

3 EXPERIMENTAL

This chapter provides details on the various epoxy resin-amine systems used for this study, as well as sample preparation and methods of analysis.

3.1 MATERIALS

The systems to be studied were chosen after collaboration with the ACLAIM partners, and in particular the partners at Birmingham University. Four commercial systems were supplied through the ACLAIM partners, with mixing details and safety data sheets. A model system (bisphenol-A-based epoxy) was chosen to be studied by both universities as well as each university having its own model system (bisphenol-A/F-based) to study.

Although all the systems investigated are epoxy-amine-based there are important differences in the functionalities of the systems and this affects the cure. The main difference is the ratio of the primary to secondary amine. The primary amine has an effective functionality of two compared to the secondary amine which has an effective functionality of one. Primary amines are expected to be more reactive than secondary amines and hence will create linear rather than branched chain structures. The less reactive secondary amine however plays a critical role in the creation of the network structure.

3.1.1 Strathclyde Model System

This model system was PY302-2, a bisphenol-A/F-based epoxy resin, cured with triethylenetetramine (TETA), an aliphatic amine. See Table 1 for details. The epoxy resin and hardener were chosen as they each have a relatively low viscosity, so can be handled with ease, and the system was known to cure at room temperature. This system has 2 primary and 4 secondary amines, giving a ratio of 1:2 (primary:secondary).

Table 1. Details of DGEBA/F model system.

	<u>Chemical</u>	<u>Supplier</u>	<u>Batch No.</u>	<u>CAS No.</u>	<u>Appearance</u>
<u>Resin</u>	PY302-2	Vantico	AA10061-798	40216-08-8	Clear liquid
<u>Hardener</u>	Triethylenetetramine (TETA)	Fluka	1082939-44904396	112-24-3	Clear liquid

The epoxide equivalent of the PY302-2 was given on accompanying data sheets as 169–177, and the average of 173 was used in the calculation of the mixing ratio. TETA has a molecular weight of 146.23 and 6 equivalent hydrogens, giving an amine equivalent of 24.37. Therefore, 24.37g of TETA reacts with 173g of PY302 2, giving a mixing ratio of: **7.1 : 1** (PY302-2 : TETA). The following isothermal temperatures were chosen for the cure characterisation: Room Temperature (RT), 25°C, 30°C, 35°C, 40°C, 45°C and 50°C, where RT was normally 23°C ± 2°C.

3.1.2 Shared Model System

The chosen shared model system, to be studied by both universities, was a diglycidyl ether of bisphenol A (DGEBA) cured with 1,6-hexanediamine, an aliphatic amine. Both were supplied from Aldrich. This system has two each of primary and secondary amines giving a ratio of 1:1. See Table 2 for details.

Table 2. Details of DGEBA model system.

	<u>Chemical</u>	<u>CAS No.</u>	<u>Batch No.</u>	<u>Aldrich Code</u>	<u>Appearance</u>
<u>Resin</u>	Araldite® 506 epoxy resin	25068-38-6	021H0722	A3183	Clear liquid
<u>Hardener</u>	1,6-hexanediamine*	124-09-4	438919/1-33702	33000	Solid at RT

*hardener had a purity of ≥ 99.0%; mp of hardener= 39-40°C.

The epoxide equivalent of the Araldite® 506 was given on accompanying data sheets as 172–185, and the average of 178.5 was used in the calculation of the mixing ratio. 1,6-hexanediamine has a molecular weight of 116.20 and 4 equivalent hydrogens,

giving an amine equivalent of 29.05. Therefore, 29.05g reacts with 178.5g of Araldite® 506, giving a mixing ratio of: **6.14 : 1** (Araldite : diamine)

As the hardener was a solid at room temperature it was necessary to heat the epoxy and amine to 40°C before mixing. With consideration to this, the following isothermal temperatures were chosen: 45°C, 50°C, 55°C, 60°C, 65°C, 70°C, 75°C and 80°C.

