8 CURE CHARACTERISATION: COMPARISON OF METHODS

A prime objective of this study was to determine whether the dielectric technique is capable of being used as a monitor of the state of cure in the epoxy resin systems studied. As part of the study, measurements of the composition change with time were studied using Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-red (FT-IR) Spectroscopy.

The changes in viscosity with time have also been used as a method of identification of the times at which gelation and vitrification occurs, and compared to those points derived from the dielectric data.

Rates of reaction for each of the systems, as calculated through data from each of the techniques, have also been compared.

8.1 MEASUREMENT OF COMPOSITIONAL CHANGE

The change in composition both as a function of time and also as an indication of the extent of cure is directly accessible through FT-IR measurements. The extent of cure and the associated parameters are presented in Table 1. During the cure process a network is formed which will trap a certain fraction of the unreacted epoxy groups. In general, increasing the cure temperature allows a greater extent of cure to be achieved and the development of a higher value of the T_g. The rates at which cure proceeds will be different for the systems studied and reflects that change of activity with the changes in the epoxy and amines present. The DSC data also show similar trends. Each system is discussed in turn below.

Table 1. Extent of Cure Calculated from FT-IR and DSC Measurements.

System	Cure Temperature /°C	% Conversion from FT-IR study	% Conversion from DSC study
Strathclyde Model System	25	54	-
	30	24	-
	35	52	59.8
	40	57	64.5
	45	64	69.5
	50	63	76.8
Shared Model System	45	-	99.2
	50	27.2	94.7
	55	-	91.7
	60	54.6	89.1
	70	48.9	-
SK31	25	-	47.9
	30	-	42.1
	35	-	66.2
	40	-	67.7
PR55	25	62.3	-
	30	69.0	30.3
	35	70.0	70.5
	40	-	64.9
	45	-	83.8
Prime20	40	-	77.1
	50	55.6	78.4
	60	67.0	85.1
	70	77.5	85.5
SP340	40	-	51.4
	50	-	54.2
	60	-	72.1
	70	-	77.9

8.1.1 Strathclyde Model System

The extent of cure increases as the cure temperature decreases, so that the percentage of epoxy as indicated by the reduction of the 917 cm^{-1} peak with time is reduced. At all of the temperatures there is a residual peak indicating unreacted epoxy functions present in the final 'cured' system. The values obtained from the DSC investigation are higher than those observed using the FT-IR. The compositional changes measured using the DSC are based on an enthalpy of reaction determined using a dynamic scan. It is assumed that in the dynamic scan all of the reactive groups will have been consumed. However, if there are groups trapped within the matrix and unavailable for reaction, then these will not be able to contribute to the overall enthalpy of reaction and therefore the value observed from the dynamic scan will be higher than the theoretical maximum. It is therefore not surprising to find that the values observed are consistently higher than those obtained from FT-IR measurements.

8.1.2 Shared Model System

As with the Strathclyde model system, complete consumption of the epoxy functionalities is not observed for the shared model system. However, in contrast to the other systems studied, the degree of conversion decreases with increasing cure temperature. This system is based on a reasonably flexible diamine and at low temperatures the network formation will be slow and allow high molecular weight species to be created before crosslinking occurs. This is in contrast to the Strathclyde model system where the amine is a fairly short molecule and high density clusters will be created at an early stage of the cure. Increasing the temperature will allow the secondary crosslinking and auto catalytic reactions to become more effective and hence network formation to occur more easily. The net result of the change in activity is to increase the probability of epoxy trapping in the matrix.

8.1.3 SK31

This system was not studied by FT-IR due to the viscous nature and difficulty of achieving a representative sample. This system differs from the model systems in that it containes an aliphatic linked epoxy material (butanediol-diglycidyl ether) in addition to the DGEBA, and the hardener is a hindered amine. The final percent conversion for this system is lower than for the other systems, likely due to the hindered amine, but does generally follow the expected increase with increasing cure temperature.

