POLYMERIZATION KINETICS OF THERMOSETS WITH AN EPOXIDE-FUNCTIONALIZED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE
POLYMERIZATION KINETICS OF THERMOSETS WITH AN EPOXIDE-
FUNCTIONALIZED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE

By JOSEPH KHOURI, B.A.Sc.

A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Applied Science

McMaster University
© Copyright by Joseph Khouri, February 2012
MASTER OF APPLIED SCIENCE (2012) McMaster University
(Department of Materials Science and Engineering) Hamilton, Ontario

TITLE: Polymerization Kinetics of Thermosets with an Epoxide-Functionalized Polyhedral Oligomeric Silsesquioxane

AUTHOR: Joseph Khouri, B.A.Sc. (Queen’s University, Kingston, Ontario)

SUPERVISOR: Professor Gyan P. Johari

NUMBER OF PAGES: 180
Abstract

Effects of a nanometer-size, reactive polyhedral oligomeric silsesquioxane (POSS) on a thermoset’s polymerization kinetics and dielectric relaxation have been investigated by using differential scanning calorimetry (DSC) and dielectric spectroscopy. Four amines, hexylamine (HA), ethylene diamine (EDA), isophorone diamine (IPDA), and diethylene triamine (DETA) were used to crosslink epoxy resin DGEBA and a multi functionalized -glycidyl POSS. The polymers formed ranged from POSS-free to POSS-only network structure, while maintaining an equal ratio of reactive groups.

Calorimetric studies of stoichiometric DETA and IPDA samples performed by ramp-heating showed that the polymerization kinetics increased with low POSS content, but progressively decreased upon further addition, and the POSS-only mixtures reacted the slowest. The same pattern of changes in the rate of polymerization was observed by isothermal polymerization of the DETA mixtures. The results have been interpreted based on changes in viscosity and diffusion coefficients according to the Stokes-Einstein and Smoluchowski equations. Furthermore, isothermal polymerization of stoichiometric DETA and EDA samples showed that the extent of reaction increased with POSS, indicating that it is easier to form a higher crosslinked thermoset with higher amounts of POSS.

Non-isothermal polymerization of POSS-IPDA mixtures was also investigated under off-stoichiometric conditions. Unlike the reaction mechanisms of non-
stoichiometric DGEBA-IPDA mixtures, a significant difference in reactivity of primary and secondary amines in the POSS-IPDA reaction was not observed.

Dielectric relaxation studies were performed in real time during polymerization. The distribution of relaxation rates increased with an increase in POSS, and the duration of polymerization required to reach a specific relaxation time increased. Furthermore, the time at which the dielectric loss minimum and peak occurred increased with POSS, however, when only POSS was reacted with the amine, an $\alpha$-relaxation peak was not observed. A frequency-dependent increase in permittivity during polymerization was observed with the POSS-only EDA, DETA, and HA samples, and a corresponding change in the loss was not detected. It was attributed to a structure-dependent increase in interfacial polarization.

Although not related to the polymerization study, work done on the residual entropy of glasses is included here. To help resolve the controversy of the residual entropy of glassy materials, specific heat data taken from the literature were analyzed. The changes in entropy of a glass on cooling and heating paths were determined, and it was found that the upper and lower limits of entropy differed by no more than 2 %. This showed that although the thermodynamic path through the glass transition is irreversible, this irreversibility has a negligibly small effect on determining the entropy.
Acknowledgements

I would to thank Dr. Gyan Johari, who not only provided a great amount of support and guidance which ultimately made this body of work what it is, but for his inspiration. I consider him not just as a supervisor, but as a mentor and friend. I am forever grateful.

I thank Dr. Daisman Aji, whose friendship and discussions assisted me over the past two years, and especially for the dielectric assembly interface software which he spent many hours programming while writing his thesis at the same time. I also thank Diana Maltese, Nanci Cole, Doug Culley and Ed McAffrey, for the little things.

But most importantly, I thank my father, for his everlasting friendship and shared love of chemistry, and for the sacrifices made over the years for my better education - my mother for her love, nurturing, and encouragement - and my sister who has shown me just how much she cares.
# Table of Contents

Abstract ........................................................................................................................................ iii

Acknowledgements .......................................................................................................................... v

List of Tables .................................................................................................................................. viii

List of Figures ................................................................................................................................. ix

Chapter 1 : An Introduction to Epoxy Polymers & Research Scope ........................................ 1

1.1 Background and Literature Review of Epoxies ................................................................. 6

1.1.1 Epoxy reaction scheme and kinetics .............................................................................. 6

1.1.2 Changes in properties during polymerization ............................................................... 9

1.2 Background and Literature Review of Silsesquioxanes .................................................... 12

1.2.1 History, synthesis and properties ................................................................................... 12

1.2.2 POSS in polymers ........................................................................................................ 14

1.3 Materials ................................................................................................................................. 18

Chapter 2 : Calorimetry .............................................................................................................. 22

2.1 Literature Review .................................................................................................................... 22

2.1.1 Epoxy reaction kinetic models .................................................................................... 22

2.1.2 Model-free analytical methods using DSC measurements ........................................... 25

2.2 Experimental .......................................................................................................................... 26

2.2.1 DSC assembly and measurements .............................................................................. 26

2.2.2 Experiment procedure and sample preparation ............................................................ 28

2.3 Results .................................................................................................................................... 30

2.3.1 Analysis of DSC plots .................................................................................................. 30

2.3.2 DGEBA-POSS-DETA ................................................................................................. 31

2.3.3 DGEBA-POSS-IPDA .................................................................................................. 40

2.3.4 DGEBA-POSS-EDA .................................................................................................. 48

2.3.5 Sources of error ............................................................................................................ 50

2.4 Discussion ............................................................................................................................... 51

2.4.1 Endothermic effect from impurities in POSS ............................................................... 51

2.4.2 Effects of POSS on thermodynamic properties .......................................................... 53
2.4.3 Influence of POSS on polymerization kinetics ............................................. 60
2.4.4 Static heterogeneity of nanoscopic POSS and dynamic heterogeneity. ....... 68
2.4.5 Analysis of polymerization kinetics using the Corezzi model ..................... 72

Chapter 3 : Real Time Dielectric Spectroscopy of Polymerization ..................... 77

3.1 Background and Literature Review of Dielectric Spectroscopy ..................... 77
3.1.1 Dielectric theory ......................................................................................... 77
3.1.2 Application of real-time dielectric spectroscopy to polymerizing systems .... 79
3.1.3 Analysis of relaxation observed during polymerization ........................... 82
3.2 Experimental ................................................................................................. 85
3.2.1 Dielectric measurement assembly ............................................................. 85
3.2.2 Experiment procedure .............................................................................. 88
3.3 Results ........................................................................................................... 89
3.3.1 DGEBA-POSS-DETA .............................................................................. 89
3.3.2 DGEBA-POSS-HA .................................................................................. 92
3.3.3 DGEBA-POSS-EDA .............................................................................. 93
3.3.4 Analysis of Cole-Cole and complex plane plots ...................................... 105
3.4 Discussion ..................................................................................................... 122
3.4.1 Effects of nm heterogeneities on gelation time, kinetics and dc conductivity 122
3.4.2 Effects on relaxation time, distribution of relaxation rates and dynamic heterogeneity ................................................................. 126
3.4.3 Change in the dielectric features with polymerization time and temperature 131

Chapter 4 : Resolution of the Residual Entropy on Heating and Cooling Through the
Glass Region ........................................................................................................ 137
4.1 Residual Entropy of Glasses ........................................................................ 137
4.2 Data Analysis and Results .......................................................................... 139
4.3 Discussion ..................................................................................................... 148

Chapter 5 : Conclusion ...................................................................................... 152
Appendix .............................................................................................................. 155
References ........................................................................................................... 171
List of Tables

Table 1.1 - POSS mole percentage and weight percentage of the mixtures, and the experimental technique used to study the four amine-DGEBA-POSS systems............... 20

Table 1.2 - Chemical structures and properties of the amines, epoxy resin and POSS .... 21

Table 2.1 - Enthalpy of Reaction (in J/g) of stoichiometric DGEBA-POSS-DETA........ 38

Table 2.2 - ΔH_{polym} (in J/g) for DGEBA-IPDA, DGEBA-POSS-IPDA, and POSS-IPDA polymerized at different heating rates......................................................... 48

Table 2.3 - ΔH_{polym} (in J/g) of stoichiometric DGEBA-POSS-EDA cured at 318K. .... 49

Table 2.4 - Average values of ΔH_q of the DGEBA-POSS-DETA mixtures and corresponding scaled values estimated using Eqn. 2.13. ......................................................... 58

Table 2.5 - Estimated activation energy values of the DGEBA-POSS-DETA mixtures using the isoconversional method................................................................. 60

Table 2.6 - Parameters k_0, k_{cl}, k'_{cl}, ξ, m, and n, from the best fit of Eqn. 2.5 to the dcd/dt data of DGEBA-EDA and 2% POSS mixture.................................................. 76

Table 3.1 – Values of ε' (t_{polym}→0), ε' (t_{polym}→∞), t_{polym}(ε^"_{peak}), ε" (t_{polym}→∞) and logσ (t_{polym}→0) .................................................................................................................. 105

Table 3.2 - Parameters from the KWW analysis of the DETA isochrones. .................. 110

Table 3.3 - Parameters from the KWW analysis of the DETA spectra data. ............... 111

Table 3.4 - Parameters from the KWW analysis of the HA isochrones. ....................... 114

Table 3.5 - Parameters from the KWW analysis of the HA spectra data. ..................... 114

Table 3.6 - Parameters from the KWW analysis of the EDA isochrones. .................... 117

Table 3.7 - Parameters from the KWW analysis of the EDA spectra data.................... 117

Table 4.1 - The cooling and heating rates q, the temperature limits of integration T_{glass} and T_{liq}, the C_p dT and C_p dlnT integrals denoted as ΔH and Δσ measured for cooling and for heating and the percentage difference between the respective integrals, x_H and x_σ. ...... 144
List of Figures

Figure 1.1 – Epoxy-Amine reaction scheme. The new bonds formed are shown in bold and the hydrogen bonds are shown by vertical dotted lines. ............................................. 8

Figure 1.2 – Silsesquioxane structures (Li et al. 2007) ..................................................... 15

Figure 2.1 – Heat flux DSC with turret-type measuring system (TA Instruments), 1 elevated constant platform for sample and reference sample, 2 chromel area thermocouple, 3 constantan body, 4 chromel – constantan thermocouple, 5 silver furnace, S sample substance, R.[Höhne et al. 2003] ................................................................. 27

Figure 2.2 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-DETA ($x_{\text{POSS}} = 0 \%$), polymerized at three heating rates, and (B) corresponding extent of reaction........................................................................................................... 33

Figure 2.3 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$), polymerized at four heating rates, and (B) corresponding extent of reaction........................................................................................................... 33

Figure 2.4 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3 \%$), polymerized at four heating rates, and (B) corresponding extent of reaction................................................................. 33

Figure 2.5 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7 \%$), polymerized at four heating rates, and (B) corresponding extent of reaction. ................................................................. 33

Figure 2.6 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 21.2 \%$), polymerized at four heating rates, and (B) corresponding extent of reaction................................................................. 34

Figure 2.7 – (A) $dH/dT$ plotted against temperature of stoichiometric POSS-DETA, polymerized at four heating rates, and (B) corresponding extent of reaction................................................................. 34

Figure 2.8 – Plots of $dH/dT$ against temperature for the six DETA mixtures polymerized at rates of (A) 5K/min and (B) 30 K/min. $x_{\text{POSS}}$ is indicated next to the curves................................. 34

Figure 2.9 – Extent of reaction plotted against temperature for the six DETA mixtures polymerized at a rate: (A) $q = 5K/min$ and (B) $q = 30 K/min$. $x_{\text{POSS}}$ is indicated next to the curves................................. 35

Figure 2.10 – The temperature at which $\alpha$ reaches 0.4, 0.6, 0.8 and 0.98, plotted against $x_{\text{POSS}}$ for the sample heated at (A) 5 K/min and (B) 30 K/min................................. 35
Figure 2.11 – (A) A plot of dH/dt plotted against polymerization time for six stoichiometric [DGEBA-POSS]-DETA samples isothermally cured at 323 K, where $x_{\text{POSS}}$ is indicated next to the curves, and (B) corresponding extent of reaction. .......................... 38

Figure 2.12 – A plot of dH/dT against temperature for the post-polymerization at 10 K/min of six stoichiometric [DGEBA-POSS]-DETA mixtures, and $x_{\text{POSS}}$ is indicated next to the curves. .......................................................... 39

Figure 2.13 – (A) The plots of the temperature of the exothermic minimum, $T_{\text{min,exo}}$ for DGEBA-POSS-DETA polymerized by ramp heating at rates of 5, 10, 20 and 30 K min rate against $x_{\text{POSS}}$. (B) The plots of the onset temperature of glass-softening, $T_{g}$, and of the peak temperature, $T_{\text{peak,iso}}$ observed by post-polymerization at 10 K/min. ...................... 39

Figure 2.14 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r$ = 1) polymerized at four heating rates and (B) corresponding extent of reaction. .............. 41

Figure 2.15 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r$ = 1.25) polymerized at four heating rates and (B) corresponding extent of reaction. ...... 41

Figure 2.16 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r$ = 0.75) polymerized at four heating rates and (B) corresponding extent of reaction. ...... 41

Figure 2.17 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r$ = 0.33) polymerized at four heating rates and (B) corresponding extent of reaction. ...... 41

Figure 2.18 – (A) A plot of $dH/dT$ against temperature for DGEBA-IPDA polymerized at a rate, $q$ = 30 K/min, where the numbers next to the curves are the epoxide-to-amine ratio, $r$ and (B) corresponding plot at $q$ = 5 K/min. .......................................................... 42

Figure 2.19 – (A) Extent of reaction, $\alpha$, plotted against temperature for DGEBA-IPDA polymerized at a rate, $q$ = 30 K/min, where the numbers next to the curves are the epoxide-to-amine ratio, $r$ and (B) corresponding plot at $q$ = 5 K/min. ................................. 42

Figure 2.20 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}}$ = 2 %) polymerized at four heating rates and (B) corresponding extent of reaction.......................................................... 44

Figure 2.21 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}}$ = 5.6 %) polymerized at four heating rates and (B) corresponding extent of reaction.......................................................... 44

Figure 2.22 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}}$ = 15.2 %) polymerized at four heating rates and (B) corresponding extent of reaction.......................................................... 44
Figure 2.23 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{POSS} = 35\%$) polymerized at four heating rates and (B) corresponding extent of reaction. ................................................. 44

Figure 2.24 – (A) Plots of $dH/dT$ against temperature for the six stoichiometric DGEBA-POSS-IPDA polymerized at rates of (A) 30 K/min and (B) 5 K/min. $x_{POSS}$ increases in the direction of the arrows. ..................................................... 45

Figure 2.25 – (A) Extent of reaction plotted against temperature for the six stoichiometric DGEBA-POSS-IPDA polymerized at a heating rate of (A) 30 K/min and (B) 5 K/min. $x_{POSS}$ is indicated by the arrows. ................................................................. 45

Figure 2.26 – (A) $dH/dT$ plotted against temperature of stoichiometric POSS-IPDA ($r = 1$) polymerized at four heating rates and (B) corresponding extent of reaction. .................. 46

Figure 2.27 – (A) $dH/dT$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 1.33$) polymerized at four heating rates and (B) corresponding extent of reaction. .. 46

Figure 2.28 – (A) $dH/dT$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 1.25$) polymerized at four heating rates and (B) corresponding extent of reaction. .. 46

Figure 2.29 – (A) $dH/dT$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 0.8$) polymerized at four heating rates and (B) corresponding extent of reaction. .... 46

Figure 2.30 – (A) $dH/dT$ plotted against temperature of reaction of non-stoichiometric POSS-IPDA ($r = 0.75$) polymerized at four heating rates and (B) corresponding extent. 47

Figure 2.31 – (A) Plots of $dH/dT$ against temperature for the five POSS-IPDA mixtures polymerized at a heating rate of (A) 30 K/min and (B) 5 K/min. The epoxide-to-proton ratio, $r$, is indicated next to the curves. ................................................................. 47

Figure 2.32 – Extent of reaction plotted against temperature of DGEBA-IPDA mixtures polymerized at a rates of (A) 30 K/min and (B) 5 K/min. The numbers next to the curves are the epoxide-to-amine ratio, $r$. ................................................................. 47

Figure 2.33 – (A) Plots of $dH/dt$ against polymerization time for DGEBA-POSS-EDA samples polymerized at 318 K and (B) corresponding extent of reaction. ................ 49

Figure 2.34 – Post-polymerization $dH/dT$ plots against temperature of the DGEBA-POSS-EDA mixtures, heated at 10 K/min. ................................................................. 50

Figure 2.35 – Plots of $dH/dt$ against temperature of EP0409 heated at 10 K/min, at a starting temperature of (A) 220 K (B) 273 K and (C) 300 K. The enthalpy change associated with the endotherm is given in the plots. ................................................. 52
Figure 2.36 – Enthalpy of reaction of DGEBA-POSS-DETA (in kJ / mole epoxide) plotted against $x_{POSS}$, for the different polymerization conditions........................................... 54

Figure 2.37 – Enthalpy of reaction of DGEBA-POSS-IPDA, (in kJ / mole epoxide), plotted against $x_{POSS}$, for four heating rates................................................................. 55

Figure 2.38 – Enthalpy of reaction of POSS-IPDA, (in kJ / mole epoxide), plotted against the epoxide-to-amine proton ratio, $r$, for four heating rates........................................ 55

Figure 2.39 – Extent of reaction of stoichiometric DGEBA-DETA, non-stoichiometric DGEBA-DETA and its equivalent stoichiometric 2% POSS mixture polymerized at (A) 5 K/min and (B) 30 K/min........................................................................................................ 67

Figure 2.40 – Extent of reaction of stoichiometric DGEBA-DETA, 2% DGEBA-POSS-DETA (wet), and 2% (dry) mixture polymerized at (A) 5 K/min and (B) 30 K/min...... 67

Figure 2.41 – Depiction of the decoupling of the inverse of average diffusion coefficient (dotted line) from viscosity (continuous line) as the polymerization time increases. The dot indicates the point at which decoupling occurs. Curve (1) is a depiction for DGEBA-DETA, curves (2) and (3) are depictions for 2% POSS mixture (DGEBA-POSS-DETA) and (POSS-DETA). At the time denoted by vertical line at $p$, polymerization occurs in the viscosity controlled zone for the DGEBA–DETA mixture, but in the decoupled diffusion-controlled zone for the 2% POSS–DGEBA–DETA mixture, where it is faster, and still in the decoupled diffusion-controlled zone for the POSS–DETA mixture, where it is slower.............................................................................................................. 72

Figure 2.42 – Logarithm of $\tau$ plotted against $\alpha$ for (A) DGEBA-EDA and (B) 2% POSS - EDA sample. The dots are the experimental data and the line is the best fit from Eqn 2.17. Parameters from the equation are shown in the panels............................................ 75

Figure 2.43 – $d\alpha/dt$ plotted against $\alpha$ for (A) DGEBA-EDA and (B) 2% POSS - EDA sample. The dots are the experimental data and the line is the best fit from Eqn 2.5...... 76

Figure 3.1 – (A) Photograph of the dielectric assembly which consists of an (1) impedance analyzer, (2) multimeter, (3) ice/water bath container, (4) thermostat assembly and (5) temperature controller. (B) Photograph of the capacitor used in dielectric measurements. (C) Photograph of the thermostat assembly.............................................. 87

Figure 3.2 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-DETA plotted against the logarithm of $t_{polym}$ for 4 frequencies................................................................. 94

Figure 3.3 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-DETA plotted against the logarithm of $f$ for several $t_{polym}$ (minutes)........................................................................ 94
Figure 3.4 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (2% POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies. ........................................ 94

Figure 3.5 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (2% POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 94

Figure 3.6 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (4.3% POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies. ........................................ 95

Figure 3.7 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (4.3% POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 95

Figure 3.8 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (10.7% POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies. ........................................ 95

Figure 3.9 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (10.7% POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 95

Figure 3.10 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (21.2% POSS) plotted against the logarithm of $t_{\text{polym}}$, for 4 frequencies. ........................................ 96

Figure 3.11 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-DETA (21.2% POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 96

Figure 3.12 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of POSS-DETA plotted against the logarithm of $t_{\text{polym}}$, for 4 frequencies. ........................................ 96

Figure 3.13 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of POSS-DETA plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 96

Figure 3.14 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ plotted against the logarithm of $t_{\text{polym}}$, measured at 1 kHz, for five POSS-DGEBA-DETA mixtures polymerized at 323 K. .... 97

Figure 3.15 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-HA plotted against the logarithm of $t_{\text{polym}}$ for 5 frequencies. ........................................ 98

Figure 3.16 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-HA plotted against the logarithm of $f$ for several $t_{\text{polym}}$. ........................................ 98

Figure 3.17 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log (\sigma)$ of DGEBA-POSS-HA (2% POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies. ........................................ 99
Figure 3.18 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-HA (2 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 99

Figure 3.19 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-HA (4.3 % POSS) plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies. ................................................................. 99

Figure 3.20 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-HA (4.3 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 99

Figure 3.21 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-HA (10.7 % POSS) plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies. ...................................................... 100

Figure 3.22 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-HA (10.7 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 100

Figure 3.23 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of POSS-HA plotted against the logarithm of \( t_{\text{polym}} \) for 5 frequencies. ................................................................. 100

Figure 3.24 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of POSS-HA plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 100

Figure 3.25 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of the five DGEBA-POSS-HA mixtures cured at 313 K are plotted against the logarithm of \( t_{\text{polym}} \) for a measurement at 1 kHz. ....... 101

Figure 3.26 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-EDA plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies ................................................................. 102

Figure 3.27 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-EDA plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 102

Figure 3.28 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-EDA (xPOSS = 2 %) plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies. ................................................................. 102

Figure 3.29 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-EDA (2 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 102

Figure 3.30 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-EDA (xPOSS = 4.3 %) plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies. ................................................................. 103

Figure 3.31 – (A) \( \varepsilon' \) (B) \( \varepsilon'' \) and (C) \( \log (\sigma) \) of DGEBA-POSS-EDA (4.3 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \). ................................................................. 103
Figure 3.32 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-EDA plotted against the logarithm of $t_{\text{polym}}$, for 4 frequencies. .......................................................... 103

Figure 3.33 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-EDA plotted against the logarithm of $f$, for several $t_{\text{polym}}$. .......................................................... 103

Figure 3.34 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ plotted against the logarithm of $t_{\text{polym}}$ of the four DGEBA-POSS-EDA mixtures at 1 kHz. .......................................................... 104

Figure 3.35 – Complex plane plot of DGEBA-DETA for 6 frequencies. ....................... 107

Figure 3.36 – Cole-Cole plot of DGEBA-DETA for 6 fixed $t_{\text{polym}}$. .......................... 107

Figure 3.37 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$) for 6 frequencies ........................................................................................................ 107

Figure 3.38 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$) for 6 fixed $t_{\text{polym}}$. ........................................................................................................ 107

Figure 3.39 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3\%$) for 6 frequencies ........................................................................................................ 108

Figure 3.40 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3\%$) for 6 fixed $t_{\text{polym}}$. ........................................................................................................ 108

Figure 3.41 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7\%$) for 6 frequencies ........................................................................................................ 108

Figure 3.42 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7\%$) for 6 fixed $t_{\text{polym}}$. ........................................................................................................ 108

Figure 3.43 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 21.2\%$) for 6 frequencies ........................................................................................................ 109

Figure 3.44 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 21.2\%$) for 6 fixed $t_{\text{polym}}$. ........................................................................................................ 109

Figure 3.45 – Complex plane plot of POSS-DETA for 6 frequencies.......................... 109

Figure 3.46 – Cole-Cole plot of POSS-DETA for 6 fixed $t_{\text{polym}}$. .......................... 109

Figure 3.47 – Complex plane plot of DGEBA-HA for 6 frequencies......................... 112

Figure 3.48 – Cole-Cole plot of DGEBA-HA for 6 fixed $t_{\text{polym}}$. .......................... 112
Figure 3.49 – Complex plane plot of DGEBA-POSS-HA ($x_{POSS} = 2\%$) for 6 frequencies. ................................................................................................................................................112

Figure 3.50 – Cole-Cole plot of DGEBA-POSS-HA ($x_{POSS} = 4.3\%$) for 6 fixed $t_{polym}$. 112

Figure 3.51 – Complex plane plot of DGEBA-POSS-HA ($x_{POSS} = 4.3\%$) for 6 frequencies ................................................................................................................................................113

Figure 3.52 – Cole-Cole plot of DGEBA-POSS-HA ($x_{POSS} = 4.3\%$) for 6 fixed $t_{polym}$. 113

Figure 3.53 – Complex plane plot of DGEBA-POSS-HA ($x_{POSS} = 10.7\%$) for 6 frequencies ................................................................................................................................................113

Figure 3.54 – Cole-Cole plot of DGEBA-POSS-HA ($x_{POSS} = 10.7\%$) for 6 fixed $t_{polym}$. ................................................................................................................................................113

Figure 3.55 – Complex plane plot of DGEBA-EDA for 6 frequencies........................................115

Figure 3.56 – Cole-Cole plot of DGEBA-EDA for 6 fixed $t_{polym}$. .........................................115

Figure 3.57 – Complex plane plot of DGEBA-POSS-EDA ($x_{POSS} = 2\%$) for 6 frequencies ................................................................................................................................................115

Figure 3.58 – Cole-Cole plot of DGEBA-POSS-EDA ($x_{POSS} = 2\%$) for 6 fixed $t_{polym}$. 115

Figure 3.59 – Complex plane plot of DGEBA-POSS-EDA ($x_{POSS} = 4.3\%$) for 6 frequencies ................................................................................................................................................116

Figure 3.60 – Cole-Cole plot of DGEBA-POSS-EDA ($x_{POSS} = 4.3\%$) for 6 fixed $t_{polym}$. ................................................................................................................................................116

Figure 3.61 – Complex plane plot of POSS-EDA for 6 frequencies.................................116

Figure 3.62 – Cole-Cole plot of POSS-EDA for 6 fixed $t_{polym}$............................................116

Figure 3.63 – Log $\tau_0$ plotted against log $t_{polym}$ for (A) DETA (B) HA and (C) EDA mixtures................................................................................................................................................121

Figure 3.64 – $t_{gel}$ and $\gamma$ estimated from Eqn. 3.9, plotted against $x_{POSS}$ for (A) DETA mixtures and (B) EDA mixtures. ................................................................................................................................................123

Figure 3.65 – (A) $\varepsilon'$ plotted against $t_{polym}$ of four POSS-DETA mixtures polymerized at different temperatures and measured at 1 kHz and (B) the corresponding $\varepsilon''$ plots. ...... 136
Figure 4.1 – The molecular structures of (A) acetaminophen (B) nifedipine (C) 2-ethyl-1-hexanol and (D) triphenylolmethane triglycidyl ether and (E) vinyl acetate monomer.