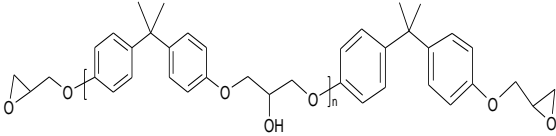
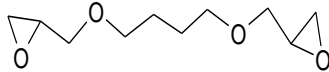
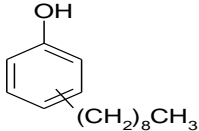
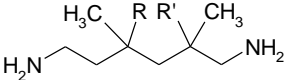
3.1.3 Sikadur®- 31 Normal (SK31)

Sikadur®- 31 Normal is manufactured by Sika Limited and was supplied by DML Devonport. It was reported as being used for rigid bonding and strengthening. The data sheets stated that it can be used as a structural adhesive for many surfaces including concrete, natural stone, wood, glass, steel, iron and aluminium, and can be used as a fast setting repair mortar, or for joint filling and crack sealing. In particular it is used in the strengthening of bridges as it is described as being thixotropic allowing it to be used on vertical and overhead surfaces.

It was also stated that the system has been designed for use at temperatures between +10°C and +30°C, and that it has a pot-life of *ca.* 90 minutes from mixing at +10°C; *ca.* 40 minutes at +20°C; and *ca.* 20 minutes at +30°C. The following isothermal temperatures for the cure characterisation were chosen with consideration to this: 25°C, 30°C, 35°C, 40°C and 45°C.

The mixing ratio used was that on the product data sheets: **3 : 1** (part A: part B, by weight or volume). The epoxy resin was white in colour with a gritty texture and resembled wet cement. The hardener was of similar texture and grey in colour. Two containers each of Parts A and B were supplied with the following batch number codes: 10949962 (Parts A and B) and 11175264 (Parts A and B). The former was used in this study. See Table 3 for the constituents of SK31- Part A (epoxy resin) and Part B (hardener) as given on the data sheets from the manufacturer. The amine part has a ratio of 1:1 (primary:secondary).

Table 3. Constituents of SK31.

	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
<u>Part A</u>	bisphenol A-(epichlorohydrin); epoxy resin (no. av. molecular wt<700)	Araldite 506 epoxy resin; DGEBA	25-50	25068-38-6	
	1,4-bis(2,3-epoxypropoxy) butane	1,4-butanediol diglycidyl ether	2.5-10	2425-79-8	
	nonyl phenol	2,6-Dimethyl-4-heptylphenol; p-Nonylphenol, branched	1-2.5	25154-52-3/ 84852-15-3	
<u>Part B</u>	Trimethyl-hexamethylene diamine	2,2,4(2,4,4)-trimethyl-1,6-hexanediamine; trimethylhexane-1,6-diamine	25-50	25620-58-0	 R = H, R' = CH ₃ or R = CH ₃ , R' = H

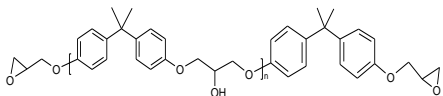
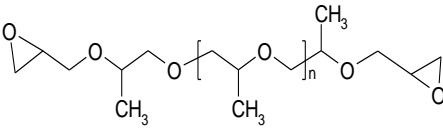
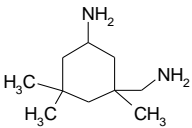
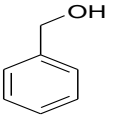
3.1.4 PR55-ST (PR55)

The PR55-ST system was also supplied by DML Devonport. It was reported as being used as the protective coating on the top of a pipe repair patch comprising a sheet of glass fibre with four sheets of carbon fibre (alternating directions) on top and then epoxy covering the area.

DML Devonport reported that the system cures at ambient temperatures and that it used the schedule of: seven days cure time at 5°C. The following isothermal temperatures for the cure characterisation were chosen with consideration to this: 25°C, 30°C, 35°C, 40°C and 45°C. The mixing ratio used was as given on the data sheets: **4.3 : 1** (resin: hardener, by weight).

The constituents of the resin and hardener can be found in Table 4. The resin was opaque and the hardener clear, and both had reasonably low viscosities, i.e. could be pipetted. The batch numbers for the resin and hardener were AA50794700 and 51195600 respectively. The amine part has a ratio of 1:1 (primary:secondary).

Table 4. Constituents of PR55.