8.1.4 PR55

As with the other systems, complete consumption of the epoxy functionalities is not observed, and the amount remaining is reduced as the cure temperature is increased. As previously observed there is not an exact match between the FT-IR and DSC results, but the overall changes with temperature are similar. This system exemplifies the complexity that can arise in the cure with the residual monomer varying somewhat erratically as a function of the increase in the temperature.

8.1.5 Prime20

As with the previous two systems, complete consumption of the epoxy functionalities is not observed for the Prime20 system, and the amount remaining is reduced as the temperature of cure is raised. As with the other systems there is not an exact match between the FT-IR and DSC results. This system is based on a mixture of epoxy and amines and it is therefore not surprising that the temperature dependence of the degree of conversion is a little complex, however increasing the temperature does produce the expected increase in the level of consumption of the epoxy functionalities.

8.1.6 SP340

This system was not studied by FT-IR due to the viscous nature and difficulty of achieving a representative sample. The epoxy component is primarily composed of DGEBA, but also has a small amount of novolac resin that increases the viscosity of the uncured resin. The reactive dilient alkylgylcidylether reduces the functionality of the system and decreases the cross-linking. The hardener is a mostly flexible chain with a mix of other constituents. Benzyl alcohol and phenol are present as diluents which are plasticising in the presence of the isophoronediamine. This system has a relatively low activation energy compared to the other systems (likely due to the phenol catalyst), but like the other systems follows a simple Arrhenius plot.

8.2 MEASUREMENT OF GELATION & VITRIFICATION

It is apparent that whilst the DSC and FT-IR measurements give an indication of the rate and extent of reaction they do not give a complete picture of the total conversion of epoxy during the cure process. In terms of the cure process, practically it is the points of gelation and vitrification that are important and the data for the systems studied are presented in Table 2. The curemeter and dielectric measurements allow these turning points to be measured by observation of different changes in physical properties. Each system has been considered in turn (below), but in summary, it is difficult to define unique times for gelation and vitrification, and the values obtained reflect the differences in physical properties that are being measured.

The curemeter gelation point is defined in terms of the viscosity reaching 10^4 Pa s. This is an arbitrary value and for one system the viscosity might be higher or lower than this value depending on the way the polymerisation creates linear or branched chain structures. Linear polymers will for the same degree of polymerisation have a larger hydrodynamic volume and hence higher viscosity than branched chain structures. Branched chain structures will be prone to forming gels and as such have very different rheological characteristics to those of the more linear structures.

Table 2. Values for gelation and vitrification from the curemeter and dielectric measurements.

System	Cure Temperature /°C	Time /s					
		Peak Max	Gel	ε’(1)	ε”(ω)	Vit	ε’(2)
Strathclyde Model System	23	7365	10245	2500	11000	13044	10000
	25	6149	8029	16000	>40000	9956	22000
	30	4596	6094	3000	8000	7667	10800
	35	3751	4907	-	-	6256	-
	40	2809	3567	2500	5000	4573	5000
	45	1899	2321	1500	2500	3106	2500
	50	1397	1716	-	-	2425	-
Shared Model System	45	4033	4652	3125	7450	5739	7500
	50	2899	3388	2900	4500	4531	5825
	55	1975	2243	1650	4000	3218	4575
	60	999	1056	1250	3700	1484	3750
	65	771	807	1200	2400	1220	2875
	70	559	587	-	-	780	-
	75	555	576	-	-	643	-
SK31	25	8398	12711	-	-	14929	-
	30	7614	11155	-	-	13789	-
	35	5109	7429	-	-	10107	-
	40	3828	5448	-	-	6412	-
	45	3335	4643	-	-	5836	-
PR55	25	16218	23726	10000	>40000	24896	23000
	30	13285	19449	9000	>40000	22450	23000
	35	10836	15853	6000	22000	17684	21000
	40	9460	13808	5500	20000	16114	19000
	45	6833	9937	4000	15000	12554	15000
Prime20	40	8641	11812	6000	15500	13772	16000
	50	5617	7666	3500	10000	9861	11000
	60	3235	4499	2050	7500	6247	7000
	70	1719	2447	1500	6000	3719	3500
	80	904	1202	1000	4500	2053	3000
SP340	25	23761	12189	-	-	36058	-
	30	17145	8824	-	-	25989	-
	35	14538	8286	-	-	23684	-
	40	10929	6199	-	-	17364	-
	50	7002	4328	-	-	14330	-
	60	3872	2540	-	-	10158	-
	70	2182	1491	-	-	8212	-
	80	1344	968	-	-	5245	-