Figure 4.2 – (A) The plot of $C_p$ against $T$ for 2-ethyl-1-hexanol on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.3 – (A) The plot of $C_p$ against $T$ for poly(vinyl acetate) on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.4 – (A) The plot of $C_p$ against $T$ for Schott Glass K7 on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.5 – The plot of $C_p$ against $T$ for Annealed Schott Glass – Na-LaK12 on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.6 – (A) The plot of $C_p$ against $T$ for nifedipine on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.7 – (A) The plot of $C_p$ against $T$ for TPTGE on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.8 – (A) The plot of $C_p$ against $T$ for acetaminophen on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against ln$T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.
Chapter 1 : An Introduction to Epoxy Polymers & Research Scope

Polymers are generally classified into two groups: thermosets and thermoplastics (elastomers/rubbers are occasionally considered in a class of their own). Thermoplastics are linear-chain compounds, which form a melt when they are heated to high temperatures, and are recyclable. A thermoset is network chain polymer, and when heated, its bonds are broken such that it decomposes and thermosets are generally non-recyclable, although developments on synthesis techniques show that certain thermosets may indeed be recycled [Zhang et al. 2009]. The two groups may also be differentiated as those which are soluble and those which gel and are in-soluble compounds, respectively.

Epoxy resins are one of the most widely used chemicals for industrial production of thermosets. The reactive group in these compounds is the epoxide, and such resins typically contain two or three epoxides located at the terminal segments of the molecule. The epoxide, otherwise known as an oxirane group or cyclic ether, is a three member ring of two carbons and one oxygen (\(\overset{\circ}{\text{O}}\), HCOCH\(_2\)R). Thermosets are formed by crosslinking the epoxy using compounds such as amines, cyclic anhydrides, polyamides and phosphites. These reagents are referred to as ‘hardeners’ or ‘curing agents’, and the polymerization process is known as ‘curing’. The most reactive and commonly used hardener is the amine [Ellis 1993].

When the liquid monomers react, the epoxide rings are opened by a series of addition reactions, and the mixture solidifies, forming a glassy material with useful mechanical and electrical properties, and good thermal stability [Ellis 1993]. Properties
are contingent on the size, functionality and electrical characteristics of the epoxy resin and hardener, and combination of certain monomers may yield high glass transition temperatures, low dielectric constants and tensile strengths that are comparable to other thermoset resins [Ellis 1993]. Epoxies are advantageous as they cure with low shrinkage and without the release of volatile matter [Kelley et al. 1994]. Applications range from decorate surfaces (coatings), adhesives, as moulds for tool shaping, as thin film coatings for protection against corrosion and electrical insulation, and encapsulation of microelectronic circuits.

An often cited disadvantage of cured epoxies is that they can have low elastic moduli, and low fracture stress at sub-ambient temperatures [Ellis 1993, Zvetkov 2008]. Elastic moduli and other properties have been improved by incorporating small amounts of filler material, forming a polymer composite. A variety of fillers and composite materials have been used to toughen epoxies (and polymers in general) and to enhance their technologically useful properties. These fillers are metal fibres [Nikkeshi et al. 1998, Lin et al. 1993], carbon fibres [Hughes 1991], rubbers [Wang et al. 1992], clays [Lan and Pinnavaia 1994, Gilman 1999], silica [Macan et al. 2006] and silsesquioxanes [Li et al. 2001]. Composites containing inorganic filler material, such as clays and silicones, are often referred to as hybrid organic-inorganic composites, or hybrid polymers. The focus of this thesis is on how incorporating one such inorganic filler, the silsesquioxane, affects polymerization kinetics of an epoxy-amine matrix.

Silsesquioxanes are compounds with the general formula \((\text{SiO}_{3/2})_n\text{R}_n\). The substituent \(R\) is covalently bonded to the silicon atoms, and there is practically no limit as
to what R might be; hydrogen, alkyl, alkyene, aryl, arylene or an organo-functional
derivative of these. Incorporation of small quantities of polyhedral oligomeric
silsesquioxanes (POSS), either by physical crosslinking, or by chemically reacting to
form covalent bonds with the base monomers, has shown to improve flame retardancy
[Franchini et al. 2009, Lu et al. 2007], elasticity [Strachota et al. 2004, Dodiuk-Kenig et
al. 2006, Zhou et al. 2008], and physical ageing [Lee and Lichtenhan 1998] of both
thermoplastics and thermosets [Li et al. 2001]. They have been found to increase crystal
melting temperature [Zhou et al. 2008] and glass transition temperature [Haddad et al.
2001, Lee 1998, Li et al. 2008, Teo et al. 2007], thus increasing the temperature range of
usage. When POSS is functionalized with a reactive substituent, an epoxide or amine, it
participates in the thermosetting reaction, and covalently bonds to the host polymer
network. Both inert and reactive POSS compounds have been found to improve the
properties of epoxies [Fu et al. 2003].

After nearly two decades of research, POSS is beginning to make its way into
industry, and a monograph on the subject provides an outline of synthesis methods and
applications of these compounds [Thompson 2011]. Companies such as Hybrid Plastics
and Sigma Aldrich supply a variety of POSS compounds in bulk quantities. If these
compounds are going to be used more in commercial products, it is important to
understand their influence on polymerization kinetics. For instance, knowing the gelation
time of a polymerizing liquid is of technical importance in the production of complicated
shapes by molding and/or extrusion, where minimization of viscous flow prior to gelation
reduces the extent to which a fracture might form.
Previous research on epoxy-amine-POSS systems have utilized empirical kinetic models and analytical methods to assess the polymerization kinetics [Gao et al. 2010, Wang et al. 2007], The scope of this study here is to provide a more physico-chemical understanding of the kinetics of polymerization of epoxy-amine mixtures containing epoxide-functionalized POSS. This thesis describes the kinetics of an epoxide-functionalized POSS reacted with one monoamine, two diamines, and one triamine by using calorimetry and dielectric relaxation spectroscopy. Both methods have been used extensively in the study of sol → gel reactive systems and relevant literature survey will be presented in the chapters of the respective methods. The thesis is divided into the following sections:

Chapter I – Introduction – contains the basic aspects of the thesis with relevant formalisms and literature review. It also describes the changes in physical properties observed during polymerization, the reaction kinetics, and the epoxy-amine reaction mechanism. This chapter also includes a brief review of the chemistry of POSS, and a literature review of POSS-epoxy systems in general. The chapter is concluded with a section on the properties of the materials used in this research.

Chapter II – Calorimetry – contains a more detailed literature review focusing on epoxy-amine reactions as studied by calorimetry, the theory of calorimetric technique, the equipment used, and the experiment conditions. The results section is divided into parts according to the different amines used, and the discussion covers the kinetics, thermodynamics and related physico-chemical interpretations of the results.
Chapter III – Dielectrics – contains a literature review of the technique as used for studying polymerization kinetics and dielectric relaxation, background on the theory of the experimental method, and the dielectric apparatus. The results section is divided into parts according to the different amines studied and the discussion covers the polymerization kinetics and relaxation processes observed in real time.

Chapter IV – Glass Transition and Entropy – contains a resolution of the currently debated issue of the entropy of glassy materials. Although the main study of this thesis is on glassy polymers, it is generally related to the thermodynamic properties of molecular glasses.

Chapter V – Conclusion – contains a summary of the calorimetric and dielectric investigation of the polymerization process with POSS in a mixture of epoxy and amine.

Part of this work has been published and part has been submitted for publication, as follows:


1.1 Background and Literature Review of Epoxies

1.1.1 Epoxy reaction scheme and kinetics

The two basic polymerization reactions are (i) condensation reactions, which leads to the release of another molecule (a condensate) and (ii) addition polymerization, which does not lead to the release of a condensate. Sub-categorical reactions are (iii) step growth polymerization, occurring from the transfer of pairs of electrons between reacting ions and molecules and (iv) chain growth polymerization which occurs from the reaction of free-radicals [Young and Lovell 1991].

The epoxy thermoset forms by addition reactions via step growth polymerization, and the overall reaction mechanism is considered complex because of the multiple reaction paths that are possible [Rozenberg 1986, Barton 1985]. The reaction mechanism between a diepoxide and a diamine can be simplified in the following manner: A proton from the primary amine (R-NH₂) bonds to a lone electron pair from the -O- of the oxirane ring, forming a hydroxyl group (OH). Concurrently, the epoxide ring opens as a nitrogen atom covalently bonds with the terminal C atom of the epoxide. Thus, the amine group acts as an electrophile in donating a proton to –O–, and as a nucleophile when it donates an electron pair as it bonds to the carbon. Next, the remaining H atom of the newly formed secondary amine (-NH- in the R-NH-(CH₂)-CH-OH-R’) reacts in the same manner with a terminal epoxide of another epoxy molecule to form a tertiary amine. Thus, by losing its amine protons, a multifunctional amine molecule provides a cross-link to several epoxide-bearing molecules. The number of OH groups formed is theoretically equal to the number of covalent bonds formed between the N and C atoms. The
diepoxide-diamine reaction scheme is depicted in Fig. 1.1. A linear chain polymer is formed when a monoamine is reacted with a diepoxide, [Johari and Pascheto 1995].

There are generally four reactions that may occur in an epoxy-amine mixture: (i) primary amine – epoxy (ii) secondary amine – epoxy (iii) epoxy – hydroxyl (etherification) and (iv) epoxy-epoxy (homopolymerization). Etherification is usually significant only when the quantity of epoxide is in excess of amine-protons, or if polymerization is performed at elevated temperatures [Riccardi and Williams 1986, Apicella et al. 1984, Düsek et al. 1977]. Homopolymerization generally occurs in the presence of Lewis base catalysts, such as a tertiary amine, and at low temperatures [Bryne et al. 1983].

Primary amines react with an epoxide to form a hydroxyl group and a secondary amine. The reactive segment of the secondary amine thus formed is comparatively more sterically hindered than that of the primary amine, and is expected to have a lower reactivity. The influence of the preceding primary amine reactions on the kinetics of the secondary amine reaction is referred to substitution effect, and is measured as the ratio of reaction constants ($k_2/k_1$). A ratio of 0.5 is the conventional value of equal reactivity, as opposed to 1, since the number of primary-amines is double that of secondary amines. A positive substitution effect would yield ratios of $k_2/k_1$ greater than 0.5, and less than 0.5 for negative substitution. The experimental findings on substitution effect has been questioned [Rozenberg 1986], however, Mijović et al. (1992) argued in favour of a temperature-independent negative substitution effect based on experiments with phenyl
Figure 1.1 – Epoxy-Amine reaction scheme. The new bonds formed are shown in bold and the hydrogen bonds are shown by vertical dotted lines.
glycidyl ether as a model compound and a monoamine. A molecule’s electrical characteristics and electrophilicity also determines the reaction kinetics. Mijović et al. (1994) have experimentally shown that amines with electron-donating substituents decrease the activation energy for reaction, which increases the polymerization rate, while electron-withdrawing substituents slow the kinetics. Electron-withdrawing substituents, such as the sulfonate group in diamino diphenylsulfone, have been found to increase the negative substitution effect [Mijović et al. 1994, Girard-Reydet et al. 1995].

Knowledge of substitution effects is of fundamental importance because kinetics influences the molecular arrangement of the vitrified structure. In an ideal case where \( k_2/k_1 \) equals 0.5, a completely random network polymer would form. When the primary amine reactivity is greater than that of secondary amines, a predominantly linear polymer forms first, followed by subsequent growth of the network structure. Thus, the morphology and properties of a polymer are determined by the polymerization kinetics.

**1.1.2 Changes in properties during polymerization**

Polymerization of an epoxy-amine mixture is a spontaneous (irreversible and exothermic) process. When a network structure forms, it may first lead to the formation of a gel, known as gelation, or sol \( \rightarrow \) gel conversion, and then vitrification or gel \( \rightarrow \) glass transition [Aronhime and Gillham 1986]. At the beginning of polymerization, the kinetics obey classic reaction laws, and the rate constant, \( k \), varies with temperature according to the Arrhenius equation

\[
k = A e^{\frac{-E_a}{RT}},
\]

(1.1)
where $A_0$ is the pre-exponential factor, $E_a$ is the activation energy, $T$ is temperature and $R$ is the gas constant, 8.13 J/(mol K). The precursors form a low molecular weight mixture and the macroscopic viscosity, $\eta$, is initially low, and the reaction is mass controlled, but as clusters of the network structure form and grow in size, $\eta$ increases. Consequently, diffusion of the reacting molecules slows, which in turn slows the progress of the reaction. At a particular instant during this process, the activation energy of diffusion exceeds that of the reaction, $E_D > E_R$, and the reaction rate becomes dependent on the rate of diffusion, and neither $k$ nor $\eta$ vary linearly with $1/T$. When this happens the reaction is said to be diffusion-controlled, and the distribution of reaction rates broadens in the diffusion-controlled regime [Wise et al. 1997]. The term negative feedback is used to describe this relationship between the polymerization rate and molecular diffusion, i.e., the decrease in one slows the other, and as the liquid vitrifies isothermally, polymerization becomes unobservable on the experiment’s time scale [Johari and Mangion 1991]. If the vitrified material is heated, $\eta$ decreases, the diffusion rates increase, and polymerization occurs again after a temperature is reached at which a chemical equilibrium between reacted and unreacted species is established. This process is known as post-curing or post-polymerization. Only a negligible portion of monomers do not react, and the network structure is assumed to be complete after the material has been post-cured.

Molecular diffusion and structure is determined by the (short range) van der Waals forces in the early stages of polymerization, and later molecular diffusion is controlled by the flexibility of, and ability to rotate about, the newly-formed covalent
bonds. The formation of covalent bonds causes the density of the liquid to increase with polymerization time, and enthalpy, $H$, and entropy, $S$, decrease as well [Johari 2004]. Thus the changes observed with the polymerization time are qualitatively similar to those observed on supercooling a liquid to form a glass [Khouri and Johari 2011]. The glass transition temperature, $T_g$, the temperature at which a material transforms from a glass to a liquid/rubber on cooling, is an intrinsic property dependent on the free volume and molecular mobility [Gibbs and DiMarzio 1957]. As the cross-link density increases, volume decreases, and consequently the $T_g$ increases as molecular mobility is reduced.

The instant (after polymerization has begun), when the irreversible sol-gel transformation from a viscoelastic liquid to a low elasticity solid of shear modulus on the order of $10^6$ Pa occurs is called the gelation time, $t_{gel}$. The viscosity formally approaches infinity at the gelled state and the polymer behaves as a Bingham solid. On a molecular basis, a gel forms at the instant when the covalent network extends throughout the volume of the sample, which typically occurs at a 55 to 80 % conversion of epoxides [Flory 1941, 1953, Stockmayer 1943]. At higher conversions, the shear modulus is in the $10^9$ Pa range, which is typical of the glassy state. The critical conversion and gel point determined empirically is found to agree with the predicted value from gelation theory, and this has been interpreted to mean that the reaction mechanism is uniform, or in other words, the reaction is homogenous [Düsek et al. 1975, Düsek 1986]. Some inhomogeneous reactions persist due to auto catalysis, however, extensive cyclization which results from an alternative reaction is not typical of diamine-diepoxy mixtures [Rozenberg 1985].
Although vitrification usually occurs after gelation, it is possible for it to occur prior. Studies of the mechanical spectra during polymerization have shown these sequences which has led to the construction of the Time-Temperature-Transformation (TTT) diagrams for isothermal polymerization by Gillham and co-workers [Enns and Gillham 1983, Aronhime and Gillham 1986]. These diagrams depict regions of the phases (liquid, gel, glass, decomposed) that exist at a given temperature in the domain of time.

Overall, the changes in physical properties of the liquid mixture from polymerization are well understood. Changes in dielectric [Johari 1994a, Johari et al. 1996, Ferrari et al. 1999, Mangion and Johari 1990, Parthun and Johari 1995, Tombari et al. 1999], calorimetric [Wasserman and Johari 1993], viscosity [Choy and Plazek 1986], acoustic [Alig et al. 1994] and mechanical [Aronhime and Gillham 1986, Wasylyshyn and Johari 1999] properties during polymerization of epoxy-amine mixtures have been investigated, by varying factors that influence polymerization rate, such as pressure, temperature, stoichiometry and phase separation.

1.2 Background and Literature Review of Silsesquioxanes

1.2.1 History, synthesis and properties

Silsesquioxane chemistry dates back to the 1940s, starting with the first documented isolation by Scott (1946). (Although, apparently these compounds were first synthesized in the late 1800s but were misidentified for silicone derivatives of carboxylic acids as described by Lickiss and Rataboul [2008]). There are two methods (or stages of reactions) used for producing silsesquioxanes. The first is the creation of the
silsesquioxane backbone by the formation of new Si-O bonds. Reaction techniques include thermolysis of polyorganyl silsesquioxanes, co-condensation of organosilicon monomers, but the traditional route is from the complete hydrolytic condensation of trifunctional organosiloxanes:

$$nXSiY_3 + 1.5nH_2O \rightarrow (XSiO_{3/2})_n + 3nHY$$

where $X$ is a stable substituent (e.g. methyl or phenyl group) and $Y$ is a reactive group (e.g. halide, -OH, -OR, -OCOR, etc...). The second synthesis method (or stage) involves substitution of functional groups bonded to the Si-atoms of the silsesquioxane, instead of the formation of new Si-O bonds. A variety of compounds functionalized with epoxide, amine, norbornyl, halide, alcohol, and isocynate have been reported in literature [Schwab et al. 2008].

Silsesquioxanes may exist in random, ladder, or caged structures (polyhedrals), as shown in Fig. 1.2, and their formation depends upon the synthesis route. Caged structures are conventionally labeled as $Tn$, where $T$ denotes polyhedral silsesquioxane, and $n$ the number of Si-atoms/vertices, which is generally an even number ranging from 2 to 12. Research groups have focused more than $T8$ structures as they are thermodynamically more stable than $T6$ and $T4$, which are difficult to synthesize and tend to form the $Si_4O_4$ rings of a $T8$ structure as opposed to the more strained $Si_3O_3$ rings. A thorough review on the properties of the different $Tn$ structures can be found in a paper by Lickiss and Rataboul (2008). The average diagonal Si—Si bond length of a $T8$ molecule is approximately 5.5 Å, and the average length of the Si—O bond is approximately 1.62 Å. The Si-O-Si and O-Si-O angles are approximately 147.3° and 109.4°, respectively. The
diameter of the T8 core is 0.5 – 0.7 nm [Gnanasekaran et al. 2009], and with the substituents the whole molecule may be as large as 2nm. POSS compounds are non-volatile, which is an advantage for its use in an age where political lobbying for the reduction of ecosystem-disrupting compounds is strong. T8 structures are thermally stable, especially under ambient conditions, although Si-O bonds are susceptible to cleavage in the presence of a strong base [Lickiss and Rataboul 2008]. T10 structures are formed by cleaving a T8 molecule and chemically reacting it with additional organosiloxane. Ladder-structures are highly resistive to oxidation, and although most research on silsesquioxanes has been conducted with ladder and T8 structures, the cage structures have received more attention because their symmetrical shape and ease of modification makes it easier to understand their effects on the properties of polymers. Baney et al. (1995) and Pielichowski et al. (2006) have written comprehensive review papers on silsesquioxane chemistry.

1.2.2 POSS in polymers

Inorganic compounds such as silica are used to improve polymer properties by combining the toughness and elasticity of polymers with the thermal stability and oxidative resistance of ceramics, forming hybrid materials [Ellis 1993, Macan et al. 2006]. In the literature, POSS is described as ‘the smallest possible silica particle’, or in other words, the smallest possible structure of a silica molecule. One may consider it as a composite of nanosilica embedded in a polymer matrix. Silsesquioxanes are an alternative to silica nanoparticles as filler materials, and are considered advantageous on the grounds that they can be tailored with organic substituents, increasing its miscibility
in the organic base material. Single phase processing, as opposed to the two-phase separation that occurs with silica, also reduces the amount of residual stress caused by significant differences in thermal expansion coefficients of silica and the polymer [Low 1990].

Figure 1.2 – Silsesquioxane structures (Li et al. 2007)
POSS can be physically crosslinked, grafted, or co-polymerized. Grafting a cage-structured POSS on a linear polymer chain would require that only one of its substituents be the same as the reactive group of the monomer. This is referred to as a monofunctional POSS, and any compound containing more than two reactive groups is called multifunctional. The potential ability to improve thermal and mechanical properties depends on the fraction of POSS in the mixture and its substituents, which effect miscibility [Haddad et al. 2001]. Mono- and multifunctionalized epoxide or amine POSS have been studied in thermosetting systems, exhibiting enhanced properties such as increased $T_g$ [Lee et al. 1998, Li et al. 2008] although a decrease in $T_g$ has also been reported [Takala et al. 2008, Ragosta et al. 2009]. Monofunctional molecules have a strong tendency to aggregate in large domains and form crystallites [Abad et al. 2003]. The nature, number, and size of the non-reactive substituents [Hadded et al. 2001, Zucchi et al. 2007], as well as pre-reacting POSS with the amine before adding the epoxy resin [Zucchi et al. 2007], influences the degree of miscibility and phase separation in the organic matrix. For example, aminophenyl and nitrophenyl functionalized POSS, both containing nitrogen, were found to form a homogeneous mixture with Diglycidyl ether of Bisphenol A (DGEBA), while a phenyl-functionalized POSS was immiscible in DGEBA [Ni et al. 2004]. Another study showed monofunctional POSS with –phenyl and –cyclopentyl substituents formed large crystal domains, while monofunctional POSS with isooctyl substituents showed considerable aggregation, but not crystal domains in a DGEBA-poly(oxypropylene) diamine mixture [Matějka et al. 2004]. By contrast, a multifunctional epoxide-POSS was found to be compatible with the same diamine, and it
has been suggested that increasing POSS functionality leads to a greater amount of dispersion of POSS and homogeneity in the epoxy-amine mixture, as indicated by WAXS results of fully cured epoxies [Matějka et al. 2004]. Ironically, it is the very formation of these crystalline domains, in which POSS serves as physical crosslinks, that tends to increase the rubbery modulus of elasticity and thermal stability [Strachota et al. 2004]. Alkyl-functionalized POSS compounds arrange in a manner such that the substituents envelope the Si-O cage and that the molecule can be assumed spherical [Larsson 1960]. Even at such low percentages, aggregation and crystal domains of multifunctional POSS on the nanoscale have been observed [Mariani et al. 2007, Strachota et al. 2007], but these nanocomposites are relatively homogenous [Matějka et al. 2004].

The general consensus in literature on the kinetics of epoxide-POSS, is that its reactivity towards amines is slower than that of DGEBA, as the bulkiness of the molecule increases steric hindrance [Strachota et al. 2007, Gao et al. 2010]. Tailoring the silsequioxane with either amine or epoxide also has an effect on kinetics with the same curing agent. Zhang et al. (2007) reported that the kinetics of a 10% mol amine functionalized POSS with DGEBA and diamino diphenyl sulfone (DDS) is slightly slower and its activation energy is slightly higher than those of the neat mixtures. Ragosta et al. (2009) used Fourier transform near infra-red spectroscopy to study the kinetics of DGEBA with DDS and found that the reactivity of 20 wt % octa glycidyl-POSS mixture is comparable with that of the neat DGEBA-DDS. By contrast, Hao et al. (2011) showed that a 1 – 5 wt % epoxide functionalized POSS exhibited faster kinetics with DDS. Only
a few papers report an increase in kinetics for epoxide-POSS in epoxy-amine mixtures (Ramirez et al. 2008, Hao et al. 2011, Khouri and Johari 2011).

Since the silsesquioxane core is inert, any catalytic behavior would be due to the functional groups. In this respect, Perrin et al. (2009) found by using calorimetry, that quaternary ammonium salt functionalized POSS acts as a catalyst in DGEBA - poly(oxypropylene)-amine mixtures. Ghaemy et al. (2007) concluded that the –OH groups from the added nanosilica particles accelerated the rate of reaction between DGEBA and a triamine, and similar effects were observed by Fu et al. (2003) which they related to the silanol groups of the phenyl-trisilanol POSS they used. A review paper on the subject of POSS nanocomposites has been written by Li et al. (2001).

1.3 Materials

In this study, four curing agents, one epoxy resin, and one POSS compound were used. Physical properties and the structures of the compounds are given in Table 1.1. Here, \( f \) refers to the functionality in terms of chemical reactive groups, i.e., the amine protons and epoxides, and EEW denotes the epoxide equivalent weight, the mass of the sample that contains one mole of the epoxide group.

The curing agents are: (i) Diethylene triamine (DETA), a symmetrical molecule which contains two terminal primary amines and one secondary amine in the centre between two ethyl groups, (ii) Isophorone diamine (IPDA), an aromatic compound which contains one alicyclic and one aromatic primary amine for a total of two primary amines, (iii) Ethylene diamine (EDA), a relatively small molecule with two primary amines separated by an ethyl group, and (iv) Hexylamine (HA), a linear chain molecule with
only one primary amine. DETA, EDA and HA, each 98%+ purity, were purchased from Sigma-Aldrich Chemicals, and IPDA, 99% purity, was purchased from Fluka. All the four amines are low viscosity liquids at room temperature.

