved to the TAM and its remaining cure reaction recorded at 80°C and compared with the cure curve of a similar mixture analysed immediately after mixing. A typical pair of curves, obtained from polymer A–B, are illustrated in Fig. 6.

Results are summarized in Table 3. The predicted and observed attenuation show reasonable agreement in the case of the less reactive mixtures at 23°C, but the half-lives predicted for polymer A–C and A–D at −32°C appear pessimistic. A further storage trial on these two mixtures was therefore performed in a water bath at 8°C.

3.6. Equating heat generation with gel time

The time for gelation to occur in these binders is of practical significance for deciding processing pot life, but the point where this occurs is not given by the calorimetric curve alone since it is not associated with any abrupt change in heat generation. Simultaneous calorimetry and viscosity experiments have been performed on some rubber

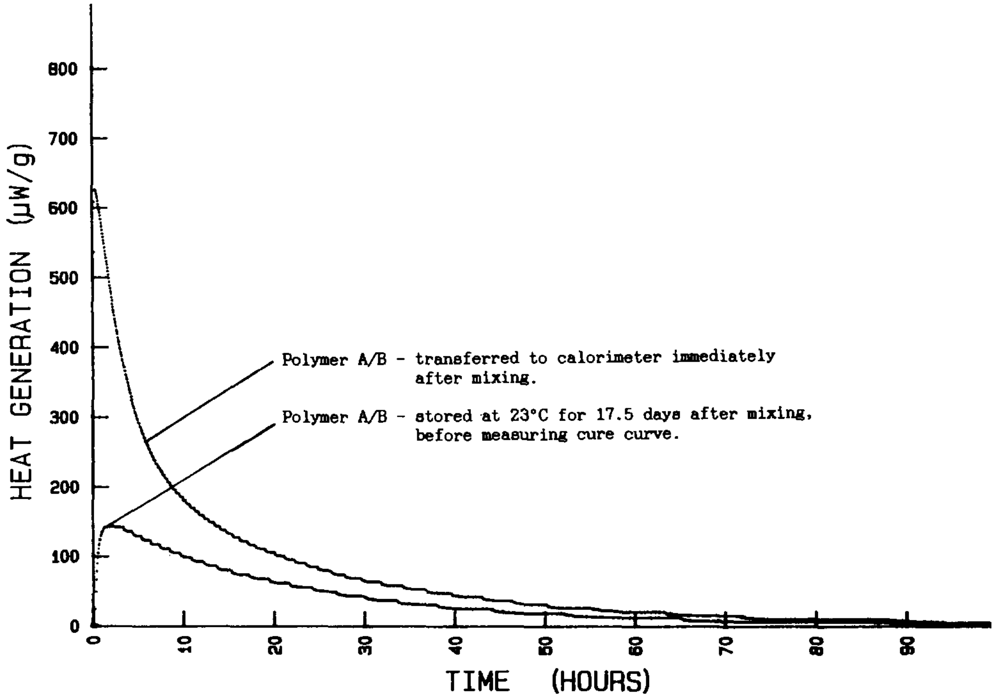


Fig. 6. Reduction in area of polymer A–B cure curve as a result of storage at room temperature.

precursors to identify the point in the cure curve which equates to the gelation point. This will assist in the selection of suitable storage conditions for premixed binder precursors.

The following rubber precursors were mixed and divided into two subsamples:

(1) a stoichiometric mixture of polymer A and polymer D;

(2) a stoichiometric mixture of polymer A and a blend of 1 part polymer D and 1 part polymer B by weight; and

(3) a stoichiometric mixture of polymer A and a blend of polymer D and polymer B containing a high proportion of polymer B.

For each precursor, one subsample had its cure curve recorded in the TAM at 80°C, as described earlier. The other subsample was transferred to a glass tube, immersed in a waterbath at 80°C and its viscosity monitored continuously using a Brookfield viscometer.