8.2.1 Strathclyde Model System

Comparison of the dielectric and curemeter data gives a clear insight into the problem of different physical properties reflecting different aspects of cure. At the lower temperatures the ionic conductivity appears to remain high right up to the end of the cure period although the viscosity has reached a level which would indicate that gelation has occurred. This implies that the matrix which is formed is fairly open and allows a significant level of conductivity to be sustained. For low levels of cure the connectivity between achieving a low level of conductivity and the development of a 3D gel structure is not very well established.

As the temperature increases more of a correlation is developed and at 45°C the viscosity (gelation) value of 2321 s and the conductivity, ε”, value of 2500 s are very comparable. At 45°C the disappearance of the low frequency contribution to ε’ at 1500 s is consistent with the reduction of the range of ionic conductivity and as a consequence an apparently more homogenous material being formed. The apparent vitrification as reflected in the amplitude of the probe motion being effectively zero does not accurately reflect the cessation of dipole relaxation. At the higher temperatures, the predictions for times for vitrification from the curemeter measurements are similar to those from dielectric observations as indicated by ε’(2).

8.2.2 Shared Model System

At all temperatures the prediction of gel formation from curemeter measurements is shorter than from ε” measurements. The principle difference between this system, and the Strathclyde model system, is the distribution of the amine groups. In the Strathclyde system, the amine hardener (TETA) has the structure $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$, whereas in the shared system it has the structure $H_2N-(CH_2)_6-NH_2$. Although the hardeners have similar molecular weights and in the case of TETA the distance between the relative terminal $–NH_2$ groups is greater, the presence of the flexible $–(CH_2)-$ entity will allow ionic mobility to be sustained to a greater extent longer into the cure process. The difference in molecular structure is reflected in the higher value of gelation as measured by ε” than detected via curemeter measurements. In fact, the predictions for gelation and vitrification using the dielectric data are greater than those from the curemeter measurements and are consistent with the cured structure being less effective at inhibiting ionic conduction and dipolar relaxation. As the cure temperature increases both sets of data show the expected decreases in time, however the degree of cure decreases with the increase in temperature. The retention of a significant level of mobility is also consistent with the significant levels of residual monomer as observed by the FT-IR measurements (Table 1). The hexanediamine, because it produces linear chains, will develop viscoelastic characteristics earlier which will influence diffusion controlled reactions and appears to increase the level of trapped monomer in the system.

8.2.3 SK31

This system was not studied by dielectric spectroscopy due to the viscous nature and difficulty of achieving a representative sample within the cell. The variation of the cure time with temperature, from the viscosity data, is not as smooth as with the previous two, simpler, systems (although as the cure temperature increases both sets of data show the expected decrease in time). This may imply that there are different mechanisms contributing to the overall reaction. The apparent change in rate, observed in the viscosity curves, would imply that the aliphatic-based epoxy (butanediol-diglycidyl ether) may be consumed initially and that the aromatic-based material is left to the later stages of the reaction to be incorporated into the matrix. It is probable that the interaction of the filler with the resin mixture is through interaction of the amine with silica surface, which will contain very few active hydroxyl groups.

