6 CURE CHARACTERISATION: FT-IR

This chapter focuses on the results of the Fourier transform infra-red (FT-IR) spectroscopy where the opening of the epoxy rings and the production of new hydroxyl groups are followed.

A heated cell was used to allow isothermal scans to be run at set time intervals, and so conversion curves could be plotted and an activation energy for each system calculated and compared to those calculated from the curemeter and DSC results. The FT-IR analysis allows the detailed changes in the chemical composition with time to be monitored and complements the studies carried out using DSC and curemeter measurements discussed in previous chapters.

6.1 INTRODUCTION

The kinetics of polymerisation are complex and even in the simplest cases do not necessarily conform to a simple set of rate equations. The polymerisation process for an amine cured epoxy resin involves the following stages:

(i) The reaction of the epoxy group with the primary amine.

(ii) The secondary amine will react further with the epoxy to form a branched chain structure.

(iii) The reaction of pendant hydroxyl groups, created as a consequence of the opening of the epoxide ring, reacting with another epoxy group to form an ether linked polymer chain. This process is often referred to as the autocatalytic process and enhances the rate of reaction once the initial coupling with the primary amine has taken place.

(iv) The reactivity of the amine depends on its chemical structure; primary amines are in general more reactive than secondary amines.

(v) The presence of tertiary amines can catalyse the polymerisation process, abstract a proton from the pendant hydroxyl group and promote the autocatalytic process.

The most popular form of analysis when considering the rate of conversion of the epoxy resin is to model the reaction using a general equation for epoxy chemistry reactions of the form [1]:

$$r = d\alpha / dt = \left(k_1 + k_2 . \alpha^m\right)\left(1 - \alpha\right)^n$$

Equation 6.1

where α is the degree of conversion, k_1 and k_2 the apparent rate constants, *r* the reaction rate, and *m* and *n* the kinetic exponents of the reactions. These parameters can be calculated according to the nonlinear fitting method proposed by Chean [2]. The two kinetic constants, k_1 and k_2, are assumed to be of the Arrhenius form:

$$k = A . \exp\left(-E_a / RT\right)$$

Equation 6.2

where *A* is the pre-exponential constant, E_a the activation energy, *R* the gas constant, and *T* the absolute temperature.

A Mathcad programme was created to simulate the dependence of dα/dt with change in the value of α. In Equation 6.2 α is the degree of conversion and initially will be expected to be first order but as cure proceeds will deviate as a consequence of the increasing importance of the various other processes influencing the kinetics.

The function dα/dt was found to be very sensitive to the precision of the individual measurements of the composition. The original data files which contained typically 150 points were edited to achieve an approximately equal spacing of the change of α and the files used in fitting contained typically 15-17 points. However it was found that the first and last points were particularly sensitive to changes in the selection of the data points. In the case of the first few data points the problem of thermal equilibration was known to have possible effects, the reference absorption changing significantly over the initial period of measurements. The last few data points were also problematic as the issue of the stability of the FT-IR over prolonged periods of time was also clearly an issue. Only the epoxy data was considered using this approach.

Due to the viscous nature and difficulty of achieving a representative sample of SK31 and SP340 these were not analysed by FT-IR spectroscopy. For each of the other systems, the results obtained and the subsequent further fitting analysis have been presented, with further details of the fitting provided within *Appendix A*.

The prime objective of this study was to explore the possible correlation between the various methods of monitoring growth of the polymer network and further investigation of the molecular significance of the kinetic data has not been undertaken. The FT-IR data does however allow comparison of the way in which other parameters are changing during the cure process.

6.2 STRATHCLYDE MODEL SYSTEM

The epoxy/amine mix was cured at room temperature (approximately 23˚C), 25˚C, 30˚C, 35˚C, 40˚C**,** 45˚C and 50˚C. Scans were performed at five minute intervals for the first three hours, and then at twenty minute intervals for a further sixteen hours and forty minutes. The peaks chosen for analysis were: the epoxy peak at 917cm^{-1}, which decreases as cure proceeds; and the hydroxy peak at 3404 cm^{-1}, which increases with cure time. The reference peak, at 1512 cm^{-1}, was chosen as it corresponds to a CH stretch and does not change throughout the cure. A wavenumber range was chosen for each peak, and written into the macro used to calculate the peak area integration.

Figure 1 shows the areas chosen for integration with the start and end spectra. The baseline was fixed by taking fixed points at the extremes of the spectral region over which integration was carried out. The integrated peak areas were normalised against the reference peak and plotted against time as shown in Figure 2 for 23ºC (room temperature) - the plots for the other temperatures can be seen in Figure 3. They all show that the peak area increases with time for 3404cm^{-1}, and decreases for 917cm^{-1} as expected.