The epoxy resin used was Diglycidyl ether of Bisphenol A (DGEBA). It contains two glycidyl groups (oxirane ring and a linear chain ether group) situated at each end, and is sold under the commercial product name Epon 828, which was supplied by Miller-Stephenson. The specified number of repeat units, \( n \), of Epon 828 is 0.14. For preparing mixtures, an average mol wt of 380 g/mol [LeMay et al. 1986] was used.

A multifunctional glycidyl-POSS compound, EP0409 was purchased from Hybrid Plastics (USA). According to the manufacturer, it contains 0.2 – 0.9 % wt of impurity water in dissolved and/or suspended state, which amounts to 50 % mole percentage. At 298 K, the viscosity of the as-received POSS (containing < 1 % water) is 48 Poise and that of DGEBA is 110 – 150 Poise. EP0409 (POSS) has a distribution of molecular sizes of approximately 60% T10, 18% T12, and 4% T8, as reported by the manufacturer and Li et al. (2008). The balance consists of larger sized silsesquioxanes, which may not be completely condensed cages. To estimate the average mol wt and the average \( f \) of POSS, the ‘larger sized, less defined silsesquioxanes’ were assumed to be cage-structure molecules comprised of 9 % T14 and 9 % T16. The calculated average mol wt is 1867 g/mol and \( f \) is 11.2. The same value of \( f \) was found by Li et al. (2008) from measurements of rubber modulus for the same POSS product. Using this molecular weight and the manufacturer-specified density of 1.25 g/ml at 298 K, the average diameter of the POSS molecule is estimated as 1.7 nm. The size of the molecule will be referred to as 2 nm-
size. By the same calculation, the diameter of a DGEBA molecule was estimated as ~1 nm.

All compounds were used as received. Table 1.2 lists the different mixtures prepared from each amine and the technique used for its study. The mixtures are labeled by the molar percentage of POSS, denoted as \( x_{\text{POSS}} \), which is calculated with respect to the sum of epoxide-containing compounds POSS and DGEBA as,

\[
x_{\text{POSS}} = \frac{n_{\text{POSS}}}{n_{\text{POSS}} + n_{\text{DGEBA}}} \times 100\%
\]  

(1.2)

where \( n_{\text{POSS}} \) and \( n_{\text{DGEBA}} \) are the number of moles of the respective compound in the mixture. Stoichiometric mixtures contain equal amounts of reactive groups, epoxides \([E]\) and amine protons \([nH]\), i.e. \([E] = [nH]\). Weight percentages of POSS in the mixtures are given with respect to the total mass,

\[
w_{\text{POSS}} = \frac{m_{\text{POSS}}}{m_{\text{POSS}} + m_{\text{DGEBA}} + m_{\text{min \, e}}} \times 100\% .
\]

(1.3)

Table 1.1 - POSS mole percentage and weight percentage of the mixtures, and the experimental technique used to study the four amine-DGEBA-POSS systems.

<table>
<thead>
<tr>
<th>( x_{\text{POSS}} ) (mol %)</th>
<th>% epoxides from POSS</th>
<th>( w_{\text{POSS}} )</th>
<th>HA</th>
<th>DETA</th>
<th>IPDA</th>
<th>EDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2.0</td>
<td>10</td>
<td>7.0</td>
<td>8.0</td>
<td>1.4</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>20</td>
<td>14.2</td>
<td>16.2</td>
<td></td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>25</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.7</td>
<td>40</td>
<td>28.9</td>
<td>33.2</td>
<td>-</td>
<td>34.1</td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.2</td>
<td>60</td>
<td>-</td>
<td>50.9</td>
<td>-</td>
<td>52.4</td>
<td></td>
</tr>
<tr>
<td>34.9</td>
<td>75</td>
<td>-</td>
<td>26.6</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>76.7</td>
<td>89.0</td>
<td>79.9</td>
<td>91.7</td>
<td></td>
</tr>
<tr>
<td>DSC</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Dielectrics Spectroscopy</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2 - Chemical structures and properties of the amines, epoxy resin and POSS

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Property</th>
<th>Density (298 K)</th>
<th>Mol Wt</th>
<th>f</th>
<th>Other Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene triamine (DETA)</td>
<td>density (298 K) = 0.955 g/mL, mol wt = 103.2, f = 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isophorone diamine (IPDA)</td>
<td>density (298 K) = 0.920 g/mL, mol wt = 170.3, f = 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene diamine (EDA)</td>
<td>density (298 K) = 0.899 g/mL, mol wt = 60.1, f = 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexylamine (HA)</td>
<td>density (298 K) = 0.766 g/mL, mol wt = 101.2, f = 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epon 828 : Diglycidyl ether of Bisphenol A (DGEBA)</td>
<td>density (298 K) = 1.16 g/mL, viscosity (298 K) = 110 – 150 P, EEW = 186-192, f = 2, n = 0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxirane, 2-[[3-(trimethoxysilyl)propoxy]methyl] – hydrolyzed EP0409 (POSS)</td>
<td>density (298 K) = 1.25 g/mL, viscosity (298 K) = 48 P, EEW = 167, f = 11.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 2 : Calorimetry

2.1 Literature Review

2.1.1 Epoxy reaction kinetic models

Based on the work of Schecter et al. (1956), and as well on his own, Smith (1961) proposed that the epoxy-amine reaction occurs via a third order mechanism, and concluded that a reaction with only those two molecules was insufficient. Impurities capable of hydrogen bonding, such as hydroxyl groups, catalyze the polymerization reaction by forming a hydrogen bond with the oxirane-oxygen, creating a dipole favorable for the nucleophilic addition of amine towards an oxirane carbon. This results in a ter-molecular complex which can be seen in the second step in Fig. 1.1. The hydroxyl formed from the reaction has the same catalytic effect as proton-donor impurities, and this effect is referred to as autocatalysis. In 1970, Horie et al. proposed the following kinetic model based on the reaction mechanism given by Smith:

\[ \frac{d\alpha}{dt} = (K_1' + K_1\alpha)(1 - \alpha)(1 - R\alpha) \]  (2.1)

where \( \alpha \) is the fraction of reacted epoxides, \( R = [E_o]/2[H_o] \), \([E_o]\) and \([H_o]\) are the epoxide and amine proton concentrations at the start of the reaction. \( K_1 = k_1 a_o e_o \) and \( K_1' = k_1' a_o c_o \), \( k_1 \) is the rate constant of the autocatalytic reaction between epoxy, primary amine and the hydroxyl formed, while \( k_1' \) is the rate constant of the reaction of epoxy, primary amine and contaminant proton donor. \( a_o \) and \( c_o \) are the initial concentrations of primary amine and proton-donor impurities. Based on DSC measurements, a generalized expression for the kinetics [Barton 1985] has been found to fit experimental data adequately:
\[
\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^n
\]  
(2.2)

where \( m \) and \( n \) are the empirical parameters related to the reaction order \((m + n = \text{overall reaction order})\) and \( K_1' \) and \( K_1 \) are proportional to the reaction rate constants for catalytic and auto-catalytic reactions. Other notable models include that of Sourour and Kamal (1976), expressed as

\[
\frac{d\alpha}{dt} = (K_1' + K_2\alpha)(1 - \alpha)(B - \alpha)
\]
(2.3)

where \( B \) is the initial ratio of amine protons to epoxides, \([\text{H}_o]/[\text{E}_o]\). \( K_1' = k'_1 c_o \), where \( c_o \) is the concentration of impurity proton-donors and \( K_2 \) is the reaction constant of the auto-catalytic reactions. In both the Horie and Sourour and Kamal models, equal reactivity between the primary and secondary amine is assumed. Side-reactions are not taken into account. Equations 2.2 and 2.3 have been found to be valid up to an \( \alpha \)-value of approximately 60\% - 70\% [Sourour and Kamal 1976, Horie et al. 1970], when the reaction mechanism is still mass-controlled.

Models incorporating diffusion-controlled reaction rates have been proposed [Corezzi et al. 2010]. In the Corezzi model, as well as in Eqns. 2.2 and 2.3, \( k_1 \) and \( k_1' \) are assumed constant throughout polymerization, which is only valid when the reaction is mass-controlled \((\alpha \sim 60\% - 70\%)\). The inconsistency between the classical models and experimental results at higher \( \alpha \) values is overcome by introducing a diffusion-corrected rate constant, \( k_d(\alpha) \), and by taking into account a crossover that occurs between \( k_c \), the mass-controlled rate constant and \( k_d \). \( k_c \) and \( k_d \) are related to the overall, or effective rate constant by \( k_{i,-1} = k_{c,i,-1} + k_{d,i,-1} \), as proposed by Rabinowitch (1937). \( k_d \) is approximately
inversely proportional to the average diffusion coefficient $D(\alpha)$, which is related to the structural relaxation time $\tau(\alpha)$. Corezzi and co-workers (2010) argue that the $D-\tau$ relationship is most accurately expressed by the power law equation, $D \tau^\xi = \text{constant}$, where $\xi$ is a fractional exponent and is assumed constant during the course of polymerization. Since $k_d^{-1} \approx D$, the diffusion rate constant is approximated by the change in $\tau$ with $\alpha$. The irreversible increase in structural relaxation time of a polymerization process has been rationalized in terms of a reduction in configurational entropy, and the change in $k_d$ with $\alpha$ is expressed as $k_d = k_0 \exp\left(-\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)$, where $\alpha_0$, $k_0$ and $B$ are constants. $\alpha_0$ is equal to $1/f$, where $f$ is the average epoxy functionality. Corezzi et al.’s model is a modification of Eqn. 2.3, and is expressed as

$$\frac{d\alpha}{dt} = (K_1' + K_\alpha \alpha^m)(1 - \alpha)^{n/2}(r - \alpha)^{n/2}. \quad (2.4)$$

By using the previously defined relationships between rate constants, $k_c$, $k_d$, and $\tau$ and $\alpha$, Eqn. 2.4 expands to

$$\frac{d\alpha}{dt} = \left[\frac{k_{c1}}{1 + k_{c1} \exp\left(\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)} + \frac{k_c'}{1 + k_c' \exp\left(\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)}\right] \alpha^m (1 - \alpha)^{n/2}(r - \alpha)^{n/2}. \quad (2.5)$$
2.1.2 Model-free analytical methods using DSC measurements

It is possible to investigate polymerization kinetics without a reaction model by only using DSC measurements. The kinetics of a condensed phase reaction may be analyzed from the following equations for either isothermal or non-isothermal conditions:

\[ \text{Isothermal: } \frac{d\alpha}{dt} = f(\alpha)k(T) \]  \hspace{1cm} (2.6)

\[ \text{Non-isothermal: } q \frac{d\alpha}{dT} = f(\alpha)A\exp\left(\frac{-E_a}{RT}\right) \]  \hspace{1cm} (2.7)

where \( k \) is the temperature dependent reaction constant according to the Arrhenius equation and \( q \) is the heating rate \((dT/dt)\). \( f(\alpha) \) is a reaction model function, and for expoy-amine systems the equation \( f(\alpha) = (1 - \alpha)^n \) generally provides a good fit with empirical data. It should be noted that Eqns. 2.6 and 2.7 are equivalent. Execution of Eqn. 2.7 requires measurements at different \( q \) be performed on the same material, and it is presumed that kinetic parameters are independent of \( q \) [Budrugeac et al. 2001].

The principle behind the model-free methods, is that at a specific \( \alpha \) the reaction rate is solely dependent on \( T \) [Sbirrazzuoli et al. 2006]. For a chemical reaction where \( E_a \) is \( \alpha \)-dependent, \( E_a \) may be determined from either the differential and the integral forms of Eqns. 2.6 and 2.7, however, the two forms yield slightly different values [Budrugeac et al. 2001]. The integral form developed by Ozawa (1965) and Flynn and Wall (1966) (obtained from manipulations of Eqn. 2.7, which will not be discussed here), leads to the following expression:
\[
\ln q = \ln \frac{AE_a}{Rg(\alpha)} - 5.33 - 1.05 \frac{E_a}{RT} \tag{2.8}
\]

where \(g(\alpha)\) is a function equal to \(AE/(qRp(E/RT))\) and \(p(E/RT)\) is the temperature integral, but neither \(g(\alpha)\) nor \(p\) are required for the evaluation of \(E_a\). At a fixed \(\alpha\), a plot of \(\ln q_i \) vs. \(T_i^{-1}\) gives a straight line whose slope equals \(-1.05E_a/R\) from which \(E_a(\alpha)\) can be estimated. Application of Eqn. 2.8 is simple, yet often yields values of \(E_a\) that may require correction [Flynn 1983]. \(E_a\) varies with \(\alpha\) for complex reactions and remains constant for single step reactions.

### 2.2 Experimental

#### 2.2.1 DSC assembly and measurements

Differential Scanning Calorimetry (DSC) allows one to measure heat exchanged with a reservoir during a physical process (glass transition, crystallization, melting etc…) or chemical reaction, and the temperature range over which the process occurs. The two common types of DSC assemblies are the ‘heat flux’ and ‘power compensation’ designs. In a heat flux DSC, the sample and reference pans reside in the same cell, on adjacent platforms. Power compensation DSCs are designed such that the reference and sample pan are heated in separate compartments. For this thesis, a turret-type heat flux DSC, was used to measure changes in heat from polymerization, and a schematic diagram of this DSC can be seen in Fig. 2.1. Turret-type DSC differs from conventional heat flux designs in the shape of the slab over which the sample and reference pans reside on. Advantages of this design include short heat conduction paths, which allows for faster thermal
responses, and minimized cross-talk between reference and sample [Höhne et al. 2003].

A thorough review on DSC designs and theoretical aspects can be found in a monograph by Höhne et al. (2003).

The DSC assembly can be described as follows: A sample and reference pan sit in a thermally insulated cell, on top of hollow, thin-walled metallic cylinders that serve as elevated platforms. The pans should be identical (composition, shape, size and mass) and can be open (uncrimped) or covered (crimped) when used. An inert gas is purged into the cell to maintain a chemically stable environment. Heat is supplied to the pans from the bottom of the furnace via a constantan alloy disc, diffusing though the jacket of the cylinders up to the top, where the pan is in contact with the cylinder. The theory behind this design is that there is a precise exchange of heat along a path of known thermal resistance, $R_D$ (e.g. heat along the constantan body, Item 3 in Fig. 2.1). Therefore, the temperature of the sample/reference and the heat provided to the pans can be correlated.
and quantified. The DSC measures the temperature difference between the sample and reference, $\Delta T$, which is proportional to the differential heat flow $dQ/dt$, $(dQ/dt) = \Delta T/R$.

Theoretical equations of heat flow measurements from heat flux DSCs can be found in Appendix A. The DSC can be operated in isothermal mode or in scanning mode by heating or cooling at a constant rate, $q$. Plots of $(dH/dt)_T$ vs. time and $(dH/dT)_q$ vs. Temperature are obtained from isothermal and scanning measurements, respectively. Changes in enthalpy are proportional to the area confined under the peaks of the $(dH/dt)_T$ and $(dH/dT)_q$ curves.

### 2.2.2 Experiment procedure and sample preparation

A Thermal Analysis DSC instrument, model Q100, was used for calorimetry experiments. The cell was purged with 99% pure, dry nitrogen at a constant rate of 50 mL/min. The DSC was calibrated regularly to maintain accuracy using indium and sapphire as standards for the temperature and cell constants. Measurements with an empty cell were taken often to assess the stability of the baseline. On one point, fluctuations appeared in the measurements, and this is elaborated on in Appendix D.

Uncrimped, aluminum pans of 10 mg nominal mass, approximately 5mm diameter, 2mm height and 0.1mm thickness were used as sample holders. To prepare the mixtures, DGEBA was weighed first in a small vial, followed by POSS, and the amine was the last compound to be added. Accuracy reading of the precision scale used for weighing the compounds is ± 0.002 g. The mixture was stirred for several minutes until the solution appeared completely homogeneous. A small portion was transferred from the stock sample into a pre-weighed aluminum pan, and the sample and reference (empty)
pans were weighed with a precision microscale of ± 0.01 mg accuracy. Sample sizes typically ranged from 10 – 25 mg. (Based on the author’s experience, a variation of 15 mg was not found to impact the results).

Polymerization by heating was performed at constant rates of 5, 10, 15, 20 and 30 K/min, starting from 303 K until a temperature was reached where the change in heat flow became negligible or undetectable. The stock sample was stored in a refrigerator at 278 K during the period over which these experiments were performed, which was less than 1 h. A freshly made mixture was used for studying the polymerization kinetics at a fixed $T$, denoted as $T_{\text{polym}}$. Immediately after isothermal polymerization, the samples were post-cured by heated from 303 K to 523 K at 10 K/min. The duration of the isothermal experiments for each amine-set was performed according to the amount of time required for the POSS-amine reaction to reach completion.

DETA mixtures were studied by ramp heating and isothermally at 323 K. EDA mixtures were only studied under isothermal conditions at 318 K, while IPDA was only studied under ramp conditions. IPDA was studied with both stoichiometric and non-stoichiometric ratios, while DETA and EDA were only studied under stoichiometric ratios. The stoichiometric samples are labeled as ‘DGEBA-POSS-amine’ and by the molar percentage of POSS in the mixture, denoted by $x_{\text{POSS}}$, which is calculated from Eqn. 1.2. The compositions ranged from the neat mixture (e.g. DGEBA-DETA) to a POSS-only mixture (e.g. POSS-DETA). Non-stoichiometric mixtures are labeled according to the ratio of [E] to [nH], denoted as $r$. 
2.3 Results

2.3.1 Analysis of DSC plots

The \((dH/dT)_q\) and \((dH/dt)_T\) curves of the epoxy reactions typically show one peak. The maximum reaction rate occurs at the temperature of the peak, \(T_{\text{peak}}\) [Kissinger 1957], or at least at a temperature slightly below \(T_{\text{peak}}\) [Reed et al. 1965]. The total heat evolved from the polymerization of a sample, \(\Delta H_{\text{polym}}\), is estimated by integrating the heat flow curves \((dH/dT)_q\) and \((dH/dt)_T\) with respect to a baseline. There are multiple choices of a baseline for the \((dH/dT)_q\) curves [Flynn 1993], and an example of the baseline used in the analysis performed here is given in Appendix C. Mathematically, the integration of the \((dH/dT)_q\) curves are expressed as

\[
\Delta H_q = \int_{T_{\text{onset}}}^{T_{\text{final}}} \left( \frac{dH}{dT} \right)_q \, dT
\]

\[
\alpha(T) = \int_{T_{\text{onset}}}^{T} \left( \frac{dH}{dT} \right)_q \, dT \quad \frac{\Delta H_q}{\Delta H_{\text{polym}}},
\]

where \(\alpha\) is the extent of reaction and is calculated as the ratio of accumulated heat released at a given temperature, to the total heat released for a complete reaction. It is known that vitrification from isothermal polymerization halts the chemical reaction before all available species have reacted. To determine the total heat of reaction and achieve full-conversion, it is necessary to post-cure the sample above its glass transition temperature. The extent of reaction for isothermal polymerization is calculated as
\[
\alpha = \frac{\int_{t_{polym}^0}^{t_{polym}^{plateau}} \left( \frac{dH}{dt} \right) dt}{\Delta H_{polym}}
\]  
(2.11)

\[
\Delta H_{polym} = \Delta H_{iso} + \Delta H_{post}
\]  
(2.12)

where \( \Delta H_{iso} \) and \( \Delta H_{post} \) are the enthalpy of isothermal polymerization and post-polymerization, respectively. The number of covalent bonds formed during the course of polymerization is estimated as \( n_{bonds}(t) = N_{lim} \times \alpha(t) \), where \( N_{lim} \) is the limiting number of reacting species.

### 2.3.2 DGEBA-POSS-DETA

Six stoichiometric mixtures of DGEBA-DETA with varying amounts of POSS were studied. The change in heat per unit temperature rise, \((dH/dT)_q\) and extent of reaction, \( \alpha \), from polymerization of the DETA mixtures by heating at fixed \( q \) are plotted against \( T \) in Figs. 2.2 to 2.7. The different curves are vertically displaced for clarity. The plots for DGEBA-POSS-DETA are qualitatively similar as they only show one peak. The reaction curves of the mixtures heated at 5 and 30 K/min are plotted in Fig. 2.8, which shows that the curves become broader and their height decreases as \( x_{POSS} \) is increased. Figure 2.9 shows plots of \( \alpha \) vs. \( T \) for the DETA mixtures polymerized at 5 and 30 K/min, and for \( q = 5 \) K/min, the curves appear in the following order from left to right: 2%, 10.7%, 4.3%, 0% and 100%. For \( q = 30 \) K/min, the curves appear in the following order from left to right: 2%, 21.2%, 4.3%, 0% and 100%. The 21.2% and 10.7% curves are
absent from Figs. 2.9 A and B to prevent crowding. The $\alpha$-axis in Fig. 2.9 starts from 0.4 since the curves do not show any cross over at lower values.

The polymerization kinetics of the mixtures, relative to each other, can be qualitatively assessed by comparing the $T$ (or time) in which $\alpha$ approaches unity. Figure 2.10 shows a plot of $T$'s against $x_{\text{POSS}}$ at which $\alpha$ reaches values of 0.4, 0.6, 0.8, and 0.98. At 5 K/min, $\alpha$ reaches 0.98 at 409 K for DGEBA-DETA, 302 K for the 2% mixture, 398 K for the 4.3 % mixture, 395 K for the 10.7 % mixture, 405 K for the 21.2 % mixture and 441 K for POSS-DETA. At 30 K/min $\alpha$ reaches 0.98 at 454 K for DGEBA-DETA, 434 K for the 2% mixture, 445 K for the 4.3 % mixture, 437 K for the 10.7 % mixture, 442 K for the 21.2 % mixture and 463 K for POSS-DETA. $\alpha$ for the 2 – 21% mixtures approaches unity before DGEBA-DETA, indicating that they polymerize faster, with the 2% mixture being the fastest. POSS-DETA polymerizes the slowest, and it can be said that POSS has a lower reactivity than DGEBA, which is consistent with findings by others [Teo et al. 2007, Strachota et al. 2007]. A U-shaped pattern is observed for a plot of $T(\alpha=0.98)$ against $x_{\text{POSS}}$ in Fig. 2.10 for heating rates of 5 and 30 K/min, and this graphically shows how the kinetics initially increase, reach a maximum, and then progressively decrease upon successive increase in $x_{\text{POSS}}$. 
Figure 2.2 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-DETA ($x_{\text{POSS}} = 0\%$), polymerized at three heating rates, and (B) corresponding extent of reaction.

Figure 2.3 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$), polymerized at four heating rates, and (B) corresponding extent of reaction.

Figure 2.4 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3\%$), polymerized at four heating rates, and (B) corresponding extent of reaction.

Figure 2.5 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7\%$), polymerized at four heating rates, and (B) corresponding extent of reaction.
Figure 2.6 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric DGEBA-POSS-DETA ($x_{\text{POSS}} = 21.2\%$), polymerized at four heating rates, and (B) corresponding extent of reaction.

Figure 2.7 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric POSS-DETA, polymerized at four heating rates, and (B) corresponding extent of reaction.

Figure 2.8 – Plots of $\frac{dH}{dT}$ against temperature for the six DETA mixtures polymerized at rates of (A) 5K/min and (B) 30 K/min. $x_{\text{POSS}}$ is indicated next to the curves.
Figure 2.9 – Extent of reaction plotted against temperature for the six DETA mixtures polymerized at a rate: (A) $q = 5\text{ K/min}$ and (B) $q = 30\text{ K/min}$. $x_{\text{POSS}}$ is indicated next to the curves.

Figure 2.10 – The temperature at which $\alpha$ reaches 0.4, 0.6, 0.8 and 0.98, plotted against $x_{\text{POSS}}$ for the sample heated at (A) 5 K/min and (B) 30 K/min.
Since DETA reacts slower with POSS than with DGEBA, a temperature of 323 K was selected for the isothermal polymerization study such that the cure would not be too slow with POSS nor too quickly with DGEBA. The selected temperature was chosen based on preliminary isothermal experiments with POSS-DETA and DGEBA-DETA at temperatures between 298 and 363 K whose plots can be found in Appendix C. Immediately after 180 minutes of polymerization at 323 K, the DETA samples were quenched to 303 K, held for a minute, and heated at 10 K/min to a final temperature of 523 K.

Plots of \((dH/dt)_T\) and \(\alpha\) vs. polymerization time, \(t_{polym}\), for the six DETA mixtures are shown in Fig. 2.11, where the \((dH/dt)_T\) curves have been vertically displaced for clarity. The initial decrease in \(dH/dt\) (increasing rate of heat released by the sample) is attributed to the formation of hydroxyl groups which autocatalyze the reactions. At longer \(t_{polym}\), the curve plateaus as the increase in viscosity renders the reactants immobile on the experimental time-scale. The \(t_{polym}\) at the exothermic minimum of the \(dH/dt\) curves decreases from 19.5 min for DGEBA-DETA to 17.7 min for the 2% sample, and thereafter moves to higher \(t_{polym}\), while the \(dH/dt\) curves broaden with further increase in POSS.

The post-polymerization \((dH/dT)_q\) curves are shown in Fig. 2.12 and have also been shifted vertically. The endothermic peaks seen at low \(T\) in the post-polymerization plots are from the softening of the vitrified material. The 2% mixture shows a more pronounced and narrower glass endotherm relative to the DGEBA-only mixture. With further addition of POSS this endotherm becomes smaller and eventually becomes
unobservable with the POSS-only mixture. This may mean the relaxations of POSS-DETA are slow and span over a broad temperature range or that a glassy material was never formed. The glass transition temperature, $T_g$, of the post-polymerized samples increases slightly with $x_{POSS}$, from 342 K for DGEBA-DETA to 346 for the 21.2% mixture.

As the material is heated through its glass transition, the viscosity decreases and the reactants begin to diffuse at a rate sufficient to overcome the $E_a$ of reaction. This is shown by an exotherm, and $(dH/dT)_q$ plateaus as the reaction comes to completion. The temperature of the post-polymerization exothermic minimum, $T_{min}$, decreases from 379 K for DGEBA-DETA to 365 K for the 2% sample, and thereafter increases with a further increase in POSS. The exothermic portion of the 2% mixture is narrower compared to that of DGEBA-DETA, and an increase in POSS causes the exotherm to broaden and become more shallow. Values for the enthalpy of reaction of the DETA samples polymerized both isothermally and non-isothermally are listed in Table 2.1.

