

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

The copyright of this thesis belongs to the author under the terms of the United Kingdom Copyright Acts as qualified by University of Strathclyde Regulation 3.50. Due acknowledgement must always be made of the use of any material contained in, or derived from, this thesis.

Signed:

Date:

ACKNOWLEDGEMENTS

I would like to thank the following people....

...my supervisor Professor R A Pethrick for the help and advice he has given me throughout my PhD.

...Dr David Hayward for answering stupid questions, fixing instruments that decided not to work when I was near them, sorting any computer-related issues, resoldering my dielectric cells...and everything else you have helped me with!

...the various students and researchers from TG315 for exciting lunches/dinners, random as well as a few sensible conversations, bubble blowing, holidays/conferences and shopping trips ...and Eric too!

...other people from the Pethrick/Liggat group for all their help including cat emails, plants, M&S information and papers with horoscopes- you should all know who you are!

...other people from the Thomas Graham building who made the three years in the lab possible/bearable/fun!!

...all the partners of the ACLAIM project, and the group at Birmingham University led by Professor Gerard Fernando: Ramani Mahendran, Rongsheng Chen and Jonathan Burns.

...my boyfriend, family and friends for continued support and enthusiasm.

ABSTRACT

The first aim of this project was to characterise the cure of several epoxy resin systems using dielectric spectroscopy, DSC, FT-IR spectroscopy and rheology measurements. It was hoped to build up an understanding of the cure process and correlate the results produced by the different methods to establish whether dielectric spectroscopy can be used to monitor the cure of epoxy resins in the field without specialist training in interpretation of the results. The second aim was to quantify moisture ingress through gravimetric measurements and dielectric spectroscopy.

Although in certain systems a close correspondence between the 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 way in which the physical properties changes are connected to the controlling molecular processes. 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.

For the water ingress study, the dielectric studies indicate the type of water and its distribution whereas the gravimetric data indicates how much moisture is absorbed. Using a combination of the two measurement methods it is possible to obtain a greater insight into the nature of the moisture uptake than using either alone.

ABBREVIATIONS

ACLAIM	Advanced composite life assessment and integrity management
BDMA	Benzyl dimethylamine
DDS	Diaminodiphenylsulphone
DGEBA	Diglycidyl ether of bisphenol A
DGEBF	Diglycidyl ether of bisphenol F
DICY	Dicyandiamide
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
EEW	Epoxy equivalent weight
EMM	Epoxy molar mass
EPA	phthalic anhydride
FT-IR	Fourier transform infra-red (spectroscopy)
IPD	Isophoronediamine
LVDT	Linear variable differential transducer
NIR	Near infra-red
TETA	Triethylenetetramine
TTT	Time-temperature-transformation (diagram)

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
ABBREVIATIONS	iv
TABLE OF CONTENTS	v
1 INTRODUCTION	1
1.1 OVERVIEW	1
1.2 COMPOSITES.....	2
1.3 EPOXY RESINS	6
1.3.1 Introduction.....	6
1.3.2 Epoxy Resins (monomer)	7
1.3.3 Curing Agents	10
1.3.4 Diluents and Fillers	12
1.4 EPOXY RESIN CURE	16
1.4.1 Cure Characterisation.....	22
1.5 WATER INGRESS.....	24
1.5.1 Introduction.....	24
1.5.2 Measurement of Water Ingress	25
1.6 AIMS OF PROJECT.....	25
1.7 REFERENCES	26
2 THEORY	32
2.1 RHEOLOGY.....	32
2.1.1 Introduction.....	32
2.1.2 Polymer Rheology	34
2.1.3 Modelling of Polymer Behaviour	37
2.1.4 Strathclyde Curemeter	42
2.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)	46
2.3 FOURIER TRANSFORM INFRA-RED (FT-IR) SPECTROSCOPY.....	48
2.4 DIELECTRIC SPECTROSCOPY.....	49
2.4.1 Dielectric Polarisation in an Alternating Field	49
2.4.2 The Debye Equations	50
2.4.3 Dielectric Response of Polymers	52
2.4.4 Dielectric Response of Heterogeneous Polymers	55
2.4.5 Dielectric Response During Epoxy Resin Cure.....	57
2.5 MOISTURE INGRESS	57
2.5.1 Moisture Ingress into Cured Epoxy Resins	57
2.5.2 Dielectric Response as a Result of Water Ingress	61
2.6 CONCLUDING REMARKS.....	63
2.7 REFERENCES	63