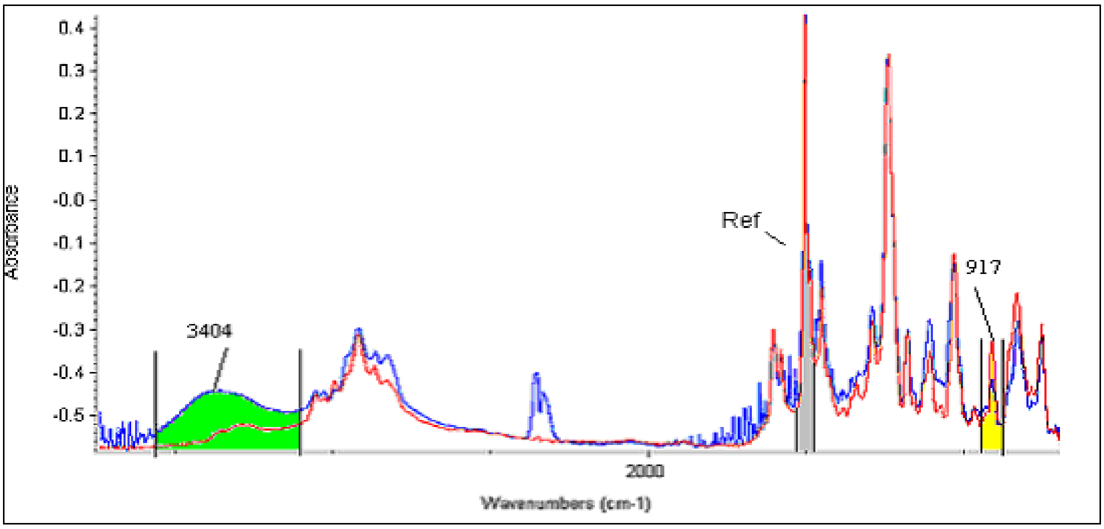

Figure 1. FT-IR start (red) and end (blue) spectra for DGEBA/F with TETA system.

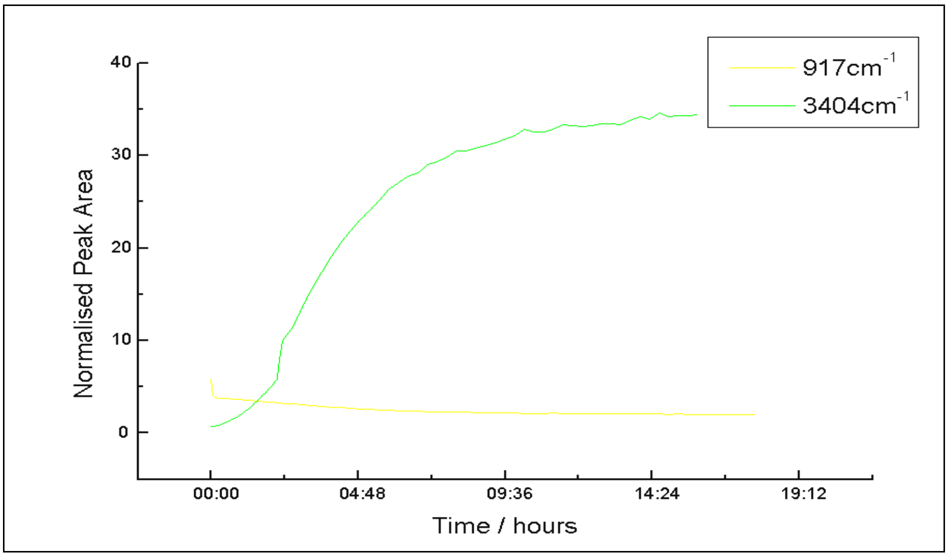

Figure 2. Plot of change in normalised peak area with time, for 23 ºC.

The results of each peak were combined for every temperature and set as '% Remaining' for the 917cm^{-1} peak and '% Formation' for the peak at 3404cm^{-1} as shown in Figure 4. In the '% Formation' plot, there is stepped region for some of the lower temperatures at approximately 2 hours. This can be attributed to the compressed air supply sometimes being turned off around 5pm. There was insufficient time to repeat all of the runs.