Figure 2.11 B shows $\alpha$ plotted against polymerization time, $t_{polym}$, and the 2% mixture achieves a final $\alpha$ of 0.85, and it is evident that it polymerizes faster than DGEBA-DETA, which achieves a final $\alpha$ of 0.81. By adding more POSS the kinetics appears to decrease, then increase up to 10.7 %, and thereafter progressively decreases until only POSS is reacted with DETA - which reacted the slowest, similar to the ramp-cure measurements. Although it is less evident whether the remaining mixtures actually vitrify before DGEBA-DETA, they do reach a higher $\alpha$, and $\alpha (t_{polym} \to \infty)$ increases from 0.85 for the 2 % mixture to 0.91 for the 21 % mixture, but then decreases to 0.88 for
POSS-DETA. The peak temperature from ramp-heat, $T_{\text{peak}}$, and post-polymerization glass and peak temperature, $T_g$ and $T_{\text{min}}$, are plotted with respect to $x_{\text{POSS}}$ in Fig. 2.13.

Table 2.1 - Enthalpy of Reaction (in J/g) of stoichiometric DGEBA-POSS-DETA.

<table>
<thead>
<tr>
<th>$x_{\text{POSS}}, %$</th>
<th>Ramp cure, $q$ [K/min]</th>
<th>Isothermal (323 K) + Post-polym (10K/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>504</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>488</td>
<td>500</td>
</tr>
<tr>
<td>4.3</td>
<td>486</td>
<td>491</td>
</tr>
<tr>
<td>10.7</td>
<td>484</td>
<td>487</td>
</tr>
<tr>
<td>21.2</td>
<td>473</td>
<td>475</td>
</tr>
<tr>
<td>100</td>
<td>462</td>
<td>440</td>
</tr>
</tbody>
</table>

Figure 2.11 – (A) A plot of $dH/dt$ plotted against polymerization time for six stoichiometric [DGEBA-POSS]-DETA samples isothermally cured at 323 K, where $x_{\text{POSS}}$ is indicated next to the curves, and (B) corresponding extent of reaction.
Figure 2.12 – A plot of \(\frac{dH}{dT}\) against temperature for the post-polymerization at 10 K/min of six stoichiometric [DGEBA-POSS]-DETA mixtures, and \(x_{\text{POSS}}\) is indicated next to the curves.

Figure 2.13 – (A) The plots of the temperature of the exothermic minimum, \(T_{\text{min,exo}}\), for DGEBA-POSS-DETA polymerized by ramp heating at rates of 5, 10, 20 and 30 K min rate against \(x_{\text{POSS}}\). (B) The plots of the onset temperature of glass-softening, \(T_g\), and of the peak temperature, \(T_{\text{peak,iso}}\) observed by post-polymerization at 10 K/min.
2.3.3 DGEBA-POSS-IPDA

Three sets of IPDA mixtures were studied. The first was a series of non-stoichiometric DGEBA-IPDA mixtures, where the ratio of epoxides [E] to amine protons [nH], \( r \), was varied from 1.25 to 1.0 (stoichiometric), 0.75, 0.5 and 0.33. The second was POSS-IPDA mixtures of varying \( r \) (= 1.33, 1.25, 1.0, 0.8, and 0.75). The third was stoichiometric DGEBA-POSS-IPDA mixtures of varying POSS content whose compositions are listed in Table 1.1. Only polymerization by ramp heating was performed for the three sets of mixtures.

\((dH/dT)_q\) and \(\alpha\) curves for the polymerization of DGEBA-IPDA mixtures are plotted against \( T \) from Figs. 2.14 to 2.17. The curves for \( r = 1.0 \) (Fig. 2.14), \( r = 1.25 \) (Fig. 2.15) and \( r = 0.75 \) (Fig. 2.16) show one large exothermic peak, and a shoulder feature at a higher temperature, and the corresponding \(\alpha\)-plots kink due to this shoulder. The curves were de-convoluted to obtain estimates of the temperatures of the peaks, which are listed in Tables C1 – C2 in Appendix C, and the analysis shows that the distance between the two peaks increases with heating rate. Figure 2.18 shows the reaction curves at 5 and 30 K/min, and when \( r > 1 \), the shoulder appears more pronounced and the primary peak appears at a lower \( T \) relative to the stoichiometric mixture. As \( r \) is decreased below unity, the distance between the two peaks decreases and the shoulder completely merges with the larger exothermic peak when \( r < 0.75 \). From the \(\alpha\)- \( T \) plots of the DGEBA-IPDA mixtures in Fig. 2.19, it is evident that the overall kinetics decreases systematically with increasing \( r \), that is, \(\alpha \rightarrow 1\) sooner for \( r = 0.33 \) and then for \( r = 1.25 \), and this trend is consistent from heating rates of 5 to 30 K/min.
Figure 2.14 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r = 1$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.15 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r = 1.25$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.16 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r = 0.75$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.17 – (A) $dH/dT$ plotted against temperature of stoichiometric DGEBA-IPDA ($r = 0.33$) polymerized at four heating rates and (B) corresponding extent of reaction.
**Figure 2.18** – (A) A plot of $\frac{dH}{dT}$ against temperature for DGEBA-IPDA polymerized at a rate, $q = 30$ K/min, where the numbers next to the curves are the epoxide-to-amine ratio, $r$ and (B) corresponding plot at $q = 5$ K/min.

**Figure 2.19** – (A) Extent of reaction, $\alpha$, plotted against temperature for DGEBA-IPDA polymerized at a rate, $q = 30$ K/min, where the numbers next to the curves are the epoxide-to-amine ratio, $r$ and (B) corresponding plot at $q = 5$ K/min.
Plots of \((dH/dT)_q\) and \(\alpha\) curves of stoichiometric DGEBA-POSS-IPDA mixtures are shown in Figs. 2.20 to 2.23. \((dH/dT)_q\) and \(\alpha\) plots for the mixtures polymerized at 5 and 30 K/min are shown in Fig. 2.24 and 2.25. A shoulder from the DGEBA-IPDA reaction is present in the \((dH/dT)_q\) plots of low \(x_{\text{POSS}}\) mixtures but diminishes with an increase, and vanishes when \(x_{\text{POSS}} > 16\%\). Figure 2.25 shows that the 2\% POSS mixture reaches a fully cured state earlier than the neat mixture at both rates. At 5 K/min, the 15.2\% mixture is slower than the neat, but still faster than the POSS-only, while the kinetics of the 35\% mixture is comparable with the POSS-only when \(\alpha > 0.9\). At 30 K/min, the kinetics of the 15\%, 35\% and POSS-only IPDA mixtures are comparable. It appears that the stoichiometric POSS-IPDA reaction sensitive to heating rate.

The \((dH/dT)_q\) curves for the reaction of stoichiometric POSS-IPDA (Fig. 2.26) only show one peak, as do the non-stoichiometric POSS-IPDA mixtures of ratio \(r = 1.33, 1.25, 0.8\) and 0.75 shown in Figs. 2.27 to 2.30. Figure 2.31 shows the \((dH/dT)_q\) curves for the POSS-IPDA mixtures cured at 5 and 30 K/min. With an increase in \(r\), the peaks become narrower and increase in height. Figure 2.32 shows \(\alpha\) plotted against \(T\) for the POSS-IPDA mixtures at 5 and 30 K/min. At 30 K/min, the excess amine mixtures approach unity prior to the amine-deficient mixtures. At 5 K/min, a systematic variation in kinetics with \(r\) is not seen, and yet, all the plots merge simultaneously as \(\alpha \to 1\). Initially the kinetics of the mixtures are different, but the plots converge at \(\alpha \approx 0.95\), and the mixtures all seem to reach completion at the same time. It can therefore be said that amine-rich POSS-IPDA mixtures cure faster when heated at high rates. The \(\Delta H\) values for all IPDA mixtures are listed in Table 2.2.
Figure 2.20 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}} = 2\%$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.21 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}} = 5.6\%$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.22 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}} = 15.2\%$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.23 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric DGEBA-POSS-IPDA ($x_{\text{POSS}} = 35\%$) polymerized at four heating rates and (B) corresponding extent of reaction.
Figure 2.24 – (A) Plots of $\frac{dH}{dT}$ against temperature for the six stoichiometric DGEBA-POSS-IPDA polymerized at rates of (A) 30 K/min and (B) 5 K/min. $x_{\text{POSS}}$ increases in the direction of the arrows.

Figure 2.25 – (A) Extent of reaction plotted against temperature for the six stoichiometric DGEBA-POSS-IPDA polymerized at a heating rate of (A) 30 K/min and (B) 5 K/min. $x_{\text{POSS}}$ is indicated by the arrows.
Figure 2.26 – (A) $\frac{dH}{dT}$ plotted against temperature of stoichiometric POSS-IPDA ($r = 1$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.27 – (A) $\frac{dH}{dT}$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 1.33$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.28 – (A) $\frac{dH}{dT}$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 1.25$) polymerized at four heating rates and (B) corresponding extent of reaction.

Figure 2.29 – (A) $\frac{dH}{dT}$ plotted against temperature of non-stoichiometric POSS-IPDA ($r = 0.8$) polymerized at four heating rates and (B) corresponding extent of reaction.
Figure 2.30 – (A) \(\frac{dH}{dT}\) plotted against temperature of reaction of non-stoichiometric POSS-IPDA (\(r = 0.75\)) polymerized at four heating rates and (B) corresponding extent.

Figure 2.31 – (A) Plots of \(\frac{dH}{dT}\) against temperature for the five POSS-IPDA mixtures polymerized at a heating rate of (A) 30 K/min and (B) 5 K/min. The epoxide-to-proton ratio, \(r\), is indicated next to the curves.

Figure 2.32 – Extent of reaction plotted against temperature of DGEBA-IPDA mixtures polymerized at a rates of (A) 30 K/min and (B) 5 K/min. The numbers next to the curves are the epoxide-to-amine ratio, \(r\).
Table 2.2 - $\Delta H_{\text{polym}}$ (in J/g) for DGEBA-IPDA, DGEBA-POSS-IPDA, and POSS-IPDA polymerized at different heating rates.

<table>
<thead>
<tr>
<th></th>
<th>DGEBA -- IPDA</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r (= \frac{[E]}{[nH]});$</td>
<td>5 K/min</td>
<td>10 K/min</td>
<td>20 K/min</td>
</tr>
<tr>
<td>0.33</td>
<td>324</td>
<td>317</td>
<td>325</td>
<td>339</td>
</tr>
<tr>
<td>0.75</td>
<td>417</td>
<td>403</td>
<td>413</td>
<td>407</td>
</tr>
<tr>
<td>1</td>
<td>426</td>
<td>437</td>
<td>433</td>
<td>404</td>
</tr>
<tr>
<td>1.25</td>
<td>347</td>
<td>336</td>
<td>374</td>
<td>361</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>DGEBA -- POSS -- IPDA</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_{\text{POSS}}, %$</td>
<td>5 K/min</td>
<td>10 K/min</td>
<td>20 K/min</td>
</tr>
<tr>
<td>2</td>
<td>439</td>
<td>418</td>
<td>392</td>
<td>391</td>
</tr>
<tr>
<td>5.6</td>
<td>409</td>
<td>407</td>
<td>403</td>
<td>392</td>
</tr>
<tr>
<td>15.2</td>
<td>394</td>
<td>408</td>
<td>396</td>
<td>401</td>
</tr>
<tr>
<td>34.9</td>
<td>414</td>
<td>426</td>
<td>411</td>
<td>411</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>POSS -- IPDA</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r (= \frac{[E]}{[nH]});$</td>
<td>5 K/min</td>
<td>10 K/min</td>
<td>20 K/min</td>
</tr>
<tr>
<td>0.75</td>
<td>445</td>
<td>444</td>
<td>399</td>
<td>426</td>
</tr>
<tr>
<td>0.8</td>
<td>471</td>
<td>431</td>
<td>427</td>
<td>409</td>
</tr>
<tr>
<td>1</td>
<td>409</td>
<td>395</td>
<td>394</td>
<td>375</td>
</tr>
<tr>
<td>1.25</td>
<td>340</td>
<td>335</td>
<td>327</td>
<td>334</td>
</tr>
<tr>
<td>1.33</td>
<td>298</td>
<td>288</td>
<td>270</td>
<td>332</td>
</tr>
</tbody>
</table>

### 2.3.4 DGEBA-POSS-EDA

EDA mixtures were isothermally polymerized at 318 K for 360 minutes, and immediately after the samples were cooled to 303 K, and then heated at 10 K/min to 523 K. The $(dH/dt)_T$ curves are plotted in Fig. 2.33, and they broaden and become more shallow as $x_{\text{POSS}}$ is increased, while the $\alpha$ curves in Fig 2.33B show that $\alpha_{\text{vit}}$ increases from 0.86 for DGEBA-EDA to 0.93 for POSS-EDA. The $\alpha$-curves of the 0% and 2% mixtures are comparable, with the neat mixture polymerizing slightly faster. It is evident that the 4.3% sample polymerizes the fastest, and POSS-EDA the slowest. The post-polymerization $(dH/dT)_q$ curves, as seen in Fig. 2.34, show a distinct glass endotherm for the low POSS samples but not for POSS-EDA. The $T_g$ increases slightly from 336 – 338 K and the temperature of the exotherm minimum, $T_{\text{min}}$, remains between 373 – 374 K for all four samples. The exotherms appear to become shallower and stretch out over a larger
temperature range with an increase in POSS. The total polymerization enthalpy increases from 478 J/g (DGEBA-EDA) to 490 J/g for \( x_{POSS} = 2\% \), and there after decreases. Enthalpy for isothermal and post-polymerization are reported in Table 2.3.

Table 2.3 - \( \Delta H_{polym} \) (in J/g) of stoichiometric DGEBA-POSS-EDA cured at 318K.

<table>
<thead>
<tr>
<th>( x_{POSS} ), %</th>
<th>Isothermal (318 K) + Post-polym (10K/min)</th>
<th>Isothem.</th>
<th>Post polym.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>390</td>
<td>88</td>
<td>478</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>420</td>
<td>70</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>410</td>
<td>77</td>
<td>487</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>349</td>
<td>49</td>
<td>398</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.33 – (A) Plots of \( dH/dt \) against polymerization time for DGEBA-POSS-EDA samples polymerized at 318 K and (B) corresponding extent of reaction.
Figure 2.34 – Post-polymerization dH/dT plots against temperature of the DGEBA-POSS-EDA mixtures, heated at 10 K/min.

2.3.5 Sources of error

The $\Delta H_{\text{polym}}$ values contain errors from composition due to mass measurements and impurities within the reagents. Sample and reference pans were uncrimped when used in the DSC which would result in heat loss by convection from the purge gas, and mass loss by evaporation of compounds with low vapor pressures and impurities with low boiling temperatures. Such losses cannot be easily be accounted for in the calculations of $\Delta H$. Errors from DSC measurements and calibration constants typically amount to no more than 2%. The small endothermic peaks and spikes that appear between 318 and 345 K, either before or during the decrease in the $(dH/dT)_q$ plots of IPDA mixtures, are likely due to impurities from IPDA evaporating, as they only appear in the DGEBA-IPDA and POSS-IPDA curves but not with any of the DETA samples.
2.4 Discussion

2.4.1 Endothermic effect from impurities in POSS

The POSS product (EP0409) was heated and cooled in a continuous cycle from 220 K to 523 K at 10 K/min so that its $T_g$ would be determined. A $T_g$ was not found, however, a broad endothermic peak was instead observed during the first scan, but was absent in the second. The same behaviour was observed for repeat-experiments using fresh POSS samples at starting temperatures of 273 and 303 K. Plots of $\frac{dH}{dT}$ for these scans in Fig. 2.35 show that the endotherms end at approximately 475, 490 and 460 K, and $\Delta H$ was estimated at 24.8, 16.3 and 17.6 J/g for measurements of increasing starting temperature. The spike at 425 K in Fig 2.35 C is an artifact of the pan shifting.

The absence of the endotherm in the second scans means the event could be combination of evaporation, crystal melting and molecular disaggregation. EP0409 contains < 1 wt % of water, either in dissolved or suspended state, according to the manufacturer. The enthalpy of evaporation of water is 2.26 kJ/g (40.65 kJ/mol) at 373 K and, in a mixture water has a lower vapor pressure and a greater boiling point. If attributed entirely to the evaporation of water, 17.6 J/g would correspond to 1 g of water in 142 g of POSS or ~ 0.7 %, which is within the specified amount of < 1 % water. Therefore the endothermic peak is attributed to loss of water from the sample. Assuming the enthalpy change of 17.6 J/g is entirely due to water evaporation, this would amount to ~ 4 % of the POSS-DETA reaction enthalpy of 450 J/g. Furthermore, water, or any –OH containing impurity compounds, will catalyze the amine-epoxide reaction.
Figure 2.35 – Plots of dH/dt against temperature of EP0409 heated at 10 K/min, at a starting temperature of (A) 220 K (B) 273 K and (C) 300 K. The enthalpy change associated with the endotherm is given in the plots.

[Schecter et al. 1956, Smith 1961], and is an important source of error to be considered. Since evaporation occurs below room temperature, a significant portion of water is expected to evaporate during the preparation of POSS-samples, which takes several minutes. Therefore, any errors in the reaction enthalpy and extent of reaction associated with water contamination are assumed negligible. The POSS product is stored in a refrigerator at 273 K. It has a viscosity of 48 Poise at 298 K while water has a viscosity of 1 CP at the same temperature, and since 1 % wt equates to a mole fraction of ~ 0.5, the true viscosity of POSS is likely to be greater than 48 P.
2.4.2 Effects of POSS on thermodynamic properties

The values from Table 2.1 have been converted to units of kJ/mol epoxide (also equal to mol amine-proton) and plotted in Fig 2.36, which shows that $\Delta H_{\text{polym}}$ of the DETA mixtures polymerized by ramp-heating, $\Delta H_q$, decreases from $109.7 \pm 2.5$ kJ/(mol epoxide) for DGEBA-DETA to $83.9 \pm 3.5$ kJ/(mol epoxide) for POSS-DETA, amounting to maximum error of $\pm 4.1\%$. These $\Delta H_q$ values lie close to, and are in the range of values typically observed for epoxy-amine systems ($100 – 120$ kJ/mol), which is close to the heat released of the epoxy ring opening [Rozenberg 1986]. Enthalpy change from isothermal polymerization, $\Delta H_{\text{iso}}$, decreased from $84.6 \pm 2.9$ kJ/(mol epoxide) to $65.5$ kJ/(mol epoxide) for 100 mole % POSS. Post-polymerization enthalpy, $\Delta H_{\text{post}}$, decreased with POSS, in the range of $16.1 \pm 5.5$ kJ/mol.

The sum of $\Delta H_{\text{iso}} + \Delta H_{\text{post}}$ is either slightly less or equal to $\Delta H_q$ for DETA-mixtures, and any differences between the two have been explained by the different reaction mechanisms that are dependent on the curing condition [Wasserman and Johari 1993]. The non-catalytic reaction has a higher $E_a$ compared to the autocatalytic reaction, and competition between the mechanisms varies according to the curing method. The non-catalytic is both thermodynamically and sterically favoured at higher temperatures [Riccardi et al. 1984] as the formation of a ternary complex becomes difficult. It has been experimentally shown that $E_a$ from ramp polymerization is different than isothermal polymerization, although it can be shown to be close to using a dynamic version of the Arrhenius equation [Prime 1973].
A decrease in $\Delta H$ is also observed with the stoichiometric EDA and IPDA samples. $\Delta H_{\text{polym}}$ of DGEBA-EDA is 98.0 kJ/mol, 99.3 kJ/mol for the 2% mixture, 97.5 kJ/mol for the 4.3% mixture, and 72.2 kJ/mol for POSS-EDA. The average $\Delta H_q$ of the stoichiometric DGEBA-IPDA is 100.5 ± 1.4 kJ/(mol epoxide) and 82.4 ± 3.7 kJ/(mol epoxide) (amounting to 4.5 % error) for POSS-IPDA, as seen in Fig. 2.37. IPDA mixtures containing more than 16 % mol POSS show a systematic trend with $q$, where a higher $\Delta H$ is observed at slower heating rates. This trend is only observed with the 16%, 35% and 100% DGEBA-POSS-IPDA mixtures, and not with the DGEBA-IPDA, DGEBA-DETA or POSS-DETA.

Figure 2.36 – Enthalpy of reaction of DGEBA-POSS-DETA (in kJ / mole epoxide) plotted against $x_{\text{POSS}}$, for the different polymerization conditions.
Figure 2.37 – Enthalpy of reaction of DGEBA-POSS-IPDA, (in kJ / mole epoxide), plotted against \( x_{\text{POSS}} \), for four heating rates.

Figure 2.38 – Enthalpy of reaction of POSS-IPDA, (in kJ / mole epoxide), plotted against the epoxide-to-amine proton ratio, \( r \), for four heating rates.
Non-stoichiometric POSS-IPDA mixtures show a decrease in $\Delta H_q$ with increasing number of epoxides, as $r$ is increased from 0.8 to 1.33 and the maximum $\Delta H$ occurs at a ratio of 0.8 ($95.6 \pm 5.5$ kJ/(mol epoxide)) - see Figure 2.38.

DSC studies on epoxy-amine-POSS systems have also shown that $\Delta H$ decreases when POSS content is increased while maintaining stoichiometry [Mariani et al. 2007, Xiao et al. 2007]. Since the enthalpy change is less for the POSS-only mixtures, this means that the energy of formation of the covalent bond between the epoxide terminal C and the amine nitrogen is less (i.e. the bond formation is less exothermic) for POSS than for the epoxy resin. If the energies of the unreacted states of the POSS-only and diepoxide-only mixtures were the same, the energy of the polymerized state with POSS would be higher than that of the polymerized state with DGEBA. If the energies of the unreacted mixtures differed, the energy of the polymerized states would be such that the decrease is less for the polymerized state with POSS than it is with the diepoxide. This can be verified by specific heat measurements of the reactants and products.

The energy released from breaking the oxirane ring is the dominant source of the total enthalpy change in the entire polymerization process. Electrical characteristics and energetic stability of the epoxy molecule also influence the net $\Delta H_{polym}$. In other words, the chemical nature of the non-reactive segments of the reactants affect the initial and final energy states. Studies with hyper-branched polymer (HBP) epoxies, which can be thought of as analogous structures to POSS, suggest that $\Delta H$ per bond of HBP mixture can be $\sim 20$ kJ/mol less than that of a DGEBA mixture [Mezzenga et al. 2000].
difference of 25 kJ/(mol epoxide) is observed between POSS-EDA and DGEBA-EDA in the study here.

Since the functionality of DETA, IPDA, and EDA is 5, 4 and 4, a maximum of $5N_A$, $4N_A$, and $4N_A$ covalent bonds would be formed from a stoichiometric mixture of 1 mol of respective amine, where $N_A$ is Avogadro’s number. Given that the energy change is dependent on the size and electrical characteristics of the reactants, one can imagine the possibility that $\Delta H$ per bond formed might vary in a successive manner as the macromolecule grows. If $\Delta H$ per bond does not change according to the previous number of covalent bonds formed, then the decrease in $\Delta H_{polym}$ with POSS would indicate that its net energy loss is indeed less than that of DGEBA. This can be investigated by determining if $\Delta H_{polym}$ scales with POSS. Scaled estimates of $\Delta H_{polym}$ from DETA mixtures were computed using the equation:

$$\Delta H_{scaled} = \left[ x_{DGEBA} \times (\Delta H_{q,avg} (DGEBA-DETA)) + x_{POSS} \times (\Delta H_{q,avg} (POSS-DETA)) \right]/100$$  

(2.13)

The enthalpy values calculated from Eqn. 2.13 are shown in Table 2.4, and the difference between the scaled and average empirical values are less than 8 %, which is within experimental errors. It is therefore assumed that the enthalpy change on bond formation with DETA is independent of macromolecule size, and that the polymerization enthalpy is additive.
Table 2.4 - Average values of $\Delta H_q$ of the DGEBA-POSS-DETA mixtures and corresponding scaled values estimated using Eqn. 2.13.

<table>
<thead>
<tr>
<th>$\chi_{\text{POSS}}$ (%)</th>
<th>$\Delta H_q,\text{average}$ (kJ/mol epoxide)</th>
<th>$\Delta H_{\text{scaled}}$ (kJ/mol epoxide)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>109.7</td>
<td>109.7</td>
<td>0</td>
</tr>
<tr>
<td>2.0</td>
<td>103.8</td>
<td>109.2</td>
<td>5.2</td>
</tr>
<tr>
<td>4.3</td>
<td>101.2</td>
<td>108.6</td>
<td>7.3</td>
</tr>
<tr>
<td>10.7</td>
<td>100.9</td>
<td>106.9</td>
<td>5.9</td>
</tr>
<tr>
<td>21.2</td>
<td>97.5</td>
<td>104.2</td>
<td>6.8</td>
</tr>
<tr>
<td>100</td>
<td>83.9</td>
<td>83.9</td>
<td>0</td>
</tr>
<tr>
<td>Non-stoichiometric DGEBA-DETA</td>
<td>107.9</td>
<td>109.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

It is also plausible that the decrease in $\Delta H$ may be a result of an incomplete reaction with POSS-epoxides. Ramirez et al. (2008) reported that some epoxide rings from their multi-glycidyl POSS did not react in a mixture with DGEBA and a diamine, based on FTIR spectroscopy experiments. Figures 2.36 and 2.37 show $\Delta H_q$ of the POSS-only mixtures vary significantly, greater than the 2 % variance limit of samples from the same batch, without any systematic trend in $q$, indicating that the repeatability of POSS-only polymerization is poor. An explanation for this is that an excess of POSS creates a significant degree of steric hindrance, and such an effect may vary if the extent of aggregation differed between samples. Agglomeration would cause epoxides to be enveloped, preventing them from being able to react, and thus, the measured $\Delta H_{\text{polym}}$ would be less than its theoretically obtainable value. However, incomplete reaction is unlikely since the mixtures are polymerized by ramp heating, which typically drives the reaction towards near completion, as well as by post polymerizing samples that have been vitrified by isothermal polymerization.
Using the integral form of the isoconversional method (Eqn. 2.8), by plotting $\ln q_i$ vs. $1/T_i$, the activation energy has been estimated for $\alpha = 0.4, 0.6,$ and $0.8$. The values are listed in Table 2.5. The linear fit for $x_{\text{POSS}} = 2$ % at $\alpha = 0.8$ is poor and $E_a$ for that mixture can be discarded. For fixed values of $\alpha$, $E_a$ initially decreases with $x_{\text{POSS}}$ but then increases when $x_{\text{POSS}} > 10.7$ %. When $\alpha$ of epoxy-amine reactions is less than $0.6 - 0.7$, the reaction constants typically obey the Arrhenius law, and therefore, a lower $E_a$ therefore signifies faster polymerization rates, and thus, the isoconversional analysis validates the initial interpretation of the reaction kinetics from Figure 2.10.