	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
<u>PR55-STR</u>	bisphenol A-(epichlorohydrin); epoxy resin (no. av. molecular wt<700)	Araldite 506 epoxy resin; DGEBA	75-85	25068-38-6	
	diglycidylether of polypropyleneglycol	PPGDGE	16-22	9072-62-2	
<u>PR55-STH</u>	isophoronediamine	3-aminomethyl-3,5,5-trimethylcyclohexylamine	80-92	2855-13-2	
	benzyl alcohol	benzenemethanol	9-15	100-51-6	

3.1.5 Prime 20/ SPX 3260 (Prime20)

Prime 20 (resin) and SPX 3260 (hardener) are manufactured by SP Systems Limited (part of the global Gurit group) and were supplied by Vestas Blades Limited. It was reported that the system is used as the infusion resin in a variety of resin infusion processes, e.g. in the production of wind turbine blades and also in the production of components for yachts.

The data sheets reported that the system has been designed for use at temperatures between +15°C and +25°C, and that it has a pot-life of. 87 minutes from mixing at +15°C; 70 minutes at +20°C; 56 minutes at +25°C; and 45 minutes at +30°C. The following isothermal temperatures for the cure characterisation were chosen with consideration to the data: 40°C, 50°C, 60°C, 70°C and 80°C.

The mixing ratio used was that on the product data sheets: **4 : 1** (resin: hardener, by weight or volume). The constituents are shown in Table 5 (resin) and Table 6 (hardener). Both materials were clear to very pale yellow in colour and could be pipetted. The batch numbers of the resin and hardener were 0000029533 and 0000026577 respectively. This is a much more complicated system compared the previous ones as the amine as well as the epoxy contains several reactive constituents.

Table 5. Constituents of Prime 20 resin.

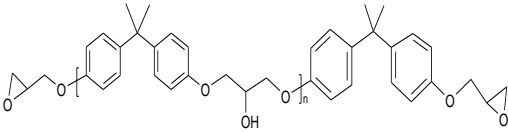
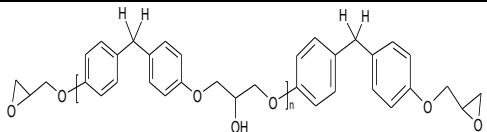
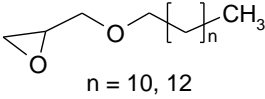
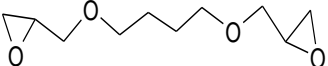
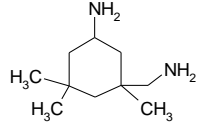
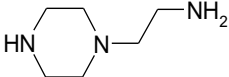
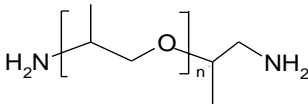
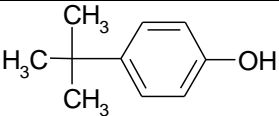
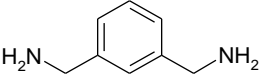
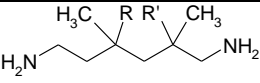
	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
Prime20 Resin	bisphenol A- (epichlorohydrin); epoxy resin (no. av. molecular wt<700)	Araldite 506 epoxy resin, DGEBA	50-100	25068-38-6	
	diglycidylether of bisphenol-F		10-25	28064-14-4	
	C12/C14 alkylglycidylether		2.5-10	68609-97-2	
	1,4-bis(2,3- epoxypropoxy)butane	1,4-butanediol diglycidyl ether	2.5-10	2425-79-8	
	solvent naphtha (petroleum), light arom.		< 0.5	64742-95-6	Mixture of principally aliphatic hydrocarbons

Table 6. Constituents of SPX3260 hardener.

	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
<u>SPX 3260</u>	isophoronediamine	3-aminomethyl-3,5,5-trimethylcyclohexylamine	25-50	2855-13-2	
	2-piperazin-1-ylethylamine		25-50	140-31-8	
	Polyoxyalkyleneamine	polypropylene glycol bis (2-aminopropyl ether); Jeffamine D	10-25	9046-10-0	
	4-tert-butylphenol		2.5-10	98-54-4	
	m-phenylenebis (methylamine)		0.5-2.5	1477-55-0	
	trimethylhexane-1,6-diamine	2,2,4(2,4,4)-trimethyl-1,6-hexanediamine; trimethylhexamethylene diamine	0.5-2.5	25620-58-0	 R = H, R' = CH ₃ or R = CH ₃ , R' = H

3.1.6 Spabond SP340 (SP340)

Spabond SP340 is manufactured by SP Systems Limited (part of the global Gurit group) and was supplied by Vestas Blades Limited. It was reported as being used as an adhesive in the wind industry.