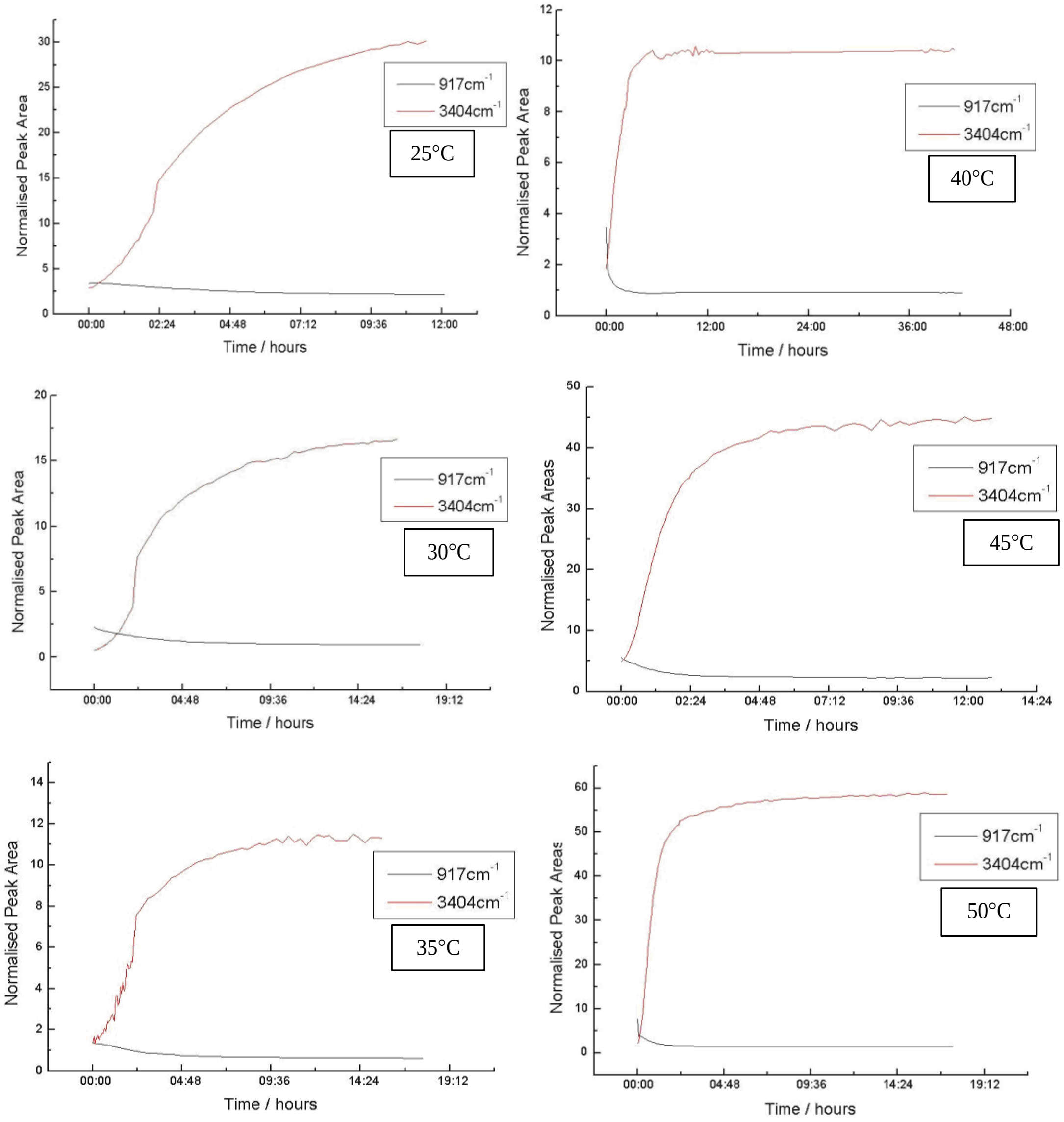

Figure 3. Plots of change in normalised peak area with time.

The initial slope of the composition against time plots (Figure 4) was used to calculate the first order rate constant. The values of k were then plotted as 'Ln k vs. 1/Temperature' for both peaks at all temperatures (Figure 5), and the slopes used to calculate the activation energies (E_a) from each peak using the Arrhenius equation. The error in the E_a was calculated in Excel using standard deviation.

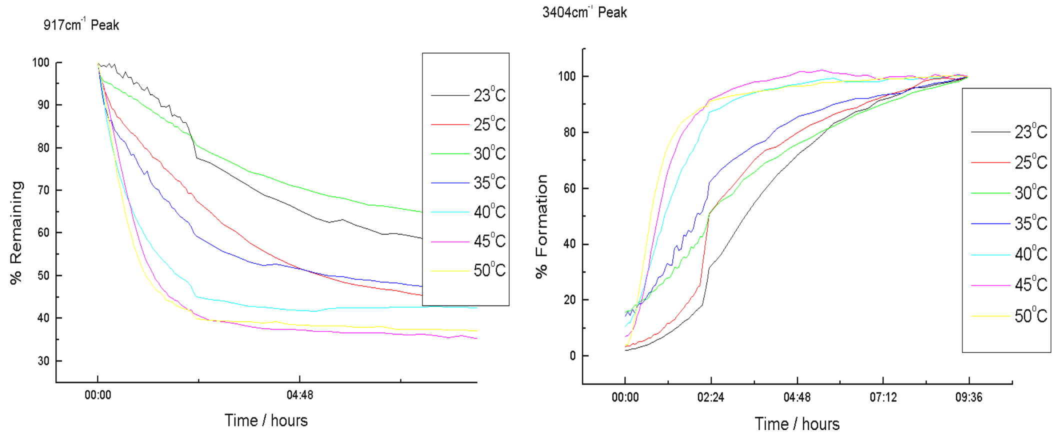

Figure 4. Plots showing % change for each peak against time.

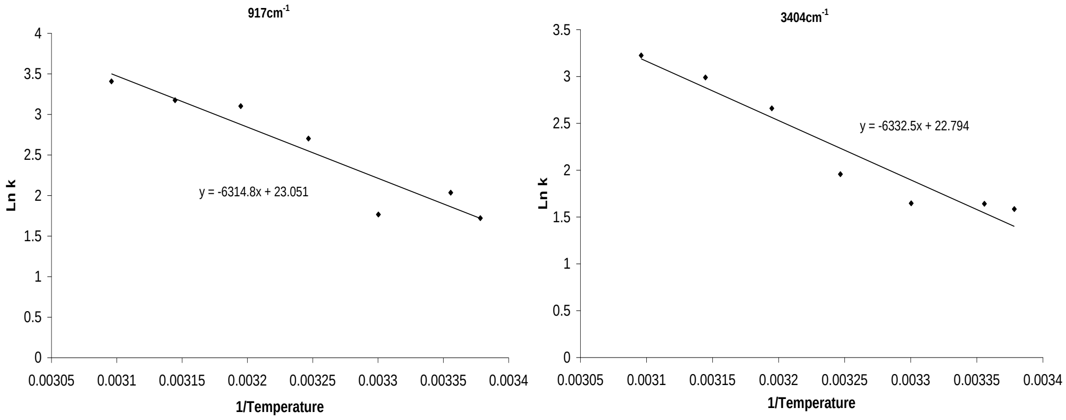

Figure 5. Plot of 'Ln k vs. 1/T' for 917cm^{-1} (left) and 3404cm^{-1} (right) peaks.

The activation energies calculated from the FT-IR measurements show good agreement with each other: E_a (917cm^{-1} peak) = 52.50 ± 0.71 kJ mol^{-1}; and E_a (3404cm^{-1} peak) = 52.65 ± 0.70 kJ mol^{-1}.

The data set was fitted using Equation 6.1 as described in *Appendix A*. The rate constants obtained are summarised in Table 1. Repeat measurements of this system were carried out allowing a comparison of the two sets of results in terms of the kinetic parameters (the results reported above being based on the average values of the two repeats). The lower temperature data (23ºC and 25ºC) were not included as they were believed to be below the operating temperature of the instrument.