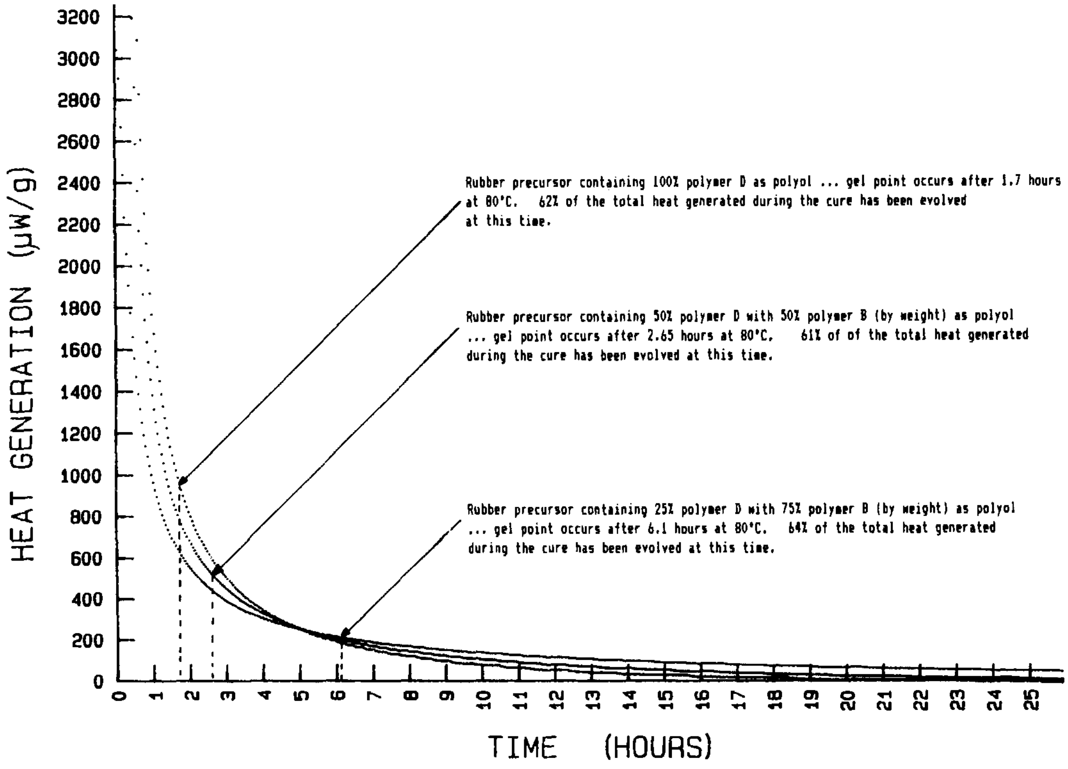
The time to gelation for each was indicated at the point where a large, rapid increase in viscosity was recorded. When the calorimetric cure curve was complete, the extent of cure at the gel point could then be deduced retrospectively from the fraction of the total heat evolved up to the gelation time. Results are summarized in Fig. 7.

It can be seen that inclusion of the more slowly reacting polymer B into the precursor mixture increases the gelation time progressively, as would be expected. However, the

Table 3
Partial cure of mixtures during storage

Sample description	Storage temp/°C	Storage time/h[a]	Heat evolved during cure reaction/(J g^{-1})		Reduction/%
			Freshly prepared	After storage	
Polymer A–B	+23	420	26.7	12.5	53.2
Polymer A–D–B	+23	109	29.14	12.37	57.5
Polymer A–C	−32	279	27.34	18.05	33.9
Polymer A–D	−32	308	33.23	26.4	20.5
Polymer A–C	+8	16.4	27.34	15.26	44.2
Polymer A–D	+8	20.2	33.23	23.6	29.0

[a] Storage time calculated to result in 50% cure reaction during storage.



Rubber precursor containing 100% polymer D as polyol ... gel point occurs after 1.7 hours at 80°C. 62% of the total heat generated during the cure has been evolved at this time.

Rubber precursor containing 50% polymer D with 50% polymer B (by weight) as polyol ... gel point occurs after 2.65 hours at 80°C. 61% of of the total heat generated during the cure has been evolved at this time.