The data sheets reported that the system has been designed for use at temperatures between +15°C and +25°C, and that it has a pot-life of. 60 minutes from mixing at +15°C; 45 minutes at +20°C; 34 minutes at +25°C; and 26 minutes at +30°C. The following isothermal temperatures for the cure characterisation were chosen: 40°C, 5°C, 60°C, 70°C and 80°C. The mixing ratio used was that on the product data sheets: **2 : 1** (resin: hardener, by weight or volume).

The constituents of the system are shown in Table 7 (resin) and Table 8 (hardener). The resin was yellow in colour, and the hardener grey coloured. Both had a sticky consistency that can be likened to set custard. No batch numbers were provided with these samples. As in the case above, both the epoxy and the amine parts contain several reactive constituents resulting in a complicated system.

Table 7. Constituents of SP340 Resin.

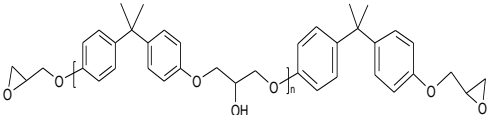
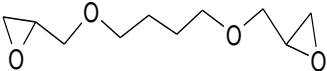
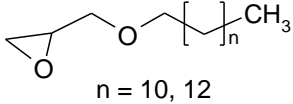
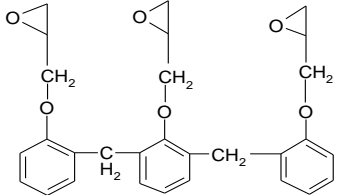
	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
SP340 Resin	bisphenol A-(epichlorohydrin); epoxy resin (no. av. molecular wt<700)	Araldite 506 epoxy resin, DGEBA	50-100	25068-38-6	
	1,4-bis(2,3-epoxypropoxy)butane	1,4-butanediol diglycidyl ether	2.5-10	2425-79-8	
	C12/C14 Alkylglycidylether		2.5-10	68609-97-2	
	epoxy novolac resin		2.5-10	9003-36-5	

Table 8. Constituents of SP340 Hardener.

	<u>Constituent</u>	<u>Synonyms</u>	<u>%</u>	<u>CAS No.</u>	<u>Structure</u>
<u>SP340 Hardener</u>	Polyoxyalkyleneamine	polypropylene glycol bis (2-aminopropyl ether); Jeffamine D	25-50	9046-10-0	
	2-piperazin-1-ylethylamine		2.5-10	140-31-8	
	benzyl alcohol	benzenemethanol	2.5-10	100-51-6	
	3-aminomethyl-3,5,5-trimethylcyclohexylamine	isophorone-diamine	2.5-10	2855-13-2	
	3,6,9-triazaundecamethylenediamine		< 0.5	112-57-2	
	phenol	hydroxybenzene	< 0.5	108-95-2	
	solvent naphtha (petroleum), light aromatic solvent.		< 0.5	64742-95-6	Mixture of principally aliphatic hydrocarbons

3.2 PREPARATION OF SAMPLES

Unless otherwise stated below, the required mass of epoxy was weighed into a suitable container and the corresponding mass of hardener added. The mixture was stirred for approximately one minute, or until a uniform colour was observed for coloured systems, and then degassed under vacuum for 5-10 minutes. The sample was used immediately.

3.2.1 Exceptions to Preparation of Samples

It was found that the PR55-STR resin became gradually more crystalline upon storage until there was very little liquid left in the container. This was believed to be due to storage conditions as discussed in *Chapter 1*. Batches of the resin were heated in an oven set at 40°C for *ca.* two hours. The melted material remained in liquid form for several months and could be pipetted and used as normal.

The hardener for the shared model system, 1,6-hexanediamine, was a solid at room temperature (mp=39-40°C). To overcome problems with mixing, the required mass of epoxy was weighed into a container. A little more than the corresponding mass of hardener was weighed into a second container. Both (covered) containers were placed in the oven at 45°C for *ca.* 30 minutes or until the amine had melted. The required quantity of liquid amine was then pipetted into the container with the epoxy using a hot pipette. The material was stirred for approximately 30 seconds, and degassed for a few minutes before use.