Table 1. Kinetic parameters obtained from fitting FT-IR data for Strathclyde model system.

Cure Temperature /°C	k_1	k_2	m	n
30	1×10^{-4}	15×10^{-2}	0.5	0.48
30- repeat	0.1×10^{-4}	17×10^{-2}	0.5	0.5
35	0.01×10^{-2}	21×10^{-2}	0.8	1
35- repeat	0.1×10^{-2}	41×10^{-2}	1.5	0.4
40	0.1×10^{-2}	41×10^{-2}	1.5	0.4
40- repeat	0.05×10^{-2}	41×10^{-2}	1.5	0.5
45	0.05×10^{-2}	62×10^{-2}	1.5	0.5
45- repeat	0.5×10^{-2}	51×10^{-2}	1.6	0.7
50	1×10^{-2}	51×10^{-2}	1.6	0.4

Although there are apparent trends appearing from the data, the lack of consistency in the values of m and n, as well as k_1 and k_2, between the original repeat set of measurements does not allow definitive conclusions to be drawn about the molecular interpretation of the constants obtained.

The rate constant k_2 plotted against the reciprocal of the temperature (Figure 6) shows a reasonably linear variation with an E_a of 47.9 kJ mol^{-1}. The k_1 is also reasonably linear but gives a very large value of E_a of 124.3 kJ mol^{-1} that seems unlikely. Removing the lower two temperatures for the rates obtained by taking the temperature variation of the initial slope gives a value of 61.5 kJ mol^{-1}. It is likely that this value and that from the k_2 fitting provide the best result and the k_1 result should be excluded from further discussion.

The values obtained are consistent with those reported for the aliphatic cure of aromatic-based epoxy resins in the literature [3]. Initial first order kinetics have been reported for a number of systems and a typical value given was ca. 55 kJ mol^{-1} for an isothermal cure study. Higher values (*ca.* 70-80 kJ mol^{-1}) were reported for dynamic cure studies from DSC analysis. An analysis of DGEBA with diamine modelled using Equation 6.1 gave a reported E_a of 55 kJ mol^{-1}, which is comparable to that obtained using the simple analysis presented.

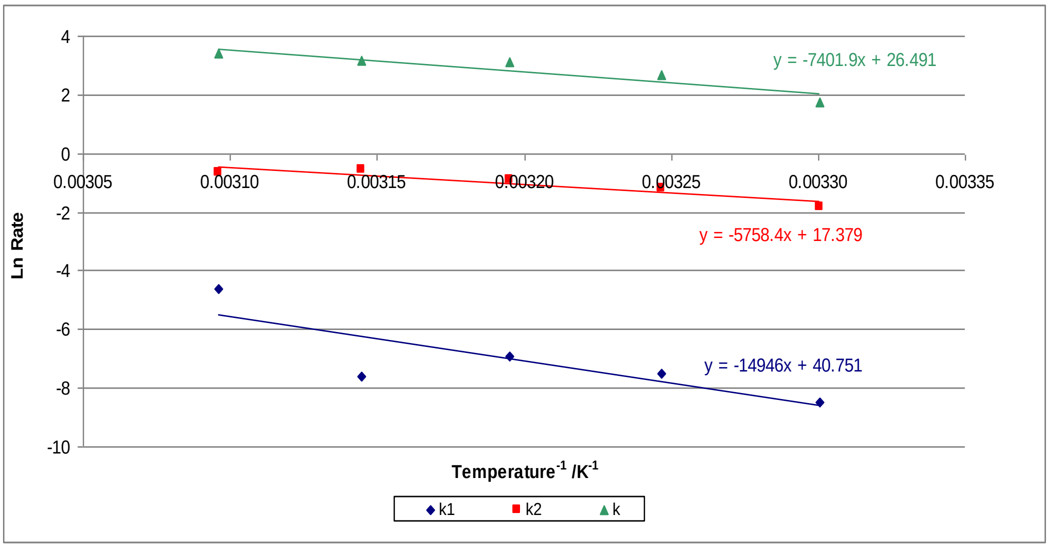

Figure 6. Plot of 'Ln k vs. 1/T' for the epoxy peak measured for the Strathclyde model system, with different values of k.

6.3 SHARED MODEL SYSTEM

The shared model system was investigated at 50˚C, 60˚C and 70˚C, and the data set was plotted as the variation of the percent epoxy (Figure 7) and hydroxyl (Figure 8) composition as a function of time.

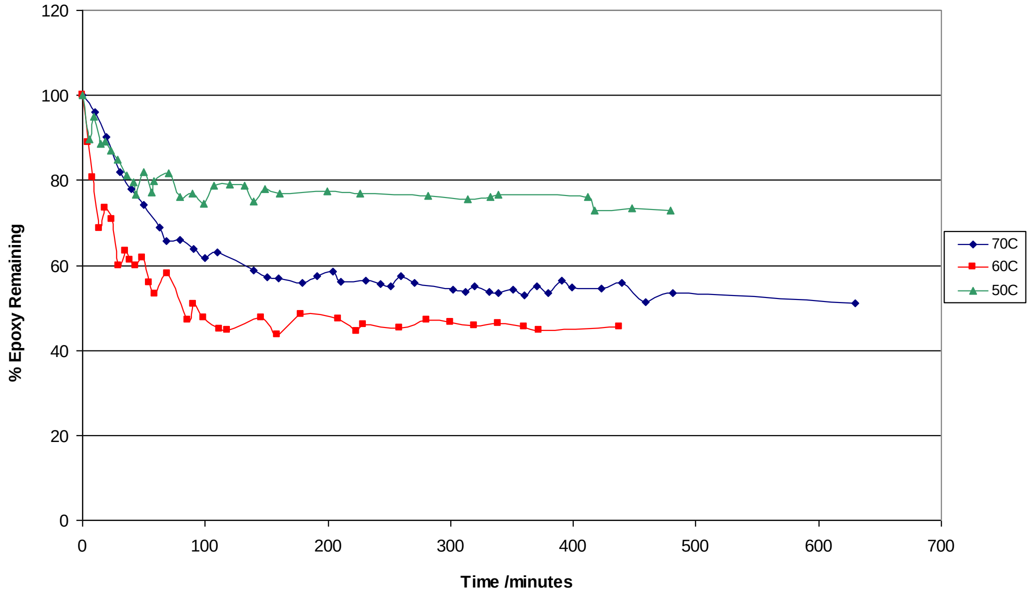

Figure 7. Plot of Epoxy Remaining against Time for the shared model system.