3	EXPERIMENTAL	66
3.1	MATERIALS	66
3.1.1	Strathclyde Model System	66
3.1.2	Shared Model System	67
3.1.3	Sikadur®- 31 Normal (SK31).....	68
3.1.4	PR55-ST (PR55)	70
3.1.5	Prime 20/ SPX 3260 (Prime20)	72
3.1.6	Spabond SP340 (SP340).....	75
3.2	PREPARATION OF SAMPLES	78
3.2.1	Exceptions to Preparation of Samples	78
3.3	METHODS OF ANALYSIS: CURE CHARACTERISATION	78
3.3.1	Rheology	78
3.3.2	Differential Scanning Calorimetry (DSC)	79
3.3.3	Fourier Transform Infra-Red (FT-IR) Spectroscopy	80
3.3.4	Dielectric Spectroscopy	80
3.4	METHODS OF ANALYSIS: WATER INGRESS	81
3.4.1	Manufacture of Blocks.....	81
3.4.2	Gravimetric Measurements.....	83
3.4.3	High Frequency Dielectric Measurements.....	83
3.4.4	Mid Frequency Dielectric Measurements	83
3.5	CONCLUDING REMARKS	83
3.6	REFERENCES	83
4	CURE CHARACTERISATION: CUREMETER	84
4.1	STRATHCLYDE MODEL SYSTEM.....	84
4.2	SHARED MODEL SYSTEM.....	89
4.3	SK31	94
4.4	PR55.....	97
4.5	PRIME20	101
4.6	SP340	104
4.7	CONCLUSIONS.....	108
4.8	REFERENCES	110
5	CURE CHARACTERISATION: DSC.....	111
5.1	STRATHCLYDE MODEL SYSTEM.....	111
5.2	SHARED MODEL SYSTEM.....	118
5.3	SK31	123
5.4	PR55.....	128
5.5	PRIME20	132
5.6	SP340	136
5.7	CONCLUSIONS.....	140
5.8	REFERENCES	143

6	CURE CHARACTERISATION: FT-IR.....	145
6.1	INTRODUCTION	145
6.2	STRATHCLYDE MODEL SYSTEM.....	147
6.3	SHARED MODEL SYSTEM.....	152
6.4	PR55.....	154
6.5	PRIME20	157
6.6	CONCLUSIONS.....	159
6.7	REFERENCES	159
7	CURE CHARACTERISATION: DIELECTRIC SPECTROSCOPY.....	160
7.1	INTRODUCTION	160
7.2	STRATHCLYDE MODEL SYSTEM.....	165
7.3	SHARED MODEL SYSTEM.....	170
7.4	PR55.....	173
7.5	PRIME20	177
7.6	ADDITIONAL ANALYSIS OF DIELECTRIC SPECTRA.....	180
7.7	CONCLUSIONS.....	185
8	CURE CHARACTERISATION: COMPARISON OF METHODS.....	186
8.1	MEASUREMENT OF COMPOSITIONAL CHANGE.....	186
8.1.1	Strathclyde Model System	188
8.1.2	Shared Model System	188
8.1.3	SK31	189
8.1.4	PR55.....	189
8.1.5	Prime20	189
8.1.6	SP340	190
8.2	MEASUREMENT OF GELATION & VITRIFICATION	190
8.2.1	Strathclyde Model System	192
8.2.2	Shared Model System	192
8.2.3	SK31	193
8.2.4	PR55.....	193
8.2.5	Prime20	194
8.2.6	SP340	195
8.3	COMPARISON OF RATES OF REACTION	195
8.3.1	Strathclyde Model System	196
8.3.2	Shared Model System	196
8.3.3	SK31	197
8.3.4	PR55.....	197
8.3.5	Prime20	197
8.3.6	SP340	198
8.4	CONCLUSIONS.....	198

9	WATER INGRESS	199
9.1	PREPARATION OF SAMPLES	199
9.2	DSC OF CURED BLOCKS	200
9.2.1	Prime20	200
9.2.2	Shared Model System	205
9.3	GRAVIMETRIC ANALYSIS	208
9.3.1	Prime20	208
9.3.2	Shared Model System	212
9.3.3	Gravimetric Conclusions	216
9.4	HIGH FREQUENCY DIELECTRICS	219
9.4.1	Prime20	219
9.4.2	Shared Model System	222
9.4.3	High Frequency Dielectrics Conclusions.....	224
9.5	MID FREQUENCY DIELECTRICS	224
9.5.1	Prime20	225
9.5.2	Shared Model System	229
9.6	COMPARISON OF ANALYSIS METHODS	233
9.6.1	Conclusions.....	235
9.7	REFERENCES	235
10	CONCLUSIONS.....	236
10.1	Epoxy Resin Characterisation.....	236
10.2	Water Ingress	237
	APPENDICES	1
	APPENDIX A: FITTING FT-IR DATA	2
	INTRODUCTION	3
	PR55.....	4
	Strathclyde Model System	6
	Shared Model System	11
	Prime20	14
	SUMMARY OF FITTED DATA	17
	Strathclyde Model System	18
	Shared Model System	19
	PR55.....	19
	Prime 20.....	20
	REFERENCES	20
	APPENDIX B: DIELECTRIC DATA	21
	APPENDIX C: WATER INGRESS SUPPLEMENTARY PLOTS.....	38
	Water Ingress HF Dielectric Plots	41
	Water Ingress Mid Frequency Dielectric Plots	47