3.3 METHODS OF ANALYSIS: CURE CHARACTERISATION

3.3.1 Rheology

The oil bath used as the heating block for the Strathclyde Curemeter was set at the required temperature and allowed to equilibrate. The epoxy-amine mix was poured into a small glass vial (10 mm diameter) to a depth of approximately 10 mm, and the vial secured into the oil bath by use of a clamp. The paddle was allowed to oscillate

then lowered into the sample so that it sat just above the bottom of the vial. A thermocouple was used to monitor the temperature of the resin during cure. In certain systems cured at high temperatures the sample may exotherm and the heat sink effect of the oil bath will be insufficient to maintain a constant temperature.

The software program Picolog was used to record the change in the real and imaginary components over time. The Origin software program was used to analyse the results and produce viscosity plots. The theory used to translate the change in amplitude and phase shift as a function of the cure time into viscosity data is given in *Chapter 2, section 2.1.4*.

3.3.2 Differential Scanning Calorimetry (DSC)

A TA Q1000 Differential Scanning Calorimeter was used with the accompanying software. Hermetic sealed aluminium pans were used throughout, with approximately 3-6 mg of epoxy-amine mix being weighed accurately into the pan before sealing. An empty, hermetic sealed pan was used as the reference. Nitrogen was used, at 20 mL min⁻¹, as the purge gas in the calorimeter.

Dynamic scans of each of the uncured mixtures were run by equilibrating the pans at -50°C and holding for 1 minute and then ramping at 10°C min⁻¹ to 250°C. This allowed the total energy of the uncured system to be calculated.

Isothermal runs at each of the cure temperatures were run by: equilibrating the pans at -50°C; holding for 1 minute; ramping at 10°C min⁻¹ to the required isothermal temperature; and holding at this temperature for a set period of time which was based on time to gelation as calculated from the rheology measurements. It took approximately ten minutes from when the sample was loaded until equilibration, at the isothermal temperature, and the data storage began.

Data analysis was carried out using TA Universal Analysis 2000 software. The theory for this method is given in *Chapter 2, section 2.2*.

3.3.3 Fourier Transform Infra-Red (FT-IR) Spectroscopy

The instrument used for the analysis of the uncured systems was a Nicolet Impact 410, operated using an Omnic software package. Samples were scanned from 4000 cm^{-1} to 500 cm^{-1} at 1 cm^{-1} resolution using a single potassium bromide (KBr) disc (32 mm x 3 mm). The heated cell which acted as a holder to the KBr disc was heated to the required temperature (not heated for room temperature scan), with a clean disc in place, and the background spectrum collected. A drop of the epoxy-amine mix (approximately 5 mg) was then drawn across the surface of the disc that was closest to the IR beam.

A macro was used to perform scans at pre-determined time intervals. The epoxy peak (diminishing) at 917 cm^{-1} and the OH peak (growing) at 3404 cm^{-1} were chosen to be followed, and the peak area integration of each was calculated. The software program Origin was used for further analysis of the results, and the method is discussed in *Chapter 2, section 2.3*. It should be noted that it was difficult to stabilise the temperature of the cell below 30°C. It is thought that the operating temperature of the instrument was approximately 30°C, and so it would not have been possible to accurately maintain temperatures below this without a cooling system.

3.3.4 Dielectric Spectroscopy

Liquid cells were produced to hold the epoxy-amine mix to allow it to cure while being analysed on the Novotronic dielectrics spectrometer. A transparency with the circuit design printed on it was placed between a circuit board and a UV light source, and the board was exposed for *ca.* 100 seconds. Each side of the board was exposed with the corresponding mask before *Develop 110* (solution) was used to expose the copper areas that the UV light had been able to reach. The circuit board was then placed in an etching tank containing ammonium persulfate solution (120g / 500 cm^3 water) at 45°C, for 5-10 minutes to etch the exposed copper areas. *Strip 120* (solution) was used to remove the remaining protecting film on the surface, leaving

the circuit etched into the board. The boards were cut and soldered together to produce the liquid cells.