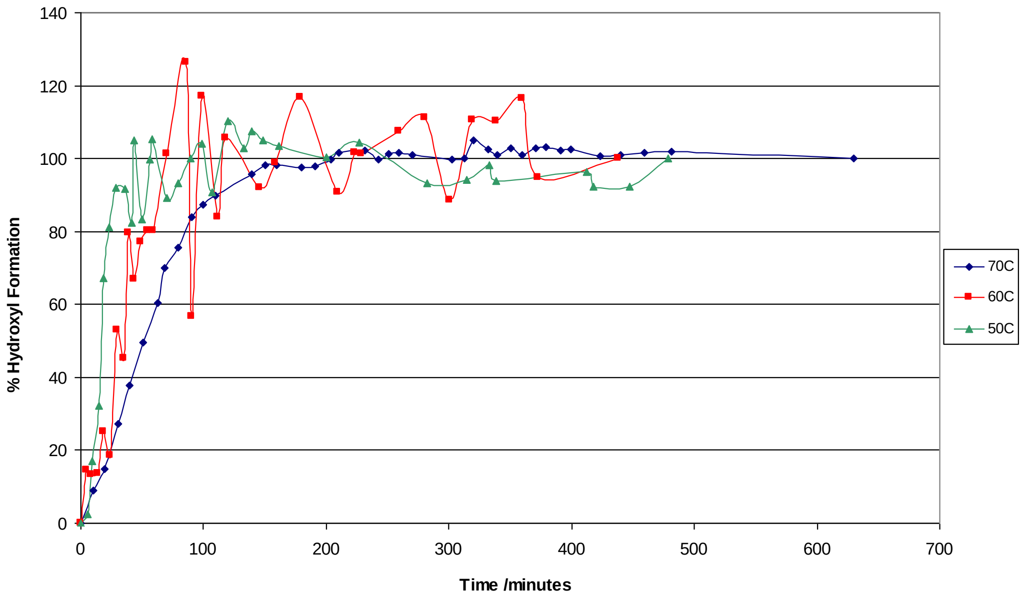

Figure 8. Plot of Hydroxyl Formation against Time for the shared model system.

The variation in the composition of the epoxy should be a monotonic function, however the instability of the FT-IR instrument may have influenced the quality of the data obtained. The rate and final percentage cure for the 60˚C compared to the 70˚C was not as expected, since, in the DSC data the final percentage conversion decreased with cure temperature, instead of increasing as was shown in the case of the other systems. This was considered to be due to the reactive groups becoming locked in place and not being able to react as a consequence of the cure schedule. A similar effect may be seen in the FT-IR data, but no repeat measurements were made to confirm the results obtained were not due to data quality as was the case with the DSC data.

The data set was fitted using Equation 6.1 as described in *Appendix A*, and the rate constants obtained are summarised in Table 2. It was observed within *Appendix A* that it was difficult to achieve a good fit with this data set. The m values remained fairly constant with temperature, and the n values decreased with increasing temperature. The k_1 and k_2 rates were plotted (Figure 9), as was the rate calculated from the gradient of the initial slope, and all gave reasonably linear plots.

Table 2. Kinetic parameters obtained from fitting FT-IR data for the shared model system.

Cure Temperature /°C	k_1	k_2	m	n
70	11×10^{-2}	180×10^{-2}	0.5	6
60	1.5×10^{-2}	16×10^{-2}	0.43	5
50	1×10^{-4}	10×10^{-2}	0.4	10

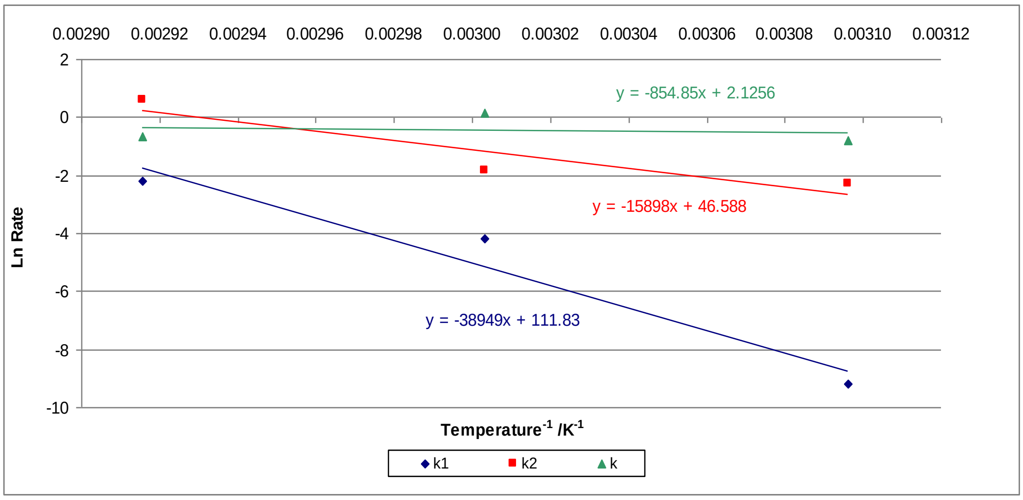

Figure 9. Plot of 'Ln k vs. 1/T' for the epoxy peak measured for the shared model system, with different values of k.