8.2.4 PR55

As with the systems described above the same trends are seen in the changes in the curemeter and dielectric data. The main difference from the model systems is the part replacement of DGEBA by diglycidylether of polypropyleneglycol and the simple aliphatic amine by the alicyclic 3-aminomethyl-3,5,5-trimethylcyclohexyl-amine. The epoxy components will not be expected to have significantly different reactivities, however the alicylic amine will be more sterically constrained than the aliphatic amines used in the model systems. The changes in the chemical structure slow down the rates of reaction and the increased flexibility of the diglycidylether of polypropyleneglycol leads to the retention of flexibility in the material cured at lower temperatures. The values from the curemeter measurements for gelation are typically ca. 6000 s lower than those from the dielectric measurements for the ε” value but are *ca*. 8500 s higher than those for the ε’(1) value. The values for vitrification are typically *ca*. 3000 s lower than for the ε’(2) value, apart from those for 25°C which falls below the operating temperature of the instrument. As with the other systems the observation of a high value of the viscosity does not necessarily reflect the cessation of dipole relaxation.

8.2.5 Prime20

The reaction mixture is predominantly a blend of bisphenol A-(epichlorohydrin) with about 10% of the dicgylcidylether of bisphenl F. The blending of these two similar epoxy systems suppresses the possibility of solidification of the epoxy and lowers the viscosity of the blend. A small amount (*ca*. 3%) of C12/C14 alkylgylcidylether introduces a flexible chain termination and helps impart a certain level of ductility to the system. The *ca*. 2% of 1,4-bis(2,3-epoxypropoxy)butane introduces a flexible chain extender and will also improve the ductility of the final product. The hardener consists of a blend of 3-aminomethyl-3,5,5-trimethylcyclohexyl-amine and 2-piperazin-1-ylethylamine. Both of these amines are based on alicyclic structures and will be expected to have low reactivity, however the presence of 10-25% polypropylene glycol bis (2-aminopropyl ether) introduces a more reactive diamine that can help initiate the cure process. This system can be cured at lower temperatures and the extent of conversion is higher than for PR55. In this system there is a closer correspondence between the curemeter and dielectric results, although the predictions from the curemeter tend to be shorter than those from the dielectric measurements.

8.2.6 SP340

This system was not studied by dielectric spectrosscopy due to the viscous nature and difficulty of achieving a representative sample within the cell. The Spabond SP340 system contains the catalyst benzyl alcohol but also contains a significant amount of the novolac-based epoxy which has raised the viscosity. This complex mixture shows through the viscosity curves changes in the rate at which the cure process occurs. The observed curves deviate from the simple linear variation found in the Strathclyde model system and show a series of discernable changes before gelation occurs reflecting the different reactivities of the components present. Despite the complexity of the cure process the overall rate of cure shows a simple variation with temperature.

8.3 COMPARISON OF RATES OF REACTION

An Activation Energy has been calculated (Table 3) for each of the systems using the data from the techniques used to study each particular system – these values reflect the rates of cure of the systems.

Table 3. Comparison of Activation Energies (in kJ mol^{-1}) derived from data for each system.

	Strathclyde Model System	Shared Model System	SK31	PR55	Prime20	SP340
FT-IR (k)	61.5	7.1	-	87.1	66.6	-
FT-IR (k_1)	124.3	323.8	-	157.8	280.4	-
FT-IR (k_2)	47.9	132.2	-	96.0	190.7	-
Gelation (curemeter)	50.5	71.2	43.0	32.8	52.3	45.5
Vitrification (curemeter)	47.5	72.7	41.6	26.8	43.7	28.3
DSC	58.1	53.3	39.9	43.9	40.9	36.7
ε”	58.3	44.0	-	31.1	27.5	-
ε’(1)	33.5	49.3	-	36.6	40.8	-
ε(2)	75.5	42.1	-	16.4	41.3	-

Whilst the FT-IR measurements allow the rates of consumption of the epoxy functions to be monitored directly, DSC measurements allow the rates of conversion to be estimated from the heat of reaction. For the FT-IR data the value above given as ‘k’ was the gradient of the initial part of the conversion slope; and ‘k_1’ and ‘k_2’ were rate constants calculated from fitting the data as described in *Appendix A*.