The cells were tested in the dielectric spectrometer, and the thickness of the gap between the two plates of the cell was found by using the dielectric constant of air which is *ca.* 1 (1.00058 in air at 20°C and 50 Hz [1]). After being filled almost to the top with the epoxy-amine mix, the cell was placed vertically into the holder within the sample chamber. The software package Win Deta was used to measure the permittivity and the dielectric loss of the sample between 1 Hz and 1 MHz at pre-determined time intervals. Each frequency sweep took 2-3 minutes, and the initial time intervals were set at 5 minutes. As the quickest overall cure time was several hours, it was felt that the time intervals were adequate to observe the cure. The instrument chosen was capable of scanning down to 10^{-3} Hz, and while this may have allowed a more accurate determination of the dc conductivity, it was felt that it was more useful to have 5 minute time intervals, and a bigger frequency sweep would have required this time to be increased. It is thought that the operating temperature of the instrument was approximately 30°C, and so it would not have been possible to accurately maintain temperatures below this without a cooling system.

For each time interval measured, a two-dimensional plot of real or imaginary permittivity against the frequency was produced in the software program Origin.

3.4 METHODS OF ANALYSIS: WATER INGRESS

3.4.1 Manufacture of Blocks

The epoxy systems were prepared as for the cure characterisation and poured into moulds which had been pre-polished using *Honey Wax* mould release (produced by Speciality Products Company), and had a 2 mm spacer between the two faces. They were cured according to the cure schedules shown below. The schedules were mostly based on the cure characterisation work carried out by the team at Birmingham University, as they started work at the start of the ACLAIM project (six

months prior to this study beginning), and it was necessary for the schedules to be the same to allow direct comparison of results in the final ACLAIM project report.

The samples were analysed on the TA Q1000 Differential Scanning Calorimeter that was used for the cure characterisation work. A dry 3-6mg sub-sample of each block was analysed using a heat-cool-reheat sequence to ascertain the glass transition temperature (T_g). The samples were heated from -50°C to 250°C , at $10^{\circ}\text{C min}^{-1}$, cooled back down to -50°C , and then reheated to 300°C . This sequence allowed the T_g to be found, and to investigate if it changed on the cooling and reheating scans.

Table 9. Cure schedules for water ingress blocks as provided through ACLAIM project.

System	Cure Temperature / $^{\circ}\text{C}$	Cure Time /hours
Shared Model	50	8
	60	6
	70	4
Prime20	50	18
	60	8
	70	7

The cured blocks were cut into smaller blocks that were 48 mm x 48 mm x 2 mm. The samples were wiped with a soft cloth and the initial gravimetric and dielectric analysis carried out prior to being submerged in deionised water at the aging temperatures of 50°C and 70°C . Samples were removed periodically, wiped dry, weighed, analysed and then returned to the water. There were three repeats of each sample.

As previously stated the free water contribution is associated with dipolar relaxations occurring above 10^6 Hz therefore a high frequency dielectric spectroscopy technique that scans above this value will allow an assessment of the free water present in the sample. As the relaxations associated with bound water occur at lower frequencies than those of the free water, the previously used mid range dielectric spectroscopy instrument will be used.

3.4.2 Gravimetric Measurements

Samples were weighed using a four point balance (Mettler Toledo AB104) with an associated error of ± 0.0001 g.

3.4.3 High Frequency Dielectric Measurements

Samples were analysed using a high frequency dielectric spectrometer, which scanned from ca. 10 MHz to 10 GHz, by holding the sample against a probe. The probe was calibrated against air, paraffin and aluminium foil prior to analysis. Five measurements were made on each block- one in each of the corners and one in the middle. As there were three repeat blocks, the average (of fifteen) was found and used in the subsequent data analysis.

3.4.4 Mid Frequency Dielectric Measurements

Following the high frequency dielectrics measurements each block was scanned from 1 Hz to 1 MHz using the Novotronic dielectric spectrometer that was used for cure characterisation. Instead of the liquid sample holder in which the produced cell had the circuitry etched on, each block was inserted between two parallel conductive plates. The average of the three repeat blocks was used in the subsequent data analysis.

3.5 CONCLUDING REMARKS

This chapter has provided details on the six epoxy resin-amine systems (two model and four commercial) used for this study, as well as sample preparation and methods of analysis.

3.6 REFERENCES

1. Elias, H.-G., *An Introduction to Polymer Science*. 1997, Weinheim & New York: VCH.