An Activation Energy was calculated from each of the sets of k values: k_1 and k_2 had very high values at 323.8 and 132.2 kJ mol^{-1} respectively; and the value from k (initial part of conversion curve) was very low at 7.1 kJ mol^{-1}. These results indicate the poor quality data for the shared model system from the FT-IR instrument.

6.4 PR55

The PR55 system was investigated at 25˚C**,** 30˚C and 35˚C, and the data set was plotted as the variation of the percent epoxy (Figure 10) and hydroxyl (Figure 11) composition as a function of time.

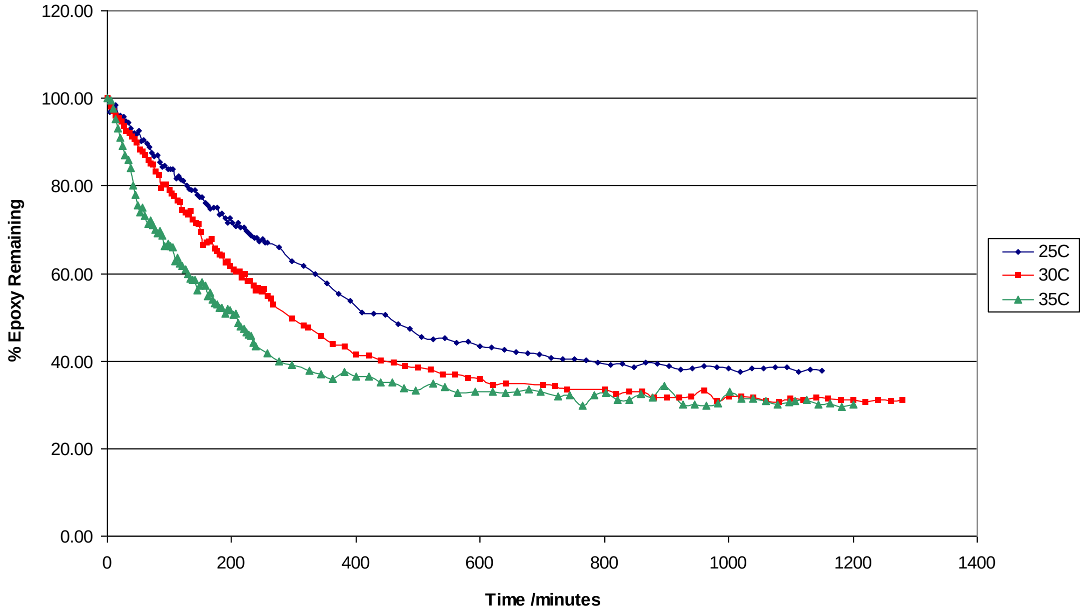

Figure 10. Plot of Epoxy Remaining against Time for the PR55 system.

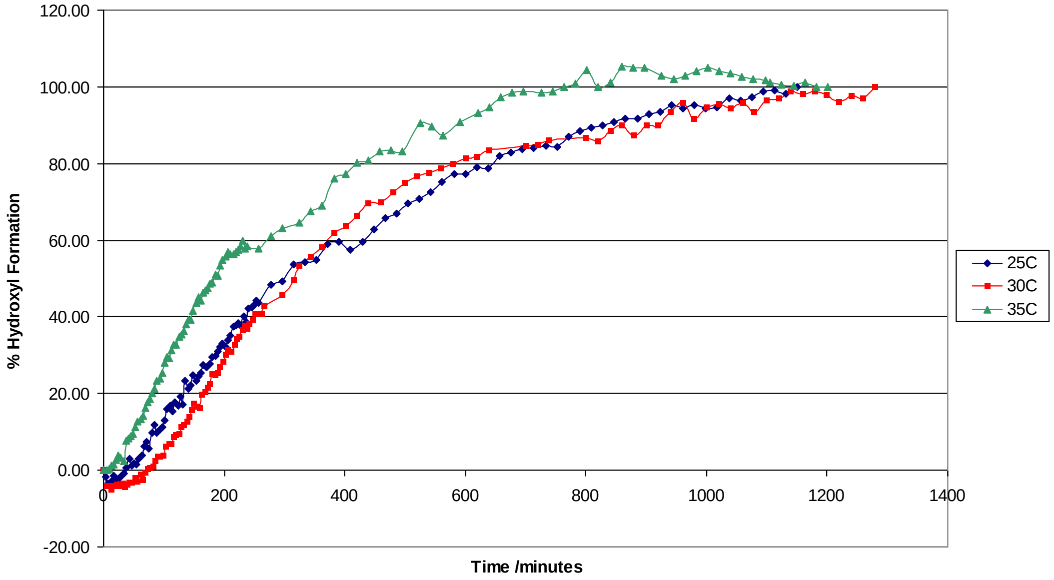

Figure 11. Plot of Hydroxyl Formation against Time for the PR55 system.

The data set was fitted using Equation 6.1 as described in *Appendix A*, and the rate constants obtained are summarised in Table 3. The values of the rate constant are subject to a high degree of uncertainty due to noise in the data, and it was noted within *Appendix A* that the fit was better at lower rather than higher degrees of conversion.

Table 3. Kinetic parameters obtained from fitting FT-IR data for PR55.