8.3.1 Strathclyde Model System

The values of the activation energies obtained by the various techniques are similar for all of the techniques studied, with the exception of the FT-IR k_1 value which is noticeably higher and is likely to be the result of a poor fit against the equation used. The low value measured for ε’(1) must be considered in light of the process being observed. The ε’(2) point is associated with the change in dipole relaxation and whilst it reflects the slowing down of the dipole rotation due to the creation of the matrix structure, it will also be influenced by the intrinsic mobility of the matrix formed. The activation energy obtained from the ε” data is relatively close to that for the viscosity and is consistent with the conductivity changes reflecting the changes in the viscosity as measured by the curemeter data.

8.3.2 Shared Model System

The activation parameters obtained for the shared model system show marked variations depending on the method of observation. The FT-IR results in particular stand out and it is believed that these values have been influenced by the poor data quality when this system was studied. The curemeter results are quite a bit higher than those of the DSC, which are also higher than the results calculated from the dielectric data. The low values of the dielectric activation parameters are at first a little surprising. The change in ε’(1) is associated with a loss of heterogeneity in the mixture and whilst this will be controlled by the reactivity of the entities involved it will also be controlled by the diffusivity of the species being generated. It would appear that it is the diffusivity which is influencing the observed activation parameter. As with the Strathclyde model system, the ε’(2) activation parameter will also involve consideration of chain mobility which for this system would be higher than for the Strathclyde model system and hence a lower activation energy is consistent. However the low value of the activation parameter for ε” is surprising as this might be expected to follow the viscosity data. However the dielectric measurements are probing the microscopic viscosity and hence will be influenced by the high mobility of the hexane chain in the diamine structure.

8.3.3 SK31

The SK31 system, due to its viscous nature, was not studied using all of the techniques. The activation energy calculated from the curemeter data was similar to that for the DSC data, and was lower than for the two model systems.

8.3.4 PR55

Overall this system had, in general, the lowest activation energies of the systems. As indicated previously there were difficulties with the FT-IR data and analysis of the activation energy parameters gave very high results in comparison to those calculated from the other techniques. In this case there is a close correspondence between the activation parameters from the curemeter data for the onset of gelation and those for the change in ε”. The DSC values are higher but this is consistent with the findings from the other systems. The relatively low value for the activation energy from DSC measurements compared with the Strathclyde and shared model systems is also consistent with the catalysed nature of this system.

8.3.5 Prime20

The very high values for the FT-IR measurements are based on a limited data set and therefore must be considered to be questionable. The DSC data are more consistent with what would be expected, especially since this system is a catalysed cure. The curemeter and DSC results are reasonably close but once again the dielectric parameters are considerably lower. The influence of the chain structure is once more evident in these data.

8.3.6 SP340

The SP340 system, due to its viscous nature, was not studied using all of the techniques. The two values from the curemeter were further apart than observed for the other systems. However, the DSC value was within the two curemeter values and it is likely that the curemeter results may have been affected by the viscous nature of the material.

8.4 CONCLUSIONS

Although in certain systems a close correspondence between the activation parameters obtained using different methods is observed this can not be generally assumed to be true in all cases. It would appear that differences can be observed which reflect the differences in the way in which the physical properties changes are connected to the controlling molecular processes. As a consequence a reasonably close correspondence is observed between the DSC and FT-IR measurements as these are both measuring directly the conversion of the monomer to the polymer. However, differences are observed between the measurements based on observations of the extent of reaction and the changes in the rheology (curemeter). The rheology depends on the type of structure that grows in the mixture and depending on whether it is a linear or branched chain growth so the changes in the viscosity will be slightly different. However the values are typically of the same order of magnitude as those found for the measurements of the monomer conversion. The dielectric measurements, although sensitive to the cure process, exhibit activation parameters which can be significantly different from those obtained by other methods. The differences observed can be rationalised on the basis of the influence of the short range molecular mobility of the matrix on the electrical properties.