Autocatalysis increases the reaction rate and $E_a$ has generally been shown to decrease with $\alpha$ [Vyazovkin and Sbirrazzuoli 1996], however, Table 2.5 shows that $E_a$ increases with $\alpha$ for each DETA mixture, which is contrary to the relationship often reported in literature. Gao et al. (2010) performed ramp-heating polymerization experiments with POSS and an anhydride, and by using the Kissinger method [Kissinger 1957], they found $E_a$ to decrease with $\alpha$. They also reported that $E_a$ and gelation temperature of the nanocomposites varied unsystematically with POSS and were slightly lower than those values from the neat mixture. Hao et al. (2011) on the other hand, reported an increase in $E_a$ with $\alpha$ for a multi-glycidyl POSS-DGEBA-DDS mixture, and found an increase in kinetics when silsesquioxane content was low. Vyazovkin and Sbirrazzuoli (1996) suggested that an increasing dependence of $E_a$ with $\alpha$ is possible if the activation energy of the reaction with an impurity HX is less than the activation energy of the autocatalytic reaction. Since $E_a$ increases with $\alpha$ for both DGEBA-DETA and POSS-DETA, impurities from the commercial hardener might be the cause, but in
order to validate this claim, the same isoconversional analysis was applied to a different system, DGEBA-IPDA and POSS-IPDA. Table C.3 in Appendix C lists $E_a$ as a function of $\alpha$ for DGEBA-IPDA and POSS-IPDA obtained from the isconversional analysis, which shows that $E_a$ increases with $\alpha$ for DGEBA-IPDA and decreases with $\alpha$ for POSS-IPDA. Vyazovkin and Sbirrazzuoli (1996) reported a decrease in $E_a$ with $\alpha$ for DGEBA-IPDA, however, their hardener came from a different manufacturer and was composed of two stereoisomers. On this account, changes of $E_a$ with $\alpha$ are less likely to be impurity based, but rather on the reaction mechanism itself.

Table 2.5 - Estimated activation energy values of the DGEBA-POSS-DETA mixtures using the isoconversional method.

<table>
<thead>
<tr>
<th>$x_{\text{poss}}$ (mol %)</th>
<th>$E_a(\alpha = 0.4)$ [kJ/mol]</th>
<th>$E_a(\alpha = 0.6)$ [kJ/mol]</th>
<th>$E_a(\alpha = 0.8)$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60.3</td>
<td>63</td>
<td>69.6</td>
</tr>
<tr>
<td>2.0</td>
<td>59</td>
<td>59.5</td>
<td>53.4*</td>
</tr>
<tr>
<td>4.3</td>
<td>58.4</td>
<td>59.4</td>
<td>60.5</td>
</tr>
<tr>
<td>10.7</td>
<td>59.5</td>
<td>59.5</td>
<td>65.6</td>
</tr>
<tr>
<td>21.2</td>
<td>61.9</td>
<td>64.7</td>
<td>66.1</td>
</tr>
<tr>
<td>100</td>
<td>70.4</td>
<td>72</td>
<td>76</td>
</tr>
</tbody>
</table>

2.4.3 Influence of POSS on polymerization kinetics

Understanding the influence of POSS on the kinetics of the DGEBA-IPDA reaction might be easier by first considering just the DGEBA-IPDA reactions. The peak and shoulder in the heating scans of stoichiometric DGEBA-IPDA (Fig. 2.14) are attributed to differences in reactivity of the secondary (RR’NH) and primary (RNH$_2$) amines, with the low temperature peak corresponding to the faster reaction of the primary amines [Sabra et al. 1986, Mounif et al. 2009]. Furthermore, IPDA contains one aliphatic
and one alicyclic primary amine, and the difference between their reactivity further complicates the reaction mechanism [Pichaud et al. 1999, Núñez et al. 1996], and the same is expected for secondary amines.

When the epoxides are in excess \((r > 1)\), the primary peak appears at a lower \(T\) than with the stoichiometric mixture, and the shoulder in Fig. 2.15 shifts to higher temperatures as if the addition of DGEBA slows the secondary amine reaction and increases the difference between the rates of reaction. Conversely, when \(r < 1\), the shoulder in Figs. 2.16 and 2.17 is observed at lower temperatures, and at \(r < 0.75\) it merges entirely with the low-temperature peak. When \(r < 0.5\), the probability of secondary amine reactions is reduced because the primary amines react faster and the epoxides are more likely to be completely consumed before having the chance to react with any secondary amines.

As the silsesquioxane content in a DGEBA-POSS-IPDA mixture is increased, a reduction in the shoulder is observed. It shifts to lower temperatures and merges entirely with the primary peak when \(x_{\text{POSS}}\) exceeds 35 \%, in a manner similar to DGEBA-IPDA as \(r\) is decreased. While this may seem that increasing \(x_{\text{POSS}}\) has the same phenomenological effect as changing stoichiometric ratio, that conclusion is incorrect. A shoulder is not visible with any of the off-stoichiometric POSS-IPDA mixtures, and it can be concluded that the alicyclic and aliphatic primary and secondary amines have similar (but not necessarily equal) reactivities towards POSS-epoxides. Therefore, the decrease in the shoulder of the POSS-containing DGEBA-IPDA mixtures is due to the change in the relative reactivities of alicyclic and aliphatic primary and secondary amines.
The curves in Figure 2.12 show how POSS affects post-polymerization after vitrification of DETA samples polymerized at 323 K. The material is heated through its glass-transition temperature, whereby the material softens while maintaining the covalent bonds previously formed. This is made evident by an endothermic peak of varying sharpness and the peak height is determined by (i) the broadness of the $T_g$ endotherm, (ii) any structural relaxation of the polymerized state during heating and the consequent overshoot in the specific heat due to enthalpy recovery, and (iii) growth of the macromolecule and the consequent loss of enthalpy immediately after $\eta$ of the liquid has decreased on heating. Processes (i) and (ii) are physical in nature, reversible and are observed for all chemically stable glasses. Process (iii) is chemical in nature, irreversible and is observed when chemical reactions occur. Peak height increases on initial addition of POSS substitution for DGEBA but then decreases and vanishes when DGEBA has been completely replaced by POSS.

The exotherm minimum shifts first to a lower $T$ and thereafter gradually to a higher $T$ as shown in Fig. 2.13. $\Delta H$ for post-polymerization decreases with $x_{\text{POSS}}$, and this indicates that the POSS-containing samples achieve a higher extent of reaction (Fig. 2.11) in comparison to the DGEBA-DETA mixture, i.e., it is easier to form an almost infinitely connected covalent bond network with POSS. This is further evidenced from the DGEBA-POSS-EDA isothermal polymerization study, whose plots of $dH/dt$ and $\alpha$ against $t_{\text{polym}}$ are shown in Fig. 2.34. $\alpha$ for DGEBA-EDA plateaus at a value of 0.86 after ~160 minutes of polymerization. After the same amount of time, the $\alpha$ reached by the 4.3% POSS mixture is 0.88, and it reaches a final value of 0.91 after 211 minutes of
polymerization. $\alpha$ of POSS-EDA remains lower than that of DGEBA-EDA up until the 165th minute of polymerization, crossing over at $\alpha = 0.86$ and increases to 0.92 until the 360th minute. In short, EDA and DETA samples isothermally polymerized with small amounts of POSS might gel faster and achieve a higher extent of reaction sooner than the neat mixture, but may take longer to vitrify. POSS-only mixtures achieve a higher $\alpha$ but polymerize slower than POSS-free mixtures. The increase in polymerization kinetics may be explained by some of the fundamental properties that govern chemical reaction rates, namely electrical characteristics, steric mobility, and translational mobility. For simplicity and to reduce redundancy, the discussion will be focused on DETA mixtures.

The U-shape pattern of $T(\alpha)$ vs. $x_{\text{POSS}}$ in Fig. 2.11 indicates that the balance of competing mechanistic factors changes at some critical $x_{\text{POSS}}$. The precise composition at which this happens is not important here; it is sufficient enough to determine what those factors are. The viscosity, $\eta$, at 298 K of POSS and DGEBA is 48 and 110 Poise, respectively. If the additivity rule for an ideal solution were to be valid for $\eta$ of a hydrogen-bonded ternary mixture, one would expect the diffusion coefficient of the DGEBA, DETA and POSS molecules in the unreacted mixture to increase with a decrease in $\eta$ as $x_{\text{POSS}}$ is increased. According to the activated complex theory for chemical reactions, chemical reactions occur when two entities come within a certain proximity to form an activated complex. When the probability is higher, or when the time taken for reaching such a distance is lower, the reaction is expected to occur faster. Therefore, assuming the additivity mixture rule of $\eta$, one would expect the polymerization rate to increase systematically by increasing $x_{\text{POSS}}$, and POSS-DETA
would polymerize the fastest. However, the plots of $\alpha$ in Fig. 2.10 show that only those mixtures with less than 21% POSS polymerize faster than DGEBA-DETA, while POSS-DETA polymerizes the slowest. This is due to the fact that these are non-ideal solutions, which do not obey the mixture rules of transport properties particularly when hydrogen-bonding occurs. The effect of impurity water on the $\eta$ of the POSS has already been discussed, and since a portion of the water evaporates during polymerization, the mixture’s macroscopic $\eta$ would instead increase with $x_{\text{POSS}}$. Moreover, dielectric studies on the effect of pressure on the rate of polymerization have shown polymerization may become faster as $\eta$ is increased on application of a hydrostatic pressure [Johari et al. 1996, Wasylyshyn and Johari 1997, Johari and Wasylyshyn 1999].

Steric hindrance is (correctly) cited as the reason for the lower reactivity of POSS towards amines [Strachota et al. 2007, Teo et al. 2007], however, this is only guaranteed to be valid for a POSS-only mixture. Hao et al. (2011) reported an increase in the reaction rate of stoichiometric DGEBA-DDS mixtures with 1 – 5% wt multiglycidyl POSS, and suspect that the glycidyl groups are softer than DGEBA, which is counter to the argument of reduced steric mobility. Another hypothesis lies with the electrical characteristics of the monomers. The average POSS molecule is ~1.7 nm and contains ~11 epoxides, and if the molecule is considered a perfect sphere, a volumetric density of 0.53 epoxides per nm$^3$ is computed based on the manufacturer specified density. By the same calculation, the epoxide density of DGEBA (~1 nm) is 0.46 epoxides per nm$^3$. Since the volumetric density of epoxides is marginally greater for POSS, it may therefore be reasonable to suspect enhanced autocatalytic activity. If the proximity of epoxides is
reduced, i.e. greater volume density, and coupled with softer chain groups, the probability that newly formed –OH groups will form an activated complex relatively sooner, increases.

In estimating the average size of a POSS molecule as 2 nm, the assumption was made that the substituent groups on the Si- vertices are folded such as to envelope the siloxane cage, and this view is held by others [Hao et al. 2011, Ramirez et al. 2008]. Therefore, even a stoichiometrically prepared mixture would resemble a non-stoichiometric mixture if activated complexes could not be formed with a significant number of POSS-epoxides. In the substituents’ unfolded state, the distance of approach for chemical reactions would vary from site to site, and it is not certain how the three types of molecules are distributed in either their pure or the mixed liquid states. Therefore, the discussion is restricted to the phenomenology of polymerization.

Ramirez et al. (2008) studied the kinetics of a multiglycidyl POSS-DGEBA-diamine mixture using FTIR and found that some of the POSS-epoxides in a 10% wt POSS mixture did not open during the reaction, yet its presence accelerated the opening of the diepoxy rings. Therefore, it seemed pertinent to further investigate whether all epoxides from POSS in the DETA mixtures chemically react. An amine-rich mixture was prepared with an [E]/[nH] ratio of 0.9, and this mixture is called the non-stoichiometric DGEBA-DETA mixture. It contains the same number of moles of DGEBA in the 2 % POSS mixture but is POSS-free. The ΔHq obtained for the non-stoichiometric DGEBA-DETA mixture is 107.9 kJ/(mol epoxide), and is comparable with its scaled estimate value of 109.7 kJ/(mol epoxide) by a difference of 1.6 %, and is slightly more than ΔHq =
103.8 kJ/(mol epoxide) for the 2% mixture ($\Delta H_{\text{scaled}} = 109.1$ kJ/mol). Plots of $\alpha$ against $T$ in Fig. 2.39 show that the non-stoichiometric mixture polymerized slower than the stoichiometric 2% mixture but faster than stoichiometric DGEBA-DETA. The relative kinetics of the stoichiometric and non-stoichiometric mixtures is consistent with earlier findings by calorimetry [Wasserman and Johari 1994] and dielectric measurements [Mangion et al. 1992, Ferrari et al. 1998] that amine-rich mixtures polymerize faster even though some partially reacted diamine persists in the polymerized mixture.

Although the buried POSS-epoxides might reduce the mixture to non-stoichiometric conditions, this effect would not increase kinetics, because the faster polymerization kinetics observed with excess amine mixtures is due to translational mobility. The amines used are less viscous than DGEBA, and therefore, $\eta$ decreases when the amount of amines is increased relative to the epoxides, which increases the diffusion coefficient of reactants and consequently the reaction constant. It is expected that the self-diffusion coefficients would depend on the relative amounts of the components in the polymerizing mixture.

The extent of the influence of impurity water on the kinetics was investigated by using a freshly prepared 2% POSS mixture. POSS was weighed first, and left at room temperature for 0.3 h. During this period, the sample lost 1% weight due to evaporation of water. DGEBA and DETA were then added to form a stoichiometric mixture which was then polymerized by ramp-curing. The results, denoted as the ‘dry’ sample, are included in Fig. 2.40. The dry sample polymerizes slower than the original sample, which
Figure 2.39 – Extent of reaction of stoichiometric DGEBA-DETA, non-stoichiometric DGEBA-DETA and its equivalent stoichiometric 2% POSS mixture polymerized at (A) 5 K/min and (B) 30 K/min.

Figure 2.40 – Extent of reaction of stoichiometric DGEBA-DETA, 2% DGEBA-POSS-DETA (wet), and 2% (dry) mixture polymerized at (A) 5 K/min and (B) 30 K/min
is expected as water catalyzes the reaction, but polymerizes faster than the POSS-free (DGEBA-DETA), thus providing further evidence that small quantities of multi-glycidyl POSS increases the polymerization rate. Based on the arguments and observations provided in the preceding paragraphs, the changes in the polymerization rate with POSS are due to the differences in steric hindrance, molecular mobility and autocatalytic effects.

2.4.4 Static heterogeneity of nanoscopic POSS and dynamic heterogeneity

The reaction mechanism at the onset of polymerization of a liquid mixture is mass-controlled, and the reaction constant $k$ and macroscopic $\eta$ vary with $T$ in an Arrhenian manner. The negative-feedback process between the macromolecule size and diffusion rate, as previously outlined in section 1.1.2, causes the reaction rate to decrease with time. When the mechanism becomes diffusion-controlled, the reaction rate is dependent on the rate of diffusion. In this regime the reactions can be modeled by Brownian diffusion in which the diffusing particles coalesce as they mutually approach, with the consequence that the particle size increases and the average diffusion coefficient, $D_{avg}$, decreases. The rate constant for a diffusion-controlled reaction between spherical solute molecules of radii $r_A$ and $r_B$ undergoing Brownian motion in a viscous liquid is related to their respective diffusivities [Smoluchowski 1916 and 1917], given by the relation:

$$k_{\text{diff}} = 4\pi(D_A + D_B)(r_A + r_B)$$  \hspace{1cm} (2.14)
where $D_A$ and $D_B$ are diffusion coefficients of species A and B. The $D_{\text{avg}}$ of a mass-controlled system is related to $\eta$ according to the Stokes-Einstein (S-E) equation:

$$D_{\text{avg}} = \frac{k_b T}{6\pi \eta r} ,$$  \hspace{1cm} (2.15)

where $k_b$ is the Boltzmann constant, $T$ is temperature, $\eta$ is viscosity and $r$ is the solute particle radius. Smoluchowki’s equation has been further expanded on by Waite (1957) and Calef and Deutch (1983) who replaced $D$ with the solvent viscosity, $\eta_s$, according to the S-E equation, rewriting Eqn. 2.14 as

$$k_{\text{diff}}(t_{\text{polym}}) = \frac{2RT}{3\eta_s(t_{\text{polym}})} \left[ \frac{(r_A(t_{\text{polym}}) + r_B(t_{\text{polym}}))^2}{r_A(t_{\text{polym}})r_B(t_{\text{polym}})} \right] ,$$  \hspace{1cm} (2.16)

where $R$ is the gas constant and the variables $\eta_s$, $r_A$ and $r_B$ of solute molecules increase with polymerization time. $k_{\text{diff}}$ is proportional to $[(r_A + r_B)^2/\eta_s r_A r_B]$, and in a polymerization process, $(r_A + r_B)^2$ increases more rapidly with $t_{\text{polym}}$ than $r_A r_B$. Therefore, for $k_{\text{diff}}$ to decrease with $t_{\text{polym}}$, $\eta_s$ must increase more rapidly than the term $[(r_A + r_B)^2/r_A r_B]$. When the reacting site of a molecule is enveloped by the non-reacting part of the remaining molecule, the reaction rate is additionally determined by the internal motions of that part of the molecule that shields the active site from reaction and it becomes difficult to establish a direct relation between the diffusion coefficients, $\eta_s$ and $k_{\text{diff}}$.

The gradual change from Arrhenius to a non-Arrhenius variation of $\eta$ with $T$ on supercooling a liquid has also been explained by postulating that heterogeneities develop in the dynamic properties of liquids [Ediger 1996, Mapes et al. 2006]. Heterogeneity is
characterized by domains that vary in mobility and diffusion rate, which can be several orders of magnitude different in two regions only a few tens of nanometers apart [Ediger 2000], resulting in a distribution of relaxation times and diffusion coefficients. When log(η) is linear with respect to 1/T, the product ηD_{avg} is constant (η = C/D_{av}, where C is the constant of proportionality according to the S-E equation). After a significant amount of heterogeneities develop, the measured viscosity is no longer predicted by the S-E, equation, and the system is said to be decoupled. Decoupling refers to the finding that ηD_{av} ceases to remain constant with changing T on supercooling as η increases, and the difference between the measured diffusion coefficient and that obtained from the S-E equation may be as much as two orders of magnitude [Mapes et al. 2006]. A plot of log(η) and log(C/D_{avg}) against 1/T for a supercooling liquid would initially show that the two increase along the same curve, but at the point of decoupling, log(C/D_{avg}) increases at a slower rate than log(η) (i.e. \( \frac{\partial(C/D_{avg})}{\partial T} < \frac{\partial\eta}{\partial T} \)).

Although these relationships were developed for physically and chemically stable liquids they can be extended to the analysis of polymerizing liquids [Khouri and Johari 2011]. The reversible increase in η and relaxation time τ by supercooling a liquid is qualitatively similar to the irreversible increase in η and τ from polymerization of a liquid at a fixed T. Application of the S-E and Smoluchowski equations can be used to provide an explanation of the changes in polymerization rate from the addition of the 2 nm-sized POSS. Since \( k_{diff} \) is inversely proportional to \( D_{avg} \), the DSC results of the DGEBA-POSS-DETA nanocomposites can be used to qualitatively predict the development of dynamic
heterogeneities and onset of decoupling. Figure 2.42 depicts changes in log($C/D_{avg}$) and log($\eta$) with $t_{polym}$ for DGEBA-DETA, the 2% POSS DGEBA-DETA mixture and POSS-DETA. The filled circles on the lines in Fig. 2.42 indicate the onset of decoupling or deviation from the S-E equation. $\eta$ of the unreacted mixtures increases with increasing amount of POSS on the assumption that the mixture is free of water and other impurities.

DGEBA-DETA is depicted as decoupling at the highest $\eta D_{avg}$ value and at a later stage in polymerization, because in the absence of POSS, dynamic heterogeneity develops intrinsically. The presence of the 2nm-static heterogeneity POSS molecules causes decoupling of the 2% mixture to occur sooner and at a lower $\eta D_{avg}$. However, the rate of polymerization of the 2% mixture is faster than DGEBA-DETA according to the analysis of DSC measurements, and therefore the line of log($C/D_{av}$) of the 2% mixture would be expected to lie below that of the POSS-free mixture, and this is depicted in Fig 2.41. In this case, a significant portion of polymerization occurs in the diffusion-controlled regime, because even after gelation has occurred, local diffusivity is sufficient enough to allow mutual diffusion of unreacted species within the experimental time scale.

Further increase in structural heterogeneities by adding POSS causes decoupling to occur sooner, and for the POSS-only mixture, POSS-DETA, log ($C/D_{av}$) intersects log($\eta$) of the other two mixtures, and polymerization mostly occurs in the diffusion-controlled zone. Addition of the static heterogeneity in the polymerization process may be treated in the same manner as the development of dynamic heterogeneity, and this conclusion may be tested by measuring viscosity, diffusion time, or the relaxation time.
Onset of decoupling \( \eta \) according to S-E eqn.

\[
\log(\eta), \log(C/D_{av})
\]

\[
\log(t_{polym})
\]

Figure 2.41 – Depiction of the decoupling of the inverse of average diffusion coefficient (dotted line) from viscosity (continuous line) as the polymerization time increases. The dot indicates the point at which decoupling occurs. Curve (1) is a depiction for DGEBA-DETA, curves (2) and (3) are depictions for 2\% POSS mixture (DGEBA-POSS-DETA) and (POSS-DETA). At the time denoted by vertical line at \( p \), polymerization occurs in the viscosity controlled zone for the DGEBA-DETA mixture, but in the decoupled diffusion-controlled zone for the 2\% POSS–DGEBA–DETA mixture, where it is faster, and still in the decoupled diffusion-controlled zone for the POSS–DETA mixture, where it is slower.

**2.4.5 Analysis of polymerization kinetics using the Corezzi model**

Several attempts have been made to incorporate the diffusion control mechanism into the epoxy-amine kinetic model [Chern and Poehlein 1987, Deng and Martin 1994, Corezzi et al. 2010]. Such models are distinguished from one another by the method in which \( \alpha \) is related to the diffusion reaction constant, \( k_d \). So far, the effective rate constant proposed by Rabinowitch (1937) has been generally accepted, although the relation between \( D \) and \( \alpha \) is not easy to formulate. Since \( k_d^{-1} \approx D \), the diffusion coefficient is assumed to be inversely proportional to the structural relaxation time, \( \tau \). Attempts have
been made to relate $\tau$ and $\alpha$ based on correlations between $\alpha$ and $T_g$ according to the free volume theory [Huguenin and Kein 1985] and configurational entropy [Havlícek 1987], since $T_g$ continually increases until vitrification, and additionally during post-polymerization. Corezzi et al. (2010) argue that previous assumptions made with the free-volume correlations are incorrect, as $T_g$ is not linearly dependent on $\alpha$. Instead, they deduce the $\tau$-$\alpha$ relationship from the reduction in configurational entropy as,

$$\tau = \tau_0 \exp\left(-\frac{\xi B \alpha}{\alpha_0 - \alpha}\right)$$

(2.17)

where $\tau_0$ is the relaxation time of the unpolymerized mixture, and the remainder of the parameters are the same as those given in section 2.1.1. $\alpha_0$ is the inverse of the average epoxy functionality given by $\bar{f} = f_c n_c/(n_c+n_a)$, where $n_c$ and $n_a$ denote the number of moles of epoxy and amine molecules. Corezzi et al use empirical dielectric relaxation data to first solve for $B$ and $\alpha_0$ from the best fit of Eqn. 2.17, followed by an iteration process to determine the remainder of parameters $k_{c1}$, $k'_{c1}$, $k_0$, $\xi$, m and n from the best fit using Eqn 2.5. This procedure is followed here using the calorimetric and dielectric data of the EDA mixtures.

The dielectric properties of DGEBA-POSS-EDA mixtures were measured in real-time during polymerization at 318 K, with the results given in section 3.3.3 and the $\tau$-analysis method in 3.1.3 and Appendix B. EDA was chosen because the calorimetry and dielectric samples came from the same batch, and experiments were performed in parallel. The logarithm of $\tau$ is plotted against $\alpha$ for the neat and 2% POSS mixture in Figs. 2.42 and 2.43, where the dots are the empirical data, and the lines are the best fit.
according to Eqn. 2.17. The values of $B$ ($\pm 0.3$), $\alpha_0$ ($\pm 0.02$) and $\tau_0$ were estimated as $7.3$, $0.9$, and $3.4 \times 10^{-9}$ s, and $7.1$, $0.89$, and $3.1 \times 10^{-10}$ s, for the two mixtures, respectively. The theoretical value of $\alpha_0$ for a stoichiometric DGEBA-EDA mixture is 0.75, and although an adequate fit could be obtained for that value, the best fit was obtained with a value close to the experimental value of $\alpha_{\max}$, $\sim 0.9$, amounting to a difference of 20%.