Rubber precursor containing 25% polymer D with 75% polymer B (by weight) as polyol ... gel point occurs after 6.1 hours at 80°C. 64% of the total heat generated during the cure has been evolved at this time.

Fig. 7. Cure curves of polymer mixtures indicating gelation times.

fraction of the total reaction which must occur to achieve gelation appears to be fairly constant over the range of conditions studied.

An equation which relates extent of a cure reaction to the functionality of the reactants was described by Stockmayer [5].

$$P_a P_b = \frac{1}{(F_e - 1)(G_e - 1)} \tag{9}$$

where P_a is the fraction of first functional group reacted; P_b is the fraction of second functional group reacted; and F_e, G_e are the functionalities of each reactant.

If the assumption is made that polymer A has a functionality of *exactly* two and polymer D has a functionality of *exactly* four, then application of this equation to the first mixture (polymer A + polymer D) predicts the gel point to occur when 57.7% of the total cure reaction is complete. Considering that these functionalities are only approximately correct, that the two components may have experienced some degradation in storage prior to the experiment and also the contribution of various experimental errors, this predicted value is considered to agree reasonably well with the observed figure of 62%.

Eq. (9) cannot be applied easily to multicomponent mixtures where the components have very different reactivities. The observation that the gel point is occurring at about the same extent of reaction in each of the experiments suggests that the nominally difunctional polymer B component also contributes to the overall crosslinking reaction in some way at 80°C.

4. Discussion

The observed relative cure reaction rates of these mixtures can be accounted for by consideration of the chemical structure of their polyol end groups. The slowest reaction occurs with polymer B. Although this prepolymer has only primary aliphatic end groups, which are expected to be more reactive than secondary ones, these are deactivated by their proximity to fluorinated units in the polymer backbone. The fastest cure is found in mixtures containing polymer C which also has primary alcohol end groups, but these have been separated from the effects of the fluorinated backbone by the insertion of short, non-fluorinated blocks. These were added during manufacture to reduce the acidity of the alcohol end groups and so facilitate its reactivity towards isocyanates. Polymer D does not show the relatively slow reaction rate of polymer B, since the hydroxy groups are also remote from the fluorinated units. However, polymer D does contain some secondary hydroxyl groups resulting in an overall slower cure rate than for mixtures containing polyol C. In principle, polyol D might have been expected to show a clear difference between the faster primary alcohol and the slower secondary alcohol reaction. However, the kinetics of these reactions are not simple, even when there is only one type of hydroxyl group present and a clear distinction between polymer D and polymer C was not apparent.

This work suggests that the time taken for a blended rubber to cure *completely* and attain its terminal mechanical strength, etc., will probably be governed by the reaction rate of its slowest reacting constituent (in the case of the 3-component mixture studied here, the reaction between polymers A and B). However, other points of practical significance, such as the point where a pre-mixed blend becomes too viscous for use in the manufacture of filled rubbers, could be reached at a time dictated by the fastest reaction (in this case the reaction between polymer A and polymer D) if this was sufficient to result in gelation by itself. The values for activation energies reported here for polyfluoroether rubbers are similar to that of 41 kJ mol^{-1} reported by Yee and Adicoff [3] for the cure reaction of another polyurethane rubber, polybutadiene, using titration techniques. The fairly low temperature-dependence of cure rate will mean that mixtures containing either of the more reactive polyols can be expected to cure extensively within a few hours when mixed at room temperature. Although this may be avoided by immediate rapid cooling, practical heat transfer considerations when processing large samples could make this difficult.

5. Conclusions

A microcalorimetric method to quantify polyurethane cure reactions has been used to record the cure curves of some polyfluoroether/polyurethane rubbers. It has enabled automatic, direct, quantitative monitoring of the entire cure reaction at moderate temperatures. The technique is non-intrusive, non-destructive and does not rely on finding a good extraction solvent.

The influence of the alcohol end group structure on cure reaction rate has been described. The ranking order of reactivity to isocyanate functionalized polymer is polymer C $>$ polymer D $\gg$ polymer B.

Fairly low activation energies in the range 38–62 kJ mol^{-1} were deduced for the cure reaction of these mixtures.

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