Cure Temperature /°C	k_1	k_2	m	n
25	1 x 10^{-3}	2.3 x 10^{-3}	0.05	2
30	1 x 10^{-3}	1.3 x 10^{-2}	0.5	3
35	8 x 10^{-3}	8 x 10^{-3}	0.5	3.3

The k_1 and k_2 rates were plotted (Figure 12), as was the rate calculated from the gradient of the initial slope, however, the plots were not as linear as those for the two model systems. An Activation Energy was calculated from each of the sets of k values: k_1 was high at 157.8 kJ mol^{-1}; k_2 was more as expected at 96.0 kJ mol^{-1}; and the value from k (initial part of conversion curve) was 87.1 kJ mol^{-1}. The high value of k_1 may be due to the noise in the data.

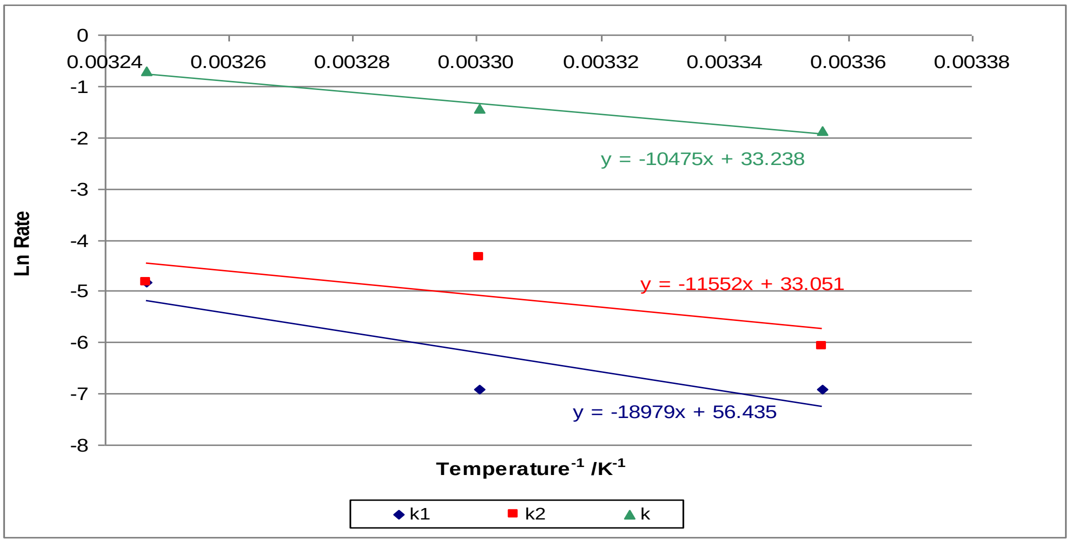

Figure 12. Plot of Ln k vs. 1/T for the epoxy peak measured for PR55 with different values of k.

6.5 PRIME20

The Prime20 system was investigated at 50˚C**,** 60˚C and 70˚C, and the data set was plotted as the variation of the percent epoxy (Figure 13) and hydroxyl (Figure 14) composition as a function of time. The plots show clear monotonic changes and as the temperature increases so the rates of reaction increase with time as expected for a first order reaction.

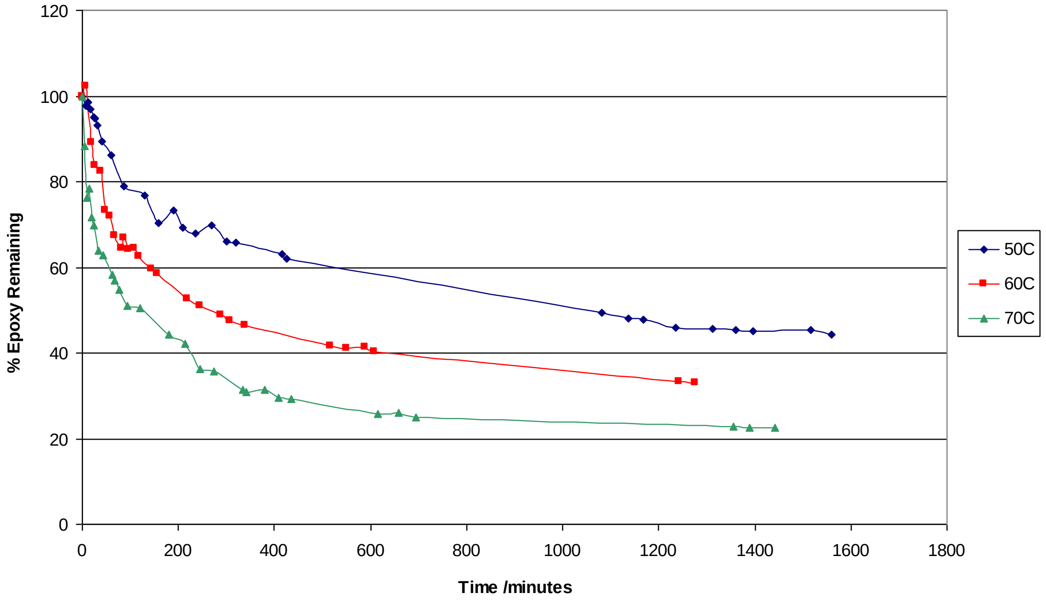

Figure 13. Plot of Epoxy Remaining against Time for the Prime20 system.