Table 2.6 lists the best-fit parameters $k_{c1}$, $k_{c1}'$, $k_0$, $\xi$, $m$ and $n$, but it must be noted, that attempting to make the fit with the $B$ parameters listed above failed, and much lower values had to be used instead. Any discrepancy between the $B$-values obtained by the fits from Eqn. 2.17 and Eqn. 2.5 could be due to an inaccurate $\tau-\alpha$ relationship. The higher values of $k_{c1}$ and $k_{c1}'$ for the neat sample indicate that DGEBA-EDA reacts faster than the 2% mixture, and it can be said that the model correctly reflects with the empirical data. Although $\xi$ bears no physical relation to the stretched exponential relaxation parameter $\beta$, Corezzi et al. (2010) claim that $\xi$ and $\beta$ are similar in value. Here, $\xi$ was estimated at $\sim 0.1$, which is significantly lower than the $\beta$ values of $\sim 0.3$ obtained from the dielectric study.

Lastly, the sum $m + n$ typically ranges between 2 and 4 [Horie et al. 1970, Barton 1985, Riccardi and Williams 1986, Wasserman and Johari 1993], however, in both cases $m + n$ summed only to 1. The expressions developed by Horie et al and Kamal and Sourour are based on the assumption that the reaction follows first or second-order autocatalytic kinetics, although others propose that the average order of reaction may be fractional with a single rate constant [Enns and Gillham 1983]. Ryan and Dutta (1979) show a temperature-dependence of $m$, decreasing from 1.2 to 0.6 with increasing $T_{\text{polym}}$. 

74
However, it is unlikely that a $T_{\text{polym}}$ of 318 K is high enough to drive $m + n$ to such low values. It is therefore concluded, that even though a reasonable graphical fit was made, the parameters obtained are unreasonable and inconsistent with literature.

Figure 2.42 – Logarithm of $\tau$ plotted against $\alpha$ for (A) DGEBA-EDA and (B) 2% POSS - EDA sample. The dots are the experimental data and the line is the best fit from Eqn 2.17. Parameters from the equation are shown in the panels.
Figure 2.43 – $d\alpha/dt$ plotted against $\alpha$ for (A) DGEBA-EDA and (B) 2% POSS - EDA sample. The dots are the experimental data and the line is the best fit from Eqn 2.5.

Table 2.6 - Parameters $k_0$, $k_{c1}$, $k_{c1}'$, $\xi$, $m$, and $n$, from the best fit of Eqn. 2.5 to the $d\alpha/dt$ data of DGEBA-EDA and 2% POSS mixture.

<table>
<thead>
<tr>
<th>$x_{POSS,%}$</th>
<th>$k_0$ [s$^{-1}$]</th>
<th>$k_{c1}$ [s$^{-1}$]</th>
<th>$k_{c1}'$ [s$^{-1}$]</th>
<th>$\xi$</th>
<th>$m$</th>
<th>$n$</th>
<th>$B$</th>
<th>$\alpha_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.5x10$^{-4}$</td>
<td>8.7x10$^{-5}$</td>
<td>1.8x10$^{-3}$</td>
<td>0.09</td>
<td>0.5</td>
<td>0.5</td>
<td>2.0</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>4.6x10$^{-4}$</td>
<td>7.8x10$^{-5}$</td>
<td>1.5x10$^{-3}$</td>
<td>0.10</td>
<td>0.5</td>
<td>0.5</td>
<td>1.9</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Chapter 3: Real Time Dielectric Spectroscopy of Polymerization

3.1 Background and Literature Review of Dielectric Spectroscopy

3.1.1 Dielectric theory

Dielectric spectroscopy allows one to observe changes in the dipolar response of a material to an electric field. A brief review of dielectric theory is provided here, and a mathematical basis behind the theory can be found in Appendix A. When a voltage is applied to a dielectric material confined between parallel electrodes, the material polarizes. Electron clouds are displaced from their original position with respect to their nuclei; polar molecules or polar segments of molecules orientate in the direction of the applied electrical potential; and charged species diffuse to the electrode of opposite charge, and thus an electric field is generated within the material. The ability of a material to polarize in response to an electric field is quantified by the dielectric constant, \( \varepsilon \), a relative measure of the charge stored per unit voltage. When the applied voltage is modulated the complex dielectric permittivity is expressed as

\[
\varepsilon' = \varepsilon' - i\varepsilon'' ,
\]  

where the real component, \( \varepsilon' \), is the dielectric permittivity, the imaginary component, \( \varepsilon'' \), is loss in the field, and \( i \) is equal to the square root of -1. \( \varepsilon' \) and \( \varepsilon'' \) are related by the phase angle difference between the alternating voltage and current, \( \delta \), by

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} .
\]

The value of \( \varepsilon' \) at which losses from dipolar relaxation begin to appear at low frequencies is called the limiting low frequency permittivity or static permittivity, \( \varepsilon_s \), while the value
of $\varepsilon'$ when losses become negligible at high frequencies is the limiting high frequency permittivity, $\varepsilon_\infty$. Dielectric measurements yield information on three processes: (i) interfacial polarization (ii) dc conductivity from mobile ions and (iii) dipolar orientations or change in the dipole vector. Processes (i) and (iii) contribute to $\varepsilon'$, while all three contribute to $\varepsilon''$,

$$\varepsilon' (f, t) = \varepsilon'_{\text{dip}}(f, t) + \varepsilon'_{\text{int}}(f, t)$$  \hspace{1cm} (3.3)

$$\varepsilon''(f, t) = \varepsilon''_{\text{dip}}(f, t) + \varepsilon''_{\text{dc}}(f, t) - \varepsilon''_{\text{int}}(f, t)$$ \hspace{1cm} (3.4)

where the subscripts dip, dc and int denote the dipolar, dc conductivity and interfacial polarization effects. $\varepsilon'$ and $\varepsilon''$ are time dependent for physically or chemically unstable systems, (i.e. systems undergoing sol $\rightarrow$ gel), but a material’s orientational response is always dependent on the frequency of the field. The sum of accumulated charges on the electrode from shifts in electron clouds and dipolar orientation is given by $\varepsilon'_{\text{dip}}$. The net dipole moment would ideally be permanent for a fixed applied voltage, but losses in the field from the diffusion of ions and free electrons constitute $\varepsilon''_{\text{dc}}$. Buildup of charges from unbound electrons and migrating ions increase the measured charge, and these constitute the interfacial polarization effects of $\varepsilon'$. In an ideal case, $\varepsilon'_{\text{int}}$ would be negligible, as it may overshadow changes in dipolar orientation, however, such effects arise during significant changes in physical structure and morphology, such as those caused by phase separation [Venkateshan and Johari 2004].
3.1.2 Application of real-time dielectric spectroscopy to polymerizing systems


At early polymerization times, $t_{\text{polym}}$, interfacial polarization effects in $\varepsilon'$ are significant, especially at low frequencies below the kHz range [Senturia and Sheppard 1986, Parthun et al. 1996]. The dipole moment of the material changes irreversibly from polymerization, and $\varepsilon'$ decreases in an inverse sigmoid manner as plots of $\varepsilon'$ vs. $\log t_{\text{polym}}$ or vs. $f$ would show. $\varepsilon'$ decreases first at high frequencies, and then at lower frequencies as the relaxation process progressively shifts to lower frequencies [Johari 1993, Tombari and Johari 1992]. It ultimately decreases to a finite value between 3 and 5 upon vitrification of the epoxy [Johari 1993], as the combined effects of atomic and electronic polarization remain unchanged during the reaction and contribute $\sim 3$ units to $\varepsilon'$. $\varepsilon_s$ decreases with the number of bonds formed [Tombari et al. 1997] by at most 10% of its initial amount [Ferrari et al. 1998], and the limiting high permittivity, $\varepsilon_\infty$, also decreases
marginally during polymerization [Soualmia et al. 1982]. $\varepsilon_\infty$ and $\varepsilon_\varepsilon$ decrease negligibly during the time taken for one spectral (frequency range) scan. Changes in the refractive index and an increase in infrared polarization from atomic vibrations prevent $\varepsilon''(t_{\text{polym}} \rightarrow \infty)$ from reaching zero [Johari 1993].

Commercial epoxy resins and hardeners contain residuals of impurity ions from the manufacturing process, and ions may also be formed in a mixture with amines by the dissociation of the proton-donating compound [Fava et al. 1968]. The viscosity of the liquid precursors is low, and consequently the high diffusion coefficient of ions means that $\varepsilon''$ values are typically high at early $t_{\text{polym}}$ [Sheppard and Senturia 1986, Mangion and Johari 1991, Alig and Johari 1993]. By using the complex electrical modulus formalism developed by Macedo et al. (1972) and Moynihan et al. (1972), the magnitude of the initially high $\varepsilon''$ relative to the dipolar relaxation peak was determined by Johari and coworkers [Mangion and Johari 1991, Mangion et al. 1992, Parthun and Johari 1992a,b,c], and concluded that dc conductivity, $\sigma_{\text{dc}}$, dominates at the initial stages of polymerization. It progressively diminishes as the increase in viscosity inhibits ion mobility, and the conductivity from dipolar relaxation, $\sigma_{\text{dip}}$ becomes more prominent. In addition to diffusion of ions, protonic conduction from an H-bonded intermolecular network contributes to dc conductivity, which is further enhanced by zwitter-ions that temporarily form during polymerization [Johari 1994a, Alig and Johari 1993]. The same effects that contribute to $\varepsilon''$ also contribute to the measured conductivity

$$\sigma = \sigma_{\text{dc}} + \sigma_{\text{dip}} - \sigma_{\text{int}}.$$  \hspace{1cm} (3.5)
where the subscripts are the same as those in Eqn. 3.4. The overall conductivity, $\sigma$, can be computed from the relationship

$$\sigma = \varepsilon'' \varepsilon_0 \omega,$$

(3.6)

where $\omega$ is angular frequency ($=2\pi f$), $\varepsilon_0$ is the permittivity of a vacuum and is equal to 8.8541 pF/m. Dynamic and static properties from near zero to optical frequencies that are affected by polymerization can be measured, however, measuring changes in dc conductivity and the average dipolar relaxation time, $<\tau>$, is simpler and sufficient for an analysis of the thermosetting process [Johari 1993]. $\tau$ irreversibly increases as the macromolecule grows [Mangion and Johari 1991, Wasylyshyn and Johari 1997] and it can be related to the extent of reaction, $\alpha$, for a fixed frequency measurement [Parthun and Johari 1992b] from the formula

$$\tau(T, t_{polym}) = \tau(T, t_{polym} = 0)e^{[S\alpha^n(T,t_{polym})]} ,$$

(3.7)

where $S (= \ln[\pi(T,t_{polym}=\infty)/\pi(T,t_{polym}=0)])$ is a constant, $n$ is an empirical parameter. Both the $\tau$ and $t_{polym}$ at which the dipolar peak appears, $t_{polym}(\varepsilon''_{peak})$, shift to lower $t_{polym}$ as the temperature of isothermal polymerization is increased [Parthun and Johari 1992a, c].

One fundamental and important phenomenological event of a thermosetting liquid is gelation. The time at which the material becomes infinitely connected, or in other words, the time at which a continuous network of covalent bonds extends throughout a sample, is the gelation time, $t_{gel}$. The process of polymerization, from the onset to $t_{gel}$, is accompanied by an increase in the mechanical modulus to a value in the MPa range and
by an increase in macroscopic viscosity towards an infinite value. The physics of gelation has been examined by Stauffer (1976, 1982) and Djabourov (1988), who have shown that a non-empirical power law equation can be used to describe changes in transport properties that ensue from gelation

\[ p(t) \propto \left( \frac{t_{gel} - t}{t_{gel}} \right)^\gamma \]  

(3.8)

where \( p(t) \) is the time-dependent transport property, and \( \gamma \) is the critical exponent, which has no physical meaning, but describes \( p(t) \)'s rate of approach towards the singularity point at \( t_{gel} \). For changes in dc conductivity during polymerization, Eqn. 3.8 is expressed as

\[ \sigma_{dc}(t_{polym}) = \sigma_{dc,0} \left[1 - \frac{t_{polym}}{t_{gel}}\right]^{-\gamma} \]  

(3.9)

where \( \sigma_{dc,0} \) is the dc conductivity of the unpolymerized mixture, \( \sigma_{dc}(t_{polym} \rightarrow 0) \). Johari and co-workers [Mangion and Johari 1991, Mangion et al. 1992, Parthun and Johari 1992a,b,c] used the transport property of conductivity from dielectric measurements and found that Eqn. 3.9 estimates \( t_{gel} \) close to the values obtained from mechanical measurements [Alig et al. 1996]. \( \sigma_{dc} \) becomes negligible but does not reach a zero-value at \( t_{gel} \), as impurity ions remain in the sample.

### 3.1.3 Analysis of relaxation observed during polymerization

A homogeneous, physically stable liquid exhibits a characteristic dielectric relaxation time, \( \tau_0 > 10^{12} \text{s} \), with a distribution of relaxation rates [Ngai 2011]. \( \tau_0 \) and the distribution of \( \tau \) continue to increase with time until a liquid vitrifies [Ngai 2011] and the parameter which characterizes this distribution, \( \beta \), typically decreases [Ferrari et al.}
An analysis of the dielectric relaxation spectra has been performed by using the empirical Cole-Davidson [Davidson and Cole 1951], Cole-Cole [Cole and Cole 1941], or Kohlrausch-Williams-Watts [Kohlrausch 1854, Williams and Watts 1972] (KWW) formalisms. The KWW formalism is

\[ \phi(t) = \phi_o \exp\left[ -\left(\frac{t}{\tau_o}\right)\beta \right] \] \tag{3.10 A}

where \( \phi \) is the relaxation function, \( t \) is the time after the removal of the electric field (or mechanical stress), and \( 0 < \beta \leq 1 \). It was originally used for analyzing mechanical creep measurements, but has generally provided the best fit to dielectric relaxation data, including epoxy-amine polymerization [Mangion and Johari 1991]. For polymerization at a fixed \( T \), the formalism is written in the form,

\[ \phi(t) = \phi_o \exp\left[ -\left(\frac{t}{\tau_o(t_{polym})}\right)\beta \right] \] \tag{3.10 B}

While the \( \beta \)-notation conventionally applies to chemically stable liquids, some authors suggest it should be replaced with another to distinguish it from polymerizing liquids [Mangion and Johari 1991]. \( \beta \) is retained here for the analysis. The general formula of the complex dielectric permittivity from dipolar relaxation is

\[ \varepsilon^* = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) \times N^*(\omega \tau) \] \tag{3.11}

where \( N^* \) is the normalized complex permittivity which is mathematically defined as the one-sided Laplacian transformation of \(-d\phi(t)/dt\)

\[ N^*(\omega \tau) = \int_0^\infty e^{-i\omega \tau} \left(-\frac{d\phi}{dt}\right) dt \] \tag{3.12}
$N^*$ is defined as

$$N^*(\omega\tau) = N'(\omega\tau) - i N''(\omega\tau),$$

(3.13)

where the real and imaginary components as are equal to

$$N' = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty},$$

(3.14)

$$N'' = \frac{\varepsilon''}{\varepsilon_s - \varepsilon_\infty}.$$

(3.15)

Values of $N^*(\omega\tau)$ for a range of $\beta$ values have been provided by Dishon et al. (1985) and Moynihan et al. (1973), which is used in the analysis here. To summarize, the increase in the density, refractive index and viscosity during polymerization has the following (irreversible) effects on the dielectric properties [Johari 1993]:

(i) A change in the dipole moment of molecules in the liquid.

(ii) A decrease in the dc conductivity as the diffusion coefficient of ions decreases.

(iii) A change from the unimodal relaxation function observed in the unpolymerized liquid to a bimodal function, and by the emergence of the $\alpha$-relaxation process on the low-frequency side of the process observed in the GHz region, and a shift of the $\alpha$-process to lower frequencies.

(iv) A decrease in $\varepsilon_s$ of the polymerizing liquids.

(v) A decrease in $\varepsilon_\infty$ as the vibrational frequencies of the optical refractive index increase.

(vi) An increase in $\tau_o$ and an increase in $\beta$. 

84
3.2 Experimental

3.2.1 Dielectric measurement assembly

The dielectric measurement assembly consists of an impedance analyzer, thermostat, temperature controller, ice bath and multimeter, as shown in Fig. 3.1. The thermostat is used to heat and maintain samples at a fixed temperature. It consists of a 6 cm diameter x 16 cm long cylindrical aluminum block, with a 0.5 cm diameter x 5 cm deep bore drilled into it for holding vials which contain the samples. High resistance nichrome wire is wrapped around the block to provide 6 kW of power for heating. The block resides in a larger metal can with 2 cm spacing between the block and can. Silica fibers and sand have been firmly packed in between the annular space to provide insulation. Heat is provided to the thermostat by a Eurotherm 818 PID controller. This setup allows for the sample to reach the set point temperature within a few minutes, and any additional heat released from the sample dissipates quickly so that the sample temperature remains constant.

T-type variable, parallel-plate capacitors manufactured by Johnson Trimmer Capacitors, with a rated geometric capacitance of 11 pF (± 0.2 pF) were used for dielectric measurements. A picture is shown in Fig. 3.1 B. Capacitor leads were soldered to RG-174/U coaxial wires, while the other end of the wires were soldered to a rectangular metallic piece that is adjoined to standard BNC plugs. This piece connects to the analyzer via RG-58/U coaxial cables. Spliced and exposed wiring were grounded and insulated with electrical tape.
A Quadtech LCR Model 7400 dielectric analyzer, interfaced with a computer for automatic data acquisition, was used for conductance and capacitance measurements. It is housed in a large metallic case to reduce extraneous, electromagnetic interference. The thermostat block was kept at the ground potential, shielding the capacitor from electromagnetic noise. The temperature of the sample was measured in real time by a Type T (copper-constantan) thermocouple immersed to a depth of approximately 2 mm in the reactant mixture, and placed adjacent to the ceramic element of the capacitor. The other end of the thermocouple, passing through a computer-interfaced multimeter, was submerged in an insulated ice-water bath. The equation used to convert voltage signals to a temperature in degrees Celsius is provided in Appendix D. And finally, a cork was used to plug the mouth of the sample vial.
Figure 3.1 – (A) Photograph of the dielectric assembly which consists of an (1) impedance analyzer, (2) multimeter, (3) ice/water bath container, (4) thermostat assembly and (5) temperature controller. (B) Photograph of the capacitor used in dielectric measurements. (C) Photograph of the thermostat assembly.
3.2.2 Experiment procedure

The thermostat block temperature was brought to the polymerization temperature one hour prior to preparing the sample, and the analyzer was zeroed before each experiment. DGEBA was weighed first in a 25-mm long, 7-mm internal diameter flat-bottom glass vial, followed by POSS and lastly the amine. The liquid precursors were thoroughly mixed at room temperature. The capacitance of air in the capacitor, $C_0$, was measured before inserting the capacitor into the mixture. Precautions were taken to ensure the absence of air bubbles in the liquid confined to the gap between the parallel plates as the capacitor was inserted into the liquid. The volume of the liquid samples (~ 1 ml) was enough to remain 2-3 mm above the electrodes in order to minimize the temperature rise during the polymerization process.

$\varepsilon'$ and $\varepsilon''$ are calculated from $C_0$, $C_p$, and $G_p$, according to Eqns. B 3.6 and B 3.7 in Appendix B. Capacitance, $C_p$, and conductance, $G_p$ in a parallel circuit were recorded in real time during the liquid’s polymerization, at 25 frequencies ranging from 10 Hz to 500 kHz. The change in properties of the polymerizing liquid would have been significant in the duration required to take measurements at frequencies lower than 10 Hz. The time taken for one spectral scan was 15 s, during which the polymerization would have progressed by a small extent, and any changes in the spectra are assumed negligible. The spectra were obtained at specific time intervals during the course of polymerization. Capacitance and conductance measurements are accurate to within 0.2 and 0.5 % respectively, while the temperature measurement is accurate to within 0.1 K.
3.3 Results

$\varepsilon'$, $\varepsilon''$, and $\sigma$ are plotted against the logarithm of polymerization time (isochrones, fixed-frequency plots) and frequency (spectra, fixed-time plots). Of the 25 frequency measurements made during each sweep, six were chosen for the analysis: 1, 2, 13, 50, 130 and 500 kHz (rounded values). Only four of these six are shown in the isochrones. $\sigma$ was computed from Eqn. 3.6 and $\sigma_{dc}$ was calculated from Eqn. 3.9 by plotting $\log \sigma_{dc}$ vs. $[1 - (t_{polym}/t_{gel})]$, which yields a straight line up to $t_{polym}(\varepsilon''_{\text{min}})$, and $\gamma$ is equal to the slope of this line. An iterative approach was taken, where $t_{gel}$ was varied until the $R^2$ value of the fit reached a maximum. $\sigma_{dc}$ is shown as a dashed line in the $\sigma$ panel of the plots of the isochrones.

3.3.1 DGEBA-POSS-DETA

DGEBA-POSS-DETA mixtures were polymerized at 323.2 K. Isochrones and spectra plots are shown in Figs. 3.2 and 3.3 for DGEBA-DETA, Figs. 3.4 and 3.5 for the 2 % mixture, Figs. 3.6 and 3.7 for the 4.3 % mixture, Figs. 3.8 and 3.9 for the 10.7 %, Figs. 3.10 and 3.11 for the 21.2 % mixture, and Figs. 3.12 and 3.13 for POSS-DETA, where the $f$ (kHz) and $t_{polym}$ (in minutes) are indicated. Figure 3.14 shows a comparison of the isochrones at 1 kHz.

The change in $\varepsilon'$ and $\varepsilon''$ of the $x_{\text{POSS}} = 0$ to 21.2 % DETA mixtures is typical for polymerizing liquids. $\varepsilon'$ decreases at a slow rate during early $t_{polym}$, and then decreases in a step-wise manner by several units and finally plateaus. The time at which the step decrease occurs is lower for higher frequencies. There is also a shallow and small step-
decrease in $\varepsilon'$ just before the larger step decrease, which is due to interfacial polarization. $\varepsilon''$ is initially high due to dc conductivity, but decreases to a local minimum, before the emergence of the dipolar relaxation peak, and finally decreases to a constant value. $\varepsilon''(t_{polym} \rightarrow 0)$ is higher at lower frequencies and $\varepsilon'' (t_{polym} \rightarrow \infty)$ is higher at higher frequencies, and the $\varepsilon''$:isochrones cross one another near the peaks as $t_{polym}(\varepsilon''_{peak})$ decreases with increasing frequency. $\sigma$ is independent of frequency at low $t_{polym}$, and the elevation and width of the $\sigma$ peaks increase with increasing frequency. The spectra plots show that $\varepsilon'$ is initially independent of $f$, except at very low $f$, but decreases and appears as an inverse-sigmoid during the emergence of the relaxation process, which is simultaneously reflected in the spectra plots of $\varepsilon''$ as the peak moves to lower frequencies as $t_{polym}$ increases.

By increasing $x_{POSS}$, the following systematic changes in $\varepsilon'$ and $\varepsilon''$ are observed:

(i) $\varepsilon(t_{polym} \rightarrow 0)$ and $\varepsilon' (t_{polym} \rightarrow \infty)$ increase.

(ii) The magnitude of $\varepsilon''_{peak}$ decreases, as determined by the difference of $\varepsilon''_{peak}$ and $\varepsilon''(t_{polym} \rightarrow \infty)$.

(iii) $\varepsilon''_{min}$ and $\varepsilon''_{peak}$ shift to higher $t_{polym}$.

Although POSS-DETA shows a continuation of the trends mentioned above, there are significant irregularities in the isochrones that distinguish it from the remainder of the DETA mixtures, particularly at frequencies less than 2 kHz, as shown in Fig. 3.12. These irregularities are:
(i) At low polymerization times, $\varepsilon'$ at lower frequencies (2 kHz and less) is significantly higher than $\varepsilon'$ at higher frequencies (13 kHz +). This is due to an increase in electrode polarization effects.

(ii) Instead of a step decrease, a spike is observed in $\varepsilon'$ at low frequencies. Spike magnitude and width increase as frequency decreases.

(iii) Instead of a sharp step-wise decrease, a sluggish decrease in $\varepsilon'$ is observed.

(iv) $\varepsilon'$ descends to a value greater than 5, and then increases once more.

(v) A dipolar $\varepsilon''$ peak is not observed at any frequency. Rather, $\varepsilon''$ decreases to a local minimum, increases and plateaus for frequencies greater than 13 kHz. At frequencies lower than 13 kHz, $\varepsilon''$ increases simultaneously along with $\varepsilon'$ at longer polymerization times.

These irregularities will be discussed further in section 3.4.3.
3.3.2 DGEBA-POSS-HA

DGEBA-POSS-HA mixtures were polymerized at 313.2 K for approximately 2000 minutes. The isochrones and spectra plots are shown in Figs. 3.15 and 3.16 for DGEBA-HA, Figs. 3.17 and 3.18 for the 2 % mixture, Figs. 3.19 and 3.20 for the 4.3 % mixture, Figs. 3.21 and 3.22 for the 10.7% mixture, and Figs. 3.23 and 3.24 for POSS-HA. A comparison of the isochrones at 1 kHz can be found in Figure 3.25. In short, the $\varepsilon'$, $\varepsilon''$, and $\sigma$ plots are typical, but a few things need attention. The $\varepsilon'$ isochrones of DGEBA-HA, 2 %, 4.3 %, and 10.7 % POSS mixtures reveal a small sigmoid-shape step decrease at low $t_{\text{polym}}$, prior to the larger decrease. $\varepsilon'$ of POSS-HA in Fig. 3.23 shows a broad increase prior to the step-decrease. The $\varepsilon'$ at 0.1 kHz is plotted in Figs. 3.15 and 3.23 to show how interfacial polarization effects drastically increase from the neat to the POSS-only mixture, as $\varepsilon'(t_{\text{polym}}\rightarrow0)$ at 0.1 kHz is significantly higher than $\varepsilon'(t_{\text{polym}}\rightarrow0)$ at 1 kHz for POSS-HA. The $\varepsilon'$ plot of the 10.7 % mixture at 1 kHz lies above that of POSS-HA, and only decreases by a value of 1 over the course of polymerization, which is unusual since $\varepsilon'$ typically decreases by about 3 or 4. It is unclear whether this is a result of a faulty capacitor or a true reflection of the changes in the sample’s dielectric properties.

When $x_{\text{POSS}}$ is increased, $\varepsilon''_{\text{peak}}$ shifts to higher $t_{\text{polym}}$ but becomes unobservable when $x_{\text{POSS}}$ exceeds 10.7 %. A weak relaxation peak for the 10.7 % mixture is observable at frequencies above 130 kHz. $\varepsilon''$ of POSS-HA decreases to a local minimum, but then increases and plateaus without any evidence of the $\alpha$-relaxation shifting to frequencies
lower than 500 kHz, as is seen in the spectra plots in Fig. 3.24. The $\varepsilon'(t_{\text{polym} \to 0})$, $\varepsilon'(t_{\text{polym} \to \infty})$, $\varepsilon''(t_{\text{polym} \to \infty})$, and $\sigma(t_{\text{polym} \to 0})$ increase with POSS.

### 3.3.3 DGEBA-POSS-EDA

EDA mixtures were polymerized at 318.2 K for approximately 360 minutes. Isochrones and spectra plots are shown in Figs. 3.26 and 3.27 for DGEBA-EDA, Figs. 3.28 and 3.29 for the 2 % mixture, Figs. 3.30 and 3.31 for the 4.3 % mixture, and Figs. 3.32 and 3.33 for POSS-EDA. Figure 3.34 shows the isochrones for the four mixtures at 1 kHz. To avoid redundancy, it will only be stated that the change in dielectric properties with time and $x_{\text{POSS}}$ are qualitatively similar to the cure of DGEBA-POSS with DETA. A small peak appears in the $\varepsilon'$ plot of POSS-EDA prior to the step-decrease at frequencies less than 2 kHz, similar to that found with POSS-DETA, though smaller in magnitude and more round in comparison. The time-dependent dielectric data at 1 kHz of DETA, HA and EDA are provided in Table 3.1, which is meant to show the effects on loss and permittivity from $x_{\text{POSS}}$ at the onset of polymerization, during relaxation and after vitrification, as previously described in section 3.3.1.
Figure 3.2 – (A) ε’, (B) ε” and (C) log (σ) of DGEBA-DETA plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies.

Figure 3.3 – (A) ε’, (B) ε” and (C) log (σ) of DGEBA-DETA plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \) (minutes).

Figure 3.4 – (A) ε’, (B) ε” and (C) log (σ) of DGEBA-POSS-DETA (2 % POSS) plotted against the logarithm of \( t_{\text{polym}} \) for 4 frequencies.

Figure 3.5 – (A) ε’, (B) ε” and (C) log (σ) of DGEBA-POSS-DETA (2 % POSS) plotted against the logarithm of \( f \) for several \( t_{\text{polym}} \)
Figure 3.6 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (4.3 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.7 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (4.3 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.

Figure 3.8 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (10.7 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.9 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (10.7 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.  

95
Figure 3.10 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (21.2 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.11 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-DETA (21.2 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.

Figure 3.12 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-DETA plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.13 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-DETA plotted against the logarithm of $f$ for several $t_{\text{polym}}$. 
Figure 3.14 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ plotted against the logarithm of $t_{\text{polym}}$, measured at 1 kHz, for five POSS-DGEBA-DETA mixtures polymerized at 323 K.
Figure 3.15 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-HA plotted against the logarithm of $t_{\text{polym}}$ for 5 frequencies.

Figure 3.16 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-HA plotted against the logarithm of $f$ for several $t_{\text{polym}}$. 

98
Figure 3.17 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-HA (2 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.18 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-HA (2 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.

Figure 3.19 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-HA (4.3 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.20 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-HA (4.3 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$. 
Figure 3.21 – (A) ε’ (B) ε” and (C) log (σ) of DGEBA-POSS-HA (10.7 % POSS) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.22 – (A) ε’ (B) ε” and (C) log (σ) of DGEBA-POSS-HA (10.7 % POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.

Figure 3.23 – (A) ε’ (B) ε” and (C) log (σ) of POSS-HA plotted against the logarithm of $t_{\text{polym}}$ for 5 frequencies.

Figure 3.24 – (A) ε’ (B) ε” and (C) log (σ) of POSS-HA plotted against the logarithm of $f$ for several $t_{\text{polym}}$. 

Figure 3.25 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of the five DGEBA-POSS-HA mixtures cured at 313 K are plotted against the logarithm of $t_{polym}$ for a measurement at 1 kHz.
Figure 3.26 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) log ($\sigma$) of DGEBA-EDA plotted against the logarithm of $t_{polym}$ for 4 frequencies.

Figure 3.27 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) log ($\sigma$) of DGEBA-EDA plotted against the logarithm of $f$ for several $t_{polym}$.

Figure 3.28 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) log ($\sigma$) of DGEBA-POSS-EDA ($x_{POSS} = 2\%$) plotted against the logarithm of $t_{polym}$, for 4 frequencies.

Figure 3.29 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) log ($\sigma$) of DGEBA-POSS-EDA (2\% POSS) plotted against the logarithm of $f$, for several $t_{polym}$. 
Figure 3.30 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-EDA ($x_{\text{POSS}} = 4.3\%$) plotted against the logarithm of $t_{\text{polym}}$ for 4 frequencies.

Figure 3.31 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of DGEBA-POSS-EDA (4.3% POSS) plotted against the logarithm of $f$ for several $t_{\text{polym}}$.

Figure 3.32 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-EDA plotted against the logarithm of $t_{\text{polym}}$, for 4 frequencies.

Figure 3.33 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ of POSS-EDA plotted against the logarithm of $f$, for several $t_{\text{polym}}$. 
Figure 3.34 – (A) $\varepsilon'$ (B) $\varepsilon''$ and (C) $\log(\sigma)$ plotted against the logarithm of $t_{\text{polym}}$ of the four DGEBA-POSS-EDA mixtures at 1 kHz.
Table 3.1 – Values of $\varepsilon'(t_{\text{polym}} \to 0)$, $\varepsilon'(t_{\text{polym}} \to \infty)$, $t_{\text{polym}}(\varepsilon''_{\text{peak}})$, $\varepsilon''(t_{\text{polym}} \to \infty)$ and $\log \sigma(t_{\text{polym}} \to 0)$ from the 1 kHz measurements.

<table>
<thead>
<tr>
<th>$X_{\text{POSS}}$ (%)</th>
<th>$\varepsilon'(t_{\text{polym}} \to 0)$</th>
<th>$\varepsilon'(t_{\text{polym}} \to \infty)$</th>
<th>$t_{\text{polym}}(\varepsilon''_{\text{peak}})$ [min.]</th>
<th>$\varepsilon''(t_{\text{polym}} \to \infty)$</th>
<th>$\log \sigma(t_{\text{polym}} \to 0)$ [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DETA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9.24</td>
<td>4.25</td>
<td>34.8</td>
<td>0.016</td>
<td>-5.43</td>
</tr>
<tr>
<td>2</td>
<td>9.24</td>
<td>4.36</td>
<td>35.7</td>
<td>0.021</td>
<td>-5.38</td>
</tr>
<tr>
<td>4.3</td>
<td>9.25</td>
<td>4.49</td>
<td>38.4</td>
<td>0.028</td>
<td>-5.32</td>
</tr>
<tr>
<td>10.7</td>
<td>9.41</td>
<td>4.85</td>
<td>43.6</td>
<td>0.042</td>
<td>-5.25</td>
</tr>
<tr>
<td>21.2</td>
<td>10.08</td>
<td>5.27</td>
<td>48.3</td>
<td>0.089</td>
<td>-5.10</td>
</tr>
<tr>
<td>100</td>
<td>12.41</td>
<td>N/a</td>
<td>N/a</td>
<td>N/a</td>
<td>-4.32</td>
</tr>
<tr>
<td><strong>HA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>6.70</td>
<td>3.57</td>
<td>229</td>
<td>0.068</td>
<td>-5.78</td>
</tr>
<tr>
<td>2</td>
<td>6.96</td>
<td>3.96</td>
<td>260</td>
<td>0.143</td>
<td>-5.59</td>
</tr>
<tr>
<td>4.3</td>
<td>7.24</td>
<td>4.55</td>
<td>280</td>
<td>0.228</td>
<td>-6.01</td>
</tr>
<tr>
<td>10.7</td>
<td>7.66</td>
<td>6.03</td>
<td>N/a</td>
<td>0.468</td>
<td>-5.73</td>
</tr>
<tr>
<td>100</td>
<td>7.25</td>
<td>6.64</td>
<td>N/a</td>
<td>0.486</td>
<td>-5.16</td>
</tr>
<tr>
<td><strong>EDA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9.13</td>
<td>4.19</td>
<td>51.5</td>
<td>0.333</td>
<td>-5.42</td>
</tr>
<tr>
<td>2</td>
<td>9.52</td>
<td>4.27</td>
<td>51.5</td>
<td>0.039</td>
<td>-5.33</td>
</tr>
<tr>
<td>4.3</td>
<td>9.52</td>
<td>4.52</td>
<td>51.5</td>
<td>0.307</td>
<td>-5.42</td>
</tr>
<tr>
<td>100</td>
<td>10.61</td>
<td>6.72</td>
<td>N/a</td>
<td>0.315</td>
<td>-4.60</td>
</tr>
</tbody>
</table>

3.3.4. Analysis of Cole-Cole and complex plane plots

Dipolar relaxation was analyzed with the KWW formalism using the set of equations given in section 3.1.2 and Appendix B, from which the distribution parameter $\beta$ and relaxation time $\tau$ were obtained. First, dc conductivity effects were removed from the data by subtracting the calculated $\sigma_{\text{dc}}$ from the experimental $\sigma$, and the dipolar relaxation effects were resolved. Cole-Cole plots of $\varepsilon''_{\text{dip}}$ against $\varepsilon'$ were constructed, and $\varepsilon_n$ and $\varepsilon_\infty$ were approximated by extrapolating the skewed arc to the abscissa. Theoretical loss and permittivity, $\varepsilon''_{\text{theor}}$ and $\varepsilon'_{\text{theor}}$, were computed from the N".N' data set tables of Dishon and coworkers (1985), which have been computationally verified by Parthun (1997). $\beta$ was selected based on the most adequate fit between $\varepsilon''_{\text{theor}}$, $\varepsilon'_{\text{theor}}$ and $\varepsilon''_{\text{dip}}$-$\varepsilon'$. Lastly, $\varepsilon_n$ and $\varepsilon_\infty$
were varied slightly to give the best fit. An analysis of samples containing more than 21% POSS could not performed where a relaxation peak was either weak or absent.

This analysis was performed on the isochrones at frequencies of 1, 2, 13, 50, 130 and 500 kHz, and spectra measurements at six different instances of polymerization, which varied according to the mixture. The Cole-Cole plots of the isochrones and spectra are shown in Figs. 3.35 to 3.46 for DETA, Figs. 3.47 to 3.54 for HA, and Figs. 3.55 to 3.62 for EDA mixtures. The dots in these figures are the experimental values while the lines are from the theoretical expressions. Data-fitting was initially performed using $\varepsilon''_{\text{dip}}$, while the data in the figures are the un-subtracted $\varepsilon''$, and for this reason there appears to be a poor fit for couple of cases, (e.g. 500 kHz in Fig. 3.43). In general, the fits are adequate except at low polymerization times where dc conductivity contributes significantly to losses, and at higher polymerization times, where the change in specimen density causes $\Delta \varepsilon_{\text{IR}}$ to change and contributions from molecular vibrations prevent $\varepsilon''$ from reaching zero.
Figure 3.35 – Complex plane plot of DGEBA-DETA for 6 frequencies.

Figure 3.36 – Cole-Cole plot of DGEBA-DETA for 6 fixed $t_{\text{polym}}$.

Figure 3.37 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$) for 6 frequencies.

Figure 3.38 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 2\%$) for 6 fixed $t_{\text{polym}}$. 
Figure 3.39 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3\%$) for 6 frequencies.

Figure 3.40 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 4.3\%$) for 6 fixed $t_{\text{polym}}$.

Figure 3.41 – Complex plane plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7\%$) for 6 frequencies.

Figure 3.42 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{\text{POSS}} = 10.7\%$) for 6 fixed $t_{\text{polym}}$. 
Figure 3.43 – Complex plane plot of DGEBA-POSS-DETA ($x_{POSS} = 21.2\%$) for 6 frequencies.

Figure 3.44 – Cole-Cole plot of DGEBA-POSS-DETA ($x_{POSS} = 21.2\%$) for 6 fixed $t_{polym}$.

Figure 3.45 – Complex plane plot of POSS-DETA for 6 frequencies.

Figure 3.46 – Cole-Cole plot of POSS-DETA for 6 fixed $t_{polym}$. 
Table 3.2 - Parameters from the KWW analysis of the DETA isochrones.

<table>
<thead>
<tr>
<th>X_{POSS} (%)</th>
<th>f (kHz)</th>
<th>\varepsilon_0 (± 0.05)</th>
<th>\varepsilon_\infty (± 0.05)</th>
<th>\Delta \varepsilon (± 0.1)</th>
<th>\beta (± 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>8.02</td>
<td>4.67</td>
<td>3.35</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.04</td>
<td>4.62</td>
<td>3.42</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.07</td>
<td>4.72</td>
<td>3.35</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.1</td>
<td>4.68</td>
<td>3.42</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.23</td>
<td>4.67</td>
<td>3.56</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.25</td>
<td>4.64</td>
<td>3.61</td>
<td>0.26</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>8.16</td>
<td>4.81</td>
<td>3.35</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.12</td>
<td>4.87</td>
<td>3.25</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.18</td>
<td>4.75</td>
<td>3.43</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.27</td>
<td>4.72</td>
<td>3.55</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.3</td>
<td>4.60</td>
<td>3.70</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.38</td>
<td>4.41</td>
<td>3.97</td>
<td>0.27</td>
</tr>
<tr>
<td>4.3</td>
<td>1</td>
<td>8.23</td>
<td>5.3</td>
<td>2.93</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.23</td>
<td>5.3</td>
<td>2.93</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.31</td>
<td>4.90</td>
<td>3.41</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.39</td>
<td>4.72</td>
<td>3.67</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.44</td>
<td>4.55</td>
<td>3.89</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.63</td>
<td>4.40</td>
<td>4.23</td>
<td>0.26</td>
</tr>
<tr>
<td>10.7</td>
<td>1</td>
<td>8.53</td>
<td>5.1</td>
<td>3.43</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.5</td>
<td>5.09</td>
<td>3.41</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.53</td>
<td>5.03</td>
<td>3.5</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.62</td>
<td>4.95</td>
<td>3.67</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.64</td>
<td>4.98</td>
<td>3.66</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.69</td>
<td>4.75</td>
<td>3.94</td>
<td>0.26</td>
</tr>
<tr>
<td>21.2</td>
<td>1</td>
<td>8.8</td>
<td>5.41</td>
<td>3.39</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.82</td>
<td>5.42</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.85</td>
<td>5.4</td>
<td>3.45</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.93</td>
<td>5.35</td>
<td>3.58</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.96</td>
<td>5.4</td>
<td>3.56</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.9</td>
<td>5.3</td>
<td>3.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Table 3.3 - Parameters from the KWW analysis of the DETA spectra data.

<table>
<thead>
<tr>
<th>X_{POSS} (%)</th>
<th>t_{polym} (min.)</th>
<th>( \varepsilon_0 ) (± 0.05)</th>
<th>( \varepsilon_\infty ) (± 0.05)</th>
<th>( \Delta \varepsilon ) (± 0.1)</th>
<th>( \beta ) (± 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26</td>
<td>8.08</td>
<td>4.4</td>
<td>3.68</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>8.07</td>
<td>4.32</td>
<td>3.75</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.02</td>
<td>4.3</td>
<td>3.72</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>7.99</td>
<td>4.28</td>
<td>3.71</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>7.95</td>
<td>4.3</td>
<td>3.65</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>7.9</td>
<td>4.48</td>
<td>3.42</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>8.13</td>
<td>4.57</td>
<td>3.56</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.1</td>
<td>4.49</td>
<td>3.61</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>8.05</td>
<td>4.4</td>
<td>3.65</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>8.09</td>
<td>4.38</td>
<td>3.71</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>8.02</td>
<td>4.51</td>
<td>3.51</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>7.99</td>
<td>4.56</td>
<td>3.43</td>
<td>0.26</td>
</tr>
<tr>
<td>4.3</td>
<td>27</td>
<td>8.3</td>
<td>4.49</td>
<td>3.81</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>8.28</td>
<td>4.44</td>
<td>3.84</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.27</td>
<td>4.4</td>
<td>3.87</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>8.24</td>
<td>4.39</td>
<td>3.85</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>8.2</td>
<td>4.41</td>
<td>3.79</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>8.16</td>
<td>4.66</td>
<td>3.5</td>
<td>0.27</td>
</tr>
<tr>
<td>10.7</td>
<td>30</td>
<td>8.53</td>
<td>4.41</td>
<td>4.12</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>8.52</td>
<td>4.4</td>
<td>4.12</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>8.4</td>
<td>4.4</td>
<td>4</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>8.37</td>
<td>4.45</td>
<td>3.92</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.34</td>
<td>4.49</td>
<td>3.85</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>8.34</td>
<td>4.5</td>
<td>3.84</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 3.47 – Complex plane plot of DGEBA-HA for 6 frequencies.

Figure 3.48 – Cole-Cole plot of DGEBA-HA for 6 fixed $t_{\text{polym}}$.

Figure 3.49 – Complex plane plot of DGEBA-POSS-HA ($x_{\text{POSS}} = 2\%$) for 6 frequencies.

Figure 3.50 – Cole-Cole plot of DGEBA-POSS-HA ($x_{\text{POSS}} = 4.3\%$) for 6 fixed $t_{\text{polym}}$. 
Figure 3.51 – Complex plane plot of DGEBA-POSS-HA ($x_{POSS}=4.3\%$) for 6 frequencies.

Figure 3.52 – Cole-Cole plot of DGEBA-POSS-HA ($x_{POSS}=4.3\%$) for 6 fixed $t_{polym}$.

Figure 3.53 – Complex plane plot of DGEBA-POSS-HA ($x_{POSS}=10.7\%$) for 6 frequencies.

Figure 3.54 – Cole-Cole plot of DGEBA-POSS-HA ($x_{POSS}=10.7\%$) for 6 fixed $t_{polym}$. 
Table 3.4 - Parameters from the KWW analysis of the HA isochrones.

<table>
<thead>
<tr>
<th>χ_{POSS} (%)</th>
<th>f (kHz)</th>
<th>ε₀ (± 0.05)</th>
<th>ε∞ (± 0.05)</th>
<th>Δε (± 0.1)</th>
<th>β (± 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>5.91</td>
<td>3.6</td>
<td>2.31</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.93</td>
<td>3.58</td>
<td>2.35</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>5.98</td>
<td>3.59</td>
<td>2.39</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.02</td>
<td>3.54</td>
<td>2.48</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>6.08</td>
<td>3.62</td>
<td>2.46</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>6.2</td>
<td>3.49</td>
<td>2.71</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>6.07</td>
<td>3.68</td>
<td>2.39</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.08</td>
<td>3.63</td>
<td>2.45</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>6.12</td>
<td>3.61</td>
<td>2.51</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.21</td>
<td>3.58</td>
<td>2.63</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>6.22</td>
<td>3.55</td>
<td>2.67</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>6.31</td>
<td>3.52</td>
<td>2.79</td>
<td>0.35</td>
</tr>
<tr>
<td>4.3</td>
<td>1</td>
<td>6.39</td>
<td>4.18</td>
<td>2.21</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.42</td>
<td>4.13</td>
<td>2.29</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>6.47</td>
<td>4.11</td>
<td>2.36</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.52</td>
<td>3.98</td>
<td>2.54</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>6.6</td>
<td>3.9</td>
<td>2.7</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>6.66</td>
<td>3.84</td>
<td>2.82</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 3.5 - Parameters from the KWW analysis of the HA spectra data.

<table>
<thead>
<tr>
<th>χ_{POSS} (%)</th>
<th>t_{polym} (min.)</th>
<th>ε₀ (± 0.05)</th>
<th>ε∞ (± 0.05)</th>
<th>Δε (± 0.1)</th>
<th>β (± 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150</td>
<td>6.04</td>
<td>3.55</td>
<td>2.49</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>5.95</td>
<td>3.54</td>
<td>2.41</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>5.87</td>
<td>3.52</td>
<td>2.35</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.83</td>
<td>3.49</td>
<td>2.34</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>5.8</td>
<td>3.47</td>
<td>2.33</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>5.77</td>
<td>3.46</td>
<td>2.31</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>6.1</td>
<td>3.84</td>
<td>2.26</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>6.02</td>
<td>3.8</td>
<td>2.22</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>5.97</td>
<td>3.71</td>
<td>2.26</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>5.96</td>
<td>3.68</td>
<td>2.28</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>5.94</td>
<td>3.63</td>
<td>2.31</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>6.53</td>
<td>3.95</td>
<td>2.58</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>6.43</td>
<td>3.97</td>
<td>2.46</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>6.38</td>
<td>3.98</td>
<td>2.4</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>6.33</td>
<td>3.99</td>
<td>2.34</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>6.31</td>
<td>3.99</td>
<td>2.32</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>6.28</td>
<td>3.99</td>
<td>2.29</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Figure 3.55 – Complex plane plot of DGEBA-EDA for 6 frequencies.

Figure 3.56 – Cole-Cole plot of DGEBA-EDA for 6 fixed $t_{\text{polym}}$.

Figure 3.57 – Complex plane plot of DGEBA-POSS-EDA ($x_{\text{POSS}} = 2\%$) for 6 frequencies.

Figure 3.58 – Cole-Cole plot of DGEBA-POSS-EDA ($x_{\text{POSS}} = 2\%$) for 6 fixed $t_{\text{polym}}$. 
Figure 3.59 – Complex plane plot of DGEBA-POSS-EDA ($x_{\text{POSS}} = 4.3\%$) for 6 frequencies.

Figure 3.60 – Cole-Cole plot of DGEBA-POSS-EDA ($x_{\text{POSS}} = 4.3\%$) for 6 fixed $t_{\text{polym}}$.

Figure 3.61 – Complex plane plot of POSS-EDA for 6 frequencies.

Figure 3.62 – Cole-Cole plot of POSS-EDA for 6 fixed $t_{\text{polym}}$. 
Table 3.6 - Parameters from the KWW analysis of the EDA isochrones.

<table>
<thead>
<tr>
<th>X_{POSS} (%)</th>
<th>f (kHz)</th>
<th>\varepsilon_s (\pm 0.05)</th>
<th>\varepsilon_\infty (\pm 0.05)</th>
<th>\Delta \varepsilon (\pm 0.1)</th>
<th>\beta (\pm 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>8.47</td>
<td>4.5</td>
<td>3.97</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.5</td>
<td>4.51</td>
<td>3.99</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.48</td>
<td>4.54</td>
<td>3.94</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.51</td>
<td>4.56</td>
<td>3.95</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.6</td>
<td>4.52</td>
<td>4.08</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.7</td>
<td>4.51</td>
<td>4.19</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>8.46</td>
<td>4.72</td>
<td>3.74</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.48</td>
<td>4.7</td>
<td>3.78</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.47</td>
<td>4.73</td>
<td>3.74</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.51</td>
<td>4.72</td>
<td>3.79</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.6</td>
<td>4.69</td>
<td>3.91</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.72</td>
<td>4.66</td>
<td>4.06</td>
<td>0.3</td>
</tr>
<tr>
<td>4.3</td>
<td>1</td>
<td>8.6</td>
<td>5.1</td>
<td>3.5</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.62</td>
<td>5.06</td>
<td>3.56</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>8.62</td>
<td>5.04</td>
<td>3.58</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.65</td>
<td>5.01</td>
<td>3.64</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>8.71</td>
<td>4.92</td>
<td>3.79</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>8.78</td>
<td>4.83</td>
<td>3.95</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3.7 - Parameters from the KWW analysis of the EDA spectra data.

<table>
<thead>
<tr>
<th>X_{POSS} (%)</th>
<th>t_{polym} (min.)</th>
<th>\varepsilon_s (\pm 0.05)</th>
<th>\varepsilon_\infty (\pm 0.05)</th>
<th>\Delta \varepsilon (\pm 0.1)</th>
<th>\beta (\pm 0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>34</td>
<td>8.46</td>
<td>4.7</td>
<td>3.76</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>8.41</td>
<td>4.68</td>
<td>3.73</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.32</td>
<td>4.68</td>
<td>3.64</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>8.24</td>
<td>4.66</td>
<td>3.58</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>8.2</td>
<td>4.63</td>
<td>3.57</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.17</td>
<td>4.55</td>
<td>3.62</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>8.52</td>
<td>4.73</td>
<td>3.79</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>8.44</td>
<td>4.71</td>
<td>3.73</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.38</td>
<td>4.7</td>
<td>3.68</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>8.31</td>
<td>4.69</td>
<td>3.62</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>8.29</td>
<td>4.68</td>
<td>3.61</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.27</td>
<td>4.58</td>
<td>3.69</td>
<td>0.29</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>8.62</td>
<td>5.15</td>
<td>3.47</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>8.59</td>
<td>5.13</td>
<td>3.46</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>8.55</td>
<td>5.12</td>
<td>3.43</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>8.52</td>
<td>5.11</td>
<td>3.41</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>8.51</td>
<td>5.11</td>
<td>3.4</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.45</td>
<td>5.1</td>
<td>3.35</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Although the change in the structure and state of the polymer in the isochrones violates the Kramers-Kronig relation [Kramers 1927, de Laer Kronig 1926], the analysis of the complex-plane plots for a fixed \( f \) has been previously justified [Wasylyshyn et al. 1996, Parthun et al. 1996], because it yields values of \( \tau_0 \) and \( \beta \) which do not differ significantly from the values of the spectra analysis. \( \beta \) for the EDA mixtures from the spectra and isochrones differ by no more than 0.09.