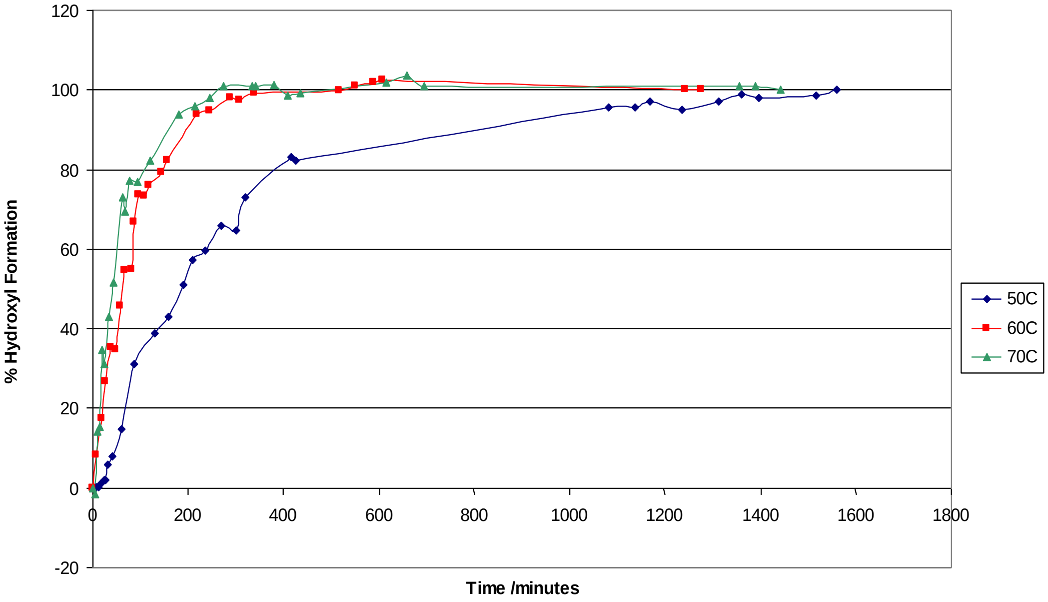

Figure 14. Plot of Hydroxyl formation against Time for the Prime20 system.

The data set was fitted using Equation 6.1 as described in *Appendix A*, and the rate constants obtained are summarised in Table 4

Table 4. Kinetic parameters obtained from fitting FT-IR data for Prime20.

Cure Temperature /°C	k_1	k_2	m	n
50	2.3×10^{-5}	42×10^{-5}	0.5	7
60	1×10^{-3}	55×10^{-3}	0.5	5
70	1×10^{-2}	25×10^{-2}	0.5	6

Analysis of the rate constants as plotted in Figure 15 gives an Activation Energy for k_1 of 280 kJ mol^{-1} and 190.7 kJ mol^{-1} for k_2. These high values of E_a reflect the large difference in values measured between 50°C and 60°C. The E_a from the k value (initial slope calculation) was 66.6 kJ mol^{-1} which appears to be closer to the expected range of values discussed above.

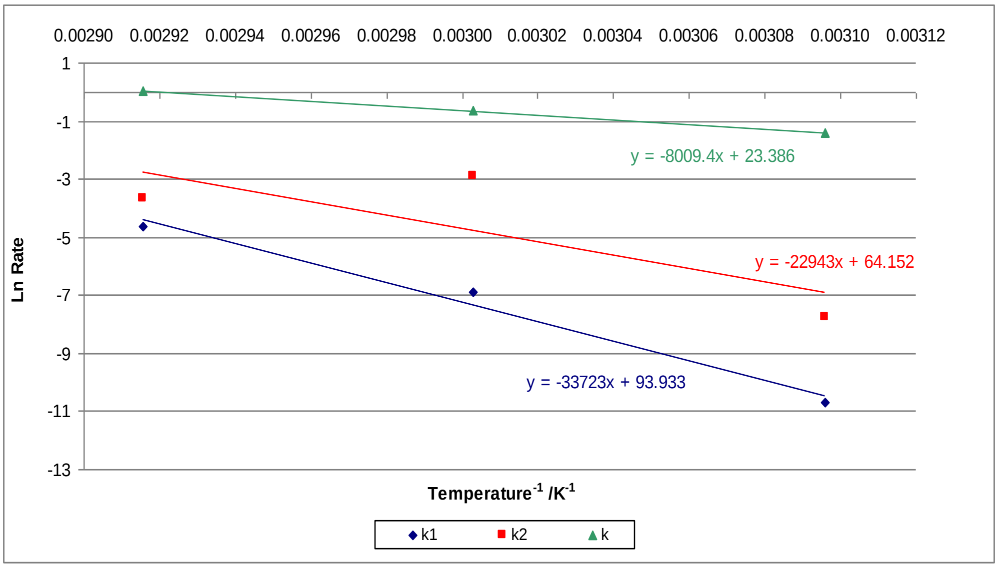

Figure 15. 'Plot of Ln k vs. 1/T' for the epoxy peak measured for Prime20 with different values of k.

6.6 CONCLUSIONS

The FT-IR study provides a measurement of the variation of the composition of the epoxy functionality with time and allows comparison of the other bulk measurements on the basis of the degree of conversion. The quality of data tended to be low using this instrument, and this caused complications when attempting to fit the data. Further discussion on comparison of the results with those of the other techniques is provided in *Chapter 8*.

6.7 REFERENCES

1. Kamal Kamal, M.R., *Thermoset Characterisation for Moldability Analysis.* Polymer Engineering Science, 1974. **14:** p. 231-239.

2. Chean, C.S., and W.M. Eamor, *Cure Kinetics and Morphology of Amine-Cured Tetraglycidyl-4,4'-diaminodiphenylmethane Epoxy Blends with Poly(ether imide)*. Polymer, 1995. **36:** p. 2883-2894.

3. Riccardi, C.C., J. Dupuy, and R.J.J. Williams, *A Simple Model to Explain the Complex Kinetic Behaviour of Epoxy/Anhydride System.* Journal of Polymer Science: Part B: Polymer Physics, 1999. **37:** p. 2799-2805.