Another apparent violation of the Kramers-Kronig relation is with the small sigmoid shape decrease in \( \varepsilon' \) of DGEBA-POSS-HA that does not show the expected corresponding peak in \( \varepsilon'' \) for a relaxation process. Kramers-Kronig relation states that the imaginary variable is proportional to the derivative of the real, and the real is proportional to the integral of the imaginary, which can be written in the form,

\[
\varepsilon''(\omega) = -\frac{\pi}{2} \left( \frac{d\varepsilon'(\omega)}{d \ln \omega} \right)
\]  

The parameters \( \varepsilon_{s}, \varepsilon_{\infty}, \Delta \varepsilon, \) and \( \beta \) from the analysis of the isochrones of DETA, HA and EDA mixtures are listed in Tables 3.2, 3.4 and 3.6. \( \varepsilon_{s} \) and \( \Delta \varepsilon \) increase with an increase in frequency, while \( \varepsilon_{\infty} \) remains relatively constant or decreases slightly, and \( \beta \) remains constant within the error limits (± 0.02) for all samples and mixtures. At a fixed frequency, both \( \varepsilon_{s} \) and \( \varepsilon_{\infty} \) increased with POSS. The time-invariant data were analyzed in the same manner as the isochrones. Tables 3.3, 3.5 and 3.7 list the relaxation parameters from the spectra analysis of DETA, HA and EDA mixtures, respectively. For DETA mixtures, a decrease was observed in \( \varepsilon_{s} \) with \( t_{\text{polymer}} \), and \( \Delta \varepsilon \) either remained constant or decreased slightly with \( t_{\text{polymer}} \). \( \varepsilon_{\infty} \) initially decreased with polymerization time, but in
some cases, a higher $\varepsilon_\infty$ at higher $t_{\text{polym}}$ had to be chosen for the analysis in order to maintain a good fit. For HA and EDA mixtures, $\varepsilon_3$ and $\varepsilon_\infty$ decrease with $t_{\text{polym}}$ and increase with $x_{\text{POSS}}$, while $\Delta \varepsilon$ decreases with $t_{\text{polym}}$ and $x_{\text{POSS}}$.

$\beta$ also appears to decrease with $t_{\text{polym}}$, or at least remains constant within the error limits. For DETA, $\beta$ decreases from 0.3 to 0.26 for the POSS-free sample, 0.3 to 0.25 for the 2 % sample, 0.3 to 0.26 for the 4.3 % sample and 0.26 to 0.2 for the 10.7 % sample, within a span of eight to fourteen minutes. For HA, $\beta$ decreases from 0.37 to 0.32 for the POSS-free sample, 0.4 to 0.32 for the 2 % sample, and 0.37 to 0.32 for the 4.3 % sample between $t_{\text{polym}} = 150$ to 300 minutes. For EDA, $\beta$ decreases from 0.34 to 0.27 for the POSS-free sample, 0.35 to 0.29 for the 2 % sample, and 0.35 to 0.3 for the 4.3 % sample between $t_{\text{polym}} = 34$ to 50 minutes.

The dielectric relaxation time was measured from the analysis of the isochronal plots. The term dielectric relaxation time is used to distinguish it from the more general structural relaxation time. Each pair of $\varepsilon'$-$\varepsilon''$ data points corresponds to a pair of $N'$-$N''$ (for a given $\beta$), which in turn corresponds to a unique value of the product $\omega \tau_0$. $\tau_0$ is plotted against $\log(t_{\text{polym}})$ in Fig. 3.63 for the three amine mixtures. By increasing POSS, the polymerization time required to reach a specific $\tau_0$ increases. The slope of the curve appears to decrease slightly with $x_{\text{POSS}}$ for DETA, but a decrease in slope is not as apparent with the HA and EDA samples. The range of $\tau_0$ obtainable from the analysis is limited to about $10^{-9}$ to $10^{-1}$ seconds, as IR vibrations keep $\varepsilon''$ above zero after
vitrification, and anything greater than $10^{-1}$ s would be an estimate from the theoretical values.

$\tau_o$ may also be obtained from the spectra, if $\omega \tau_m$ is assumed to be equal to unity, as it would be for an exponential decay with a single Debye relaxation time. $\tau_m$ is the relaxation time at $t(\varepsilon''_{\text{peak}})$, and is plotted in Fig. 3.63 for the 4.3 % DETA mixture, calculated from several spectra. The difference in $\tau_o$ and $\tau_m$ against polymerization time is $\sim 5\%$, confirming the use of the complex plane plots for analysis, despite a violation of Kramers-Kronig relation.
Figure 3.63 – Log $\tau_0$ plotted against log $t_{polym}$ for (A) DETA (B) HA and (C) EDA mixtures.
3.4. Discussion

3.4.1 Effects of nm heterogeneities on gelation time, kinetics and dc conductivity

The gelation time and exponential parameter $\gamma$ obtained by fitting Eqn. 3.9 to experimental data are shown in Fig. 3.64 for the DETA and EDA samples. $t_{gel}$ of the DETA samples increases with $x_{POSS}$, and $\gamma$ increases too, but not consistently. $t_{gel}$ and $\gamma$ increase from the DGEBA-EDA to the 2% mixture, the decrease from the 2 % to the 4.3 % mixture, while POSS-EDA gels the slowest. The validity of using Eqn. 3.9 has been discussed previously [Alig et al. 1996], but its ability to accurately estimate $t_{gel}$ will be further verified here. A $t_{gel}$ of 24 minutes for DGEBA-DETA cured at 323 K was estimated from Eqn. 3.9, while De Nograro et al. (1995) report a value of 22 minutes for the same system studied by rheological measurements. The $t_{gel}$ of DGEBA-EDA cured at 313 K was estimated at 46 minutes, while Zhou and Johari (1997) report a value of 51 minutes based on ultrasonic measurements. It can therefore be said that the $t_{gel}$’s found in this study are accurate within 5 minutes.

A network polymer does not form from a diepoxy and monoamine reaction, and for this reason Eqn. 3.9 is not applicable to the polymerization of DGEBA-HA [Wasylyshyn and Johari 1997, Wasylyshyn and Johari 1999]. When the number of POSS-epoxides in a DGEBA-POSS-monoamine mixture is significant, a predominantly network structure might prevail. Hence, only $t_{gel}$ and the parameters for the 10.7 % HA and POSS-HA mixture are reported. $t_{gel}$, $\gamma$, and $\sigma_{dc,0}$ for these two samples are 145 minutes, 2.94, 1.9 $\mu$S/m and 431 minutes, 7.12, 7.3 $\mu$S/m, respectively. Rheological
Figure 3.64 – $t_{\text{gel}}$ and $\gamma$ estimated from Eqn. 3.9, plotted against $x_{\text{POSS}}$ for (A) DETA mixtures and (B) EDA mixtures.
or mechanical measurements would be able to confirm these values.

\( \sigma_{dc,0} \) increased with an increase in POSS, but amine deprotonation is unlikely to be the cause since the ratio of epoxides to amine remains constant irrespective of the epoxy resin. It is likely due to the lower \( \eta \) of EP0409. Apart from water, the concentration of other impurities in EP0409 are not known, and therefore it can only be stated that there is either an increase in mobility from water, a greater percentage of impurity ions in the POSS product, or both, which causes \( \sigma_{dc,0} \) to increase.

In addition to \( t_{polym}(\varepsilon''_{\min}) \) and \( t_{polym}(\varepsilon''_{\text{peak}}) \), \( t_{gel} \) can be used as a qualitative indicator of polymerization kinetics, and it can therefore be said that replacing a diepoxide with a silsesquioxane molecule decreases the rate of polymerization. Recalling the calorimetry results, the reaction kinetics with DETA increased with small quantities of POSS, as \( \alpha \to 1 \) earlier for the 2 and 4 % mixtures. Hence, one would expect \( t_{gel} \) to be lower or \( \varepsilon''_{\text{peak}} \) to appear earlier for 2% POSS, but the opposite is observed instead. Unfortunately, there isn’t an accurate method of quantitatively assessing reaction kinetics from dielectric measurements [Soualmia et al. 1982, Sheppard and Senturia 1985], nor are the interpretation of the results reliable [Senturia and Sheppard 1986]. To resolve this seeming discrepancy in kinetics between dielectric and calorimetric measurements, the factors that determine \( t_{gel} \) must be brought into focus – one such factor being stoichiometry.

Amine-rich mixtures exhibit accelerated reactions relative to stoichiometric mixtures, but in a study on the dielectric relaxation of an amine-rich DGEBA-cyclohexylamine mixture, Johari (1994b) found that not only was the \( \alpha \)-relaxation peak
absent from the $\varepsilon''$ curve, but that the local minimum, $\varepsilon''_{\text{min}}$, appeared later compared to the corresponding stoichiometric mixture. The increase in $t(\varepsilon''_{\text{min}})$ was attributed to a longer $t_{\text{polym}}$ needed to reach the same $\tau_0$ in the low viscosity range where the kinetics is faster but the increase in $\tau_0$ with an increase in the extent of polymerization at a fixed $T_{\text{polym}}$ is less, i.e., $d\log(\tau_0)/d\log(t_{\text{polym}})$ is lower. Therefore, the time required for a sub-stoichiometric mixture to reach the same molecular weight or viscosity as a stoichiometric that would result in a certain degree of relaxation or phase delay might be greater, and thus $\varepsilon''_{\text{min}}$ appears later. The same reasoning can be applied to the $\varepsilon''_{\text{peak}}$ of the silsesquioxane composites.

Strachota and coworkers (2007) proposed three types of cross-linked structures for POSS-epoxy-amine systems, (i) that of an ideal epoxy-amine network, (ii) networks with oligomeric POSS junctions and (iii) isolated POSS junctions, cyclically bonded with the amine. Based on their results from SAXS and mechanical shearing experiments they argue that (ii) and (iii) are more prevalent than the ideal network structure that typically occurs in diepoxide-diamine systems. If significant cyclization occurs with POSS, then one can imagine that the amount of time required for the mixture to reach the same molecular weight, viscosity or relaxation time as the POSS-free mixture would be greater, and thus, $t_{\text{gel}}$, $t(\varepsilon''_{\text{min}})$ or $t(\varepsilon''_{\text{peak}})$ would increase with POSS. The discrepancy in kinetics between the dielectric and calorimetric measurements cannot be thoroughly resolved, because the two methods are not comparable, even though the measurements can be made simultaneously with a single apparatus [Ferrari et al. 1996].
3.4.2 Effects on relaxation time, distribution of relaxation rates and dynamic heterogeneity

Relaxation spectra provide qualitative information on changes in molecular structure and the modes of relaxation, and quantitative information on the relaxation times and the distribution of these rates. During polymerization of a thermoset, two new relaxation processes, the $\alpha$- and the JG-relaxations [Wasylyshyn et al. 1997a,b, Johari and Goldstein 1970], evolve from the unimodal GHz frequency relaxation feature, and shift to lower frequencies, while the strength of the original mode is highly reduced in the completely polymerized glassy state [Parthun and Johari 1995, Wasylyshyn et al. 1997a,b]. The characteristic relaxation time, $\tau_o$, of the $\alpha$ and JG processes increases with $t_{polym}$, but the $\alpha$ relaxation progresses more rapidly. When $\tau_o$ has exceeded the time of one’s observation, the liquid is said to vitrify isothermally [Johari 1994a]. $\tau_o$ and the distribution of rates are intrinsic of morphology, structure and molecule arrangements which depend on the size, shape, functionality, and electrical characteristics of the monomers.

The values of $\beta$ obtained from the analysis of the isochrones (Tables 3.2, 3.4 and 3.6) decreases with an increase in the amount of POSS from 0.27 for the POSS-free mixtures to 0.2 for the 21 % DETA mixture, from 0.35 to 0.33 for the HA mixtures, but remains relatively constant for the EDA mixtures at ~0.28. $\beta$ is essentially independent of $\omega$, within an error margin of ± 0.02. In the analysis performed by fixing $t_{polym}$, $\beta$
decreases with \( t_{\text{polym}} \) by no more than 0.08 within the time frame in which the analysis can be performed after the appearance of \( \alpha \)-peak, as can be seen in Tables 3.3, 3.5 and 3.7.

Although \( \beta \) was determined after subtracting the dc conductivity contributions to the spectra, and ignoring the faster relaxation that distorts the spectra at the high frequency end effects, the values determined may have an uncertainty of as much as \( \pm 0.02 \), which is significantly smaller than the change in \( \beta \) observed on changing composition of the mixture. Errors can stem from two other sources: the overlap of several relaxation processes particularly as the \( \alpha \)-relaxation process evolves from a GHz frequency process [Johari 1994a], and changes in the contributions to \( \varepsilon' \) and \( \varepsilon'' \) from changes in the low-frequency vibrational modes as the liquid densifies. \( \beta \) typically ranges from 0.6 to 0.85 for the \( \alpha \)-process of normal liquids and its value decreases as the temperature is decreased [Ngai 2011]. A higher degree of crosslinking also ensues from higher cure temperatures, \( T_{\text{polym}} \) [Parthun and Johari 1992b].

In this study, \( \beta \) decreases as a macromolecule grows at a fixed \( T \), despite its lower value of ~ 0.3, as if the temperature-dependence of \( \beta \) is analogous to molecular weight dependence of the macromolecule. The decrease in \( \beta \) with \( t_{\text{polym}} \) has been reported before and interpreted as an indication of an increase in steric hindrance causing a further increase in the distribution of times for different molecular modes of dipole relaxation [Ferrari \textit{et al.} 1998]. Parthun and Johari (1992b) reported higher \( \beta \) values for DGEBA polymerized with larger sized amines (e.g. hexamethylene diamine, HMDA, compared to propylene diamine or EDA). HMDA is a linear chain molecule with 6
adjacent C atoms, while EDA is a linear chain molecule of only 2 C atoms, and HMDA is expected to form a looser and lower crosslink density material. Based on this assumption, $\beta$ can be interpreted as an indicator of molecular packing or crosslink density as heterogeneity increases [Parthun and Johari 1992b]. As mentioned previously in section 2.4.3, the volumetric density of epoxides is marginally greater for the POSS molecule, and a tightly bonded structure with a higher crosslink density can be expected.

The statements made in the preceding paragraph seem to be validated by the decrease in $\beta$ with an increase in POSS observed in this study. A higher crosslink density, however, may not necessarily be the reason why, because the anticipated decrease was based on the assumption of ideal network bonding. Although significant phase separation is unlikely to occur in these types of nanocomposites, nano-scale phase separation has been observed [Mariani et al. 2007, Strachota et al. 2007], and heterogeneity is increased by variations in mobility between the phases [Venkateshan and Johari 2004]. The incorporation of POSS, whether via physical crosslinking or covalent bonding is expected to increase the number of regions of varying relaxation and diffusion rates, which in turn increases the distribution of reaction rates.

POSS increases static heterogeneity in a mixture, and the notion of dynamic heterogeneity arising from differences in the number of cross-links and arrangements of chain segments in different regions of its structure can be used in discussing polymerization kinetics [Khouri and Johari 2011]. Dynamic heterogeneity is anticipated to develop as $\tau_o$ and $\eta$ increase with $t_{polym}$. Figure 3.43 shows that the slope of the $\tau_o$ curves plotted against $t_{polym}$ decreases slightly with $x_{POSS}$, and the time taken to reach a
specific $\tau_0$ value increases. The reason for the shift in the $\tau_0$ curves with $x_{\text{POSS}}$ can be explained in the same manner already used to describe the changes in $t_{\text{gel}}$ and $t(\epsilon''_{\text{peak}})$ given in section 3.4.1. At a fixed $T$, the observed increase in $\tau_0$ with increase in $t_{\text{polym}}$ may be related to the decrease in the volume, enthalpy and entropy on polymerization. Accordingly, the irreversible increase in $\tau_0$ indicates that both the free volume and the configurational entropy of the liquid, $S_{\text{conf}}$, decrease on polymerization, as discussed by Venkateshan and Johari (2004).

In this study, $\tau_0$ is measured for the gelled state which does not show Newtonian flow. Because of this, its increase with $t_{\text{polym}}$ in the gelled state makes it difficult to envisage how $\tau_0$ and $\eta$ may be related. In an attempt to resolve it, one may define an intrinsic viscosity and diffusion coefficient in the gelled state which are different from the $\eta$ and the diffusion coefficient of an ultraviscous liquid and then experimentally determine $\tau_0$ and the diffusion coefficient of polymerizing liquids in real time to determine if these quantities differ in the two states. Otherwise, one could investigate the effects of POSS on the dynamic behavior of a non-polymerizing, preferably a rigid molecular, liquid. One may also attempt to resolve it by performing parallel rheological measurements with sufficient repeatability of time-dependent data. This is particularly important because $\tau_0$ continues to increase with $t_{\text{polym}}$ in the gelled state and dynamic heterogeneity does not refer to molecular dynamics in the gel state and it may shed more light on the observed distribution of rate constants in ultraviscous liquids when the reaction becomes diffusion-controlled [Maffezzoli et al. 1994].
Tables 3.2, 3.4 and 3.6 reveal that $\varepsilon_s$ and $\varepsilon_\infty$ of the isochrones increase with the amount of POSS, while a definite trend with $\Delta\varepsilon$ cannot be established. Average values over the six frequencies analyzed, however, show that all parameters increase with $x_{\text{POSS}}$. $\varepsilon_s$ increases by about ~3, 0.5 and 1.5 from the POSS-free to the POSS-only DETA, HA and EDA samples, respectively. This is attributable to higher $\varepsilon_s$ of POSS and the monotonic increase shows that the ternary mixture behaves as an ideal solution as far as $\varepsilon_s$ and $\varepsilon_\infty$ are concerned.

According to the statistical theory of electric polarization developed by Onsager (1936), Kirkwood (1939), and Fröhlich (1958), the factors that contribute to the value of $\varepsilon_s$ are (i) volumetric density of dipoles, (ii) molecular vapour phase dipole moment, (iii) orientational correlation factor and, (iv) $\varepsilon_\infty$, which is dependent on the refractive index, and (v) temperature. The Onsager-Kirkwood-Fröhlich equation [Fröhlich 1958] is given as

$$\varepsilon_s = \varepsilon_\infty + \left( \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty} \right) \frac{4\pi N_d}{3 k_b T} g \mu_0^2,$$  

(3.17)

where $N_d$ is the number density of dipoles, $g$ is the orientation correlation factor, $\mu_0$ is the vapour phase dipole moment, and $k_b$ is Boltzmann’s constant. During the polymerization of a thermoset, the increase in density [Holst et al. 2005] which would increase $\varepsilon_s$ is offset by a decrease in $g\mu_0^2$, and $\varepsilon_s$ decreases with time [Parthun 1997]. The product specified density of POSS is greater than DGEBA, as shown in Table 1.2, and assuming that factor $g\mu_0^2$ is identical for POSS-free and POSS-only systems, $N_d$ would be greater for POSS. The increase in $\varepsilon_s$ could be due to impurity water, since smaller polar
molecules have a higher susceptibility, $\chi$. On the account of water evaporation, a reduction in $\varepsilon'$ within a few minutes would be expected, but unlike the calorimetry experiments, water remains in the dielectric cell as it is a closed system.

3.4.3 Change in the dielectric features with polymerization time and temperature

Now that the kinetics and relaxation behaviour have been discussed, attention can be given to the uncharacteristic behavior of the POSS-only mixtures. There are three distinguishable features in the isochrones of these mixtures, whose occurrences are inconsistent with the phenomenological changes associated with dipolar relaxation. The first feature is a small sigmoid-shape decrease in the $\varepsilon'$ at low $t_{\text{polym}}$, prior to the large step decrease, and is most evident in the isochrones of the HA mixtures in Figs. 3.15, 3.17, 3.19 and 3.21. The second feature is the sharp increase in the $\varepsilon'$ plots against $t_{\text{polym}}$ for POSS-DETA and POSS-EDA at frequencies less than 2 kHz. $\varepsilon'$ of POSS-EDA at 1 kHz increases from 10.4 at the 29th minute of polymerization to 10.7 at 37th minute mark, and thereafter decreases to a final value of 6.8 (Fig. 3.32). In the POSS-DETA isochrone at 1 kHz (Fig. 3.12), $\varepsilon'$ increases from 10.1 at a $t_{\text{polym}}$ of 21 min to 13.2 at a $t_{\text{polym}}$ of 31 min and thereafter it decreases to 8.0 after an additional 85 minutes of polymerization. A broad, shallow increase in $\varepsilon'$ of POSS-HA is also observed, which peaks at 7.6 after ~70 minutes of polymerization. The third feature is a concurrent increase in $\varepsilon'$ and $\varepsilon''$ after the 85th minute mark for POSS-DETA.
The first feature is characterized by (i) the lack of a corresponding peak in the plot of $\varepsilon''$ against $t_{\text{polym}}$, and by (ii) a gradual diminishing of its magnitude as the frequency of measurement is increased, and it ultimately vanishes. This has been observed in other studies, where the effects from molecular dipole reorientation have been ruled out as a cause [Venkateshan and Johari 2004], and because it has been observed for single component polymerizing liquids [Alig and Johari 1993], it is also unrelated to a specific reaction mechanism between two different components [Parthun and Johari 1995]. Furthermore, the magnitude of this step-decrease in the $\varepsilon'$ against $t_{\text{polym}}$ is relatively low, and therefore seems inconsistent with the large dielectric polarization usually associated with the orientation of highly dipolar zwitter-ions that may form during the diepoxide-diamine reaction. To date, there does not seem to be an explanation as to how zwitter-ions become rapidly consumed in a short duration such that $\varepsilon'$ decreases without a significant increase in the extent of polymerization [Venkateshan and Johari 2004].

Like the first feature, the spiked-increase in $\varepsilon'$ diminishes at higher frequencies, and lacks a corresponding change in the plot of $\varepsilon''$ against $t_{\text{polym}}$. In this respect, the event violates the Kramers-Kronig relation. If a corresponding change is indeed present, then it is overshadowed by the progressive decrease in $\varepsilon''_{\text{dc}}$ that dominates within this $t_{\text{polym}}$ range. Losses in the electric field are increased by dc effects and by molecules that do not orient in the direction of the field, and is decreased by interfacial polarization, which is the accumulation of charged species at the electrode-material interface where the Maxwell-Wagner-Sillars (MWS) process occurs [Wagner 1914, Sillars 1937]. These effects occur independently of each another, and yet, the magnitude of each varies
according to the dynamic properties of the material. Contributions to charge density on the electrode from dipolar orientation continuously decrease with macromolecular growth, so any increase in $\varepsilon'$ would be due to the MWS effects. The time-dependent interfacial polarization contributions to permittivity, $\varepsilon'_{\text{int}}$, and loss, $\varepsilon''_{\text{int}}$, can be assessed with the expressions derived by Cole and coworkers [Johnson and Cole 1951, Cole and Tombari 1991]:

$$\varepsilon'_{\text{int}}(t_{\text{polym}}) = \left[ z_0(t_{\text{polym}}) \sin \left( \frac{n\pi}{2} \right) \left( \frac{\sigma_{dc}(t_{\text{polym}}) + \sigma_{\text{dip}}(\omega,t_{\text{polym}})}{\varepsilon_0^2} \right)^2 C_0 \right] \omega^{-(n+1)} \quad (3.18)$$

$$\varepsilon''_{\text{int}}(t_{\text{polym}}) = \left[ z_0(t_{\text{polym}}) \cos \left( \frac{n\pi}{2} \right) \left( \frac{\sigma_{dc}(t_{\text{polym}}) + \sigma_{\text{dip}}(\omega,t_{\text{polym}})}{\varepsilon_0^2} \right)^2 C_0 \right] \omega^{-n} \quad (3.19)$$

where $z_0$ is the frequency-independent impedance of interfacial polarization and is characteristic of the electrode material interface. $C_0$ is the capacitance in air, and $n$ is a constant of the Warburg impedance usually taken as 0.5 [Johnson and Cole 1951, Johari 1993]. The remainder of variables and constants are the same as before. Equation 3.18 was used to calculate $z_0$ of POSS-DETA at 1 kHz as a function of $t_{\text{polym}}$. Its value of 8.18 MΩ at $t_{\text{polym}} = 22.5$ min increases to 4004.27 MΩ at $t_{\text{polym}} = 31.8$ min. These calculations show that the magnitude of $z_0$ increases according to the growth of the covalently bonded structure of the polymerizing liquid. Thus, the increase in $\varepsilon'$ in the isochrones observed in the beginning of a macromolecule’s growth in the POSS-DETA and EDA samples is due to the increase in $z_0$ with $t_{\text{polym}}$. An increase in $z_0$ is also expected with the broad increase in $\varepsilon'$ of POSS-HA. Similar calculations at polymerization times before and after the
dipolar step-decrease in $\varepsilon'$ would show that $z_0$ decreases for the first feature, and increases for the third.

$z_0$ can be taken to be constant for a given material and a set of electrodes, but if the chemical structure or physical state of a material changes, its ionic and or dipolar state changes and the $z_0$ value would change. $z_0$, $\sigma_{dc}$ and $\sigma_{dip}$ do not change for a fixed $t_{polym}$, and the peak-like feature resulting from $\varepsilon'_{\text{int}}$ decreases according to $(\omega)^{(n+1)}$ in Eqn. 3.18. Addition of the POSS substituent to the polymerizing mixture increases $z_0$ that increases $\varepsilon'$. At low concentrations of POSS this increase is undetectably small and it reaches a maximum value for the POSS-only EDA and DETA samples. Before small clusters of network structure join together by covalent bonds to form a gel, (i) $z_0$ changes as the structure changes with $t_{polym}$ and (ii) $\varepsilon''_{dc}$ decreases as the viscosity increases. The feature observed in the $\varepsilon'$ isochrones depends on the manner of change in $z_0$ and the rate of decrease in $\sigma_{dc}$ and $\varepsilon''_{dc}$ before gelation occurs. It is therefore concluded that as the POSS-only-amine macromolecules grow, $z_0$ increases initially more rapidly than $\sigma_{dc}$ decreases.

To further investigate these features, POSS-DETA was cured at additional temperatures of 363, 343 and 298 K. Isochrones of $\varepsilon'$ and $\varepsilon''$ from the polymerization at these four temperatures are shown in Fig. 3.65. The sharp peak is evident in the $\varepsilon'$ plots for the cure at 323 K, 343 K and 363 K (albeit rather skewed) but is absent at 298 K. The peak shifts from a $t_{polym}$ of ~ 32 min and $\varepsilon'$ value of ~ 13.1 to ~ 4 min and 14.3 as the temperature is raised from 323 K to 363 K. A broad second peak appears in the $\varepsilon'$ plots of the mixtures polymerized at 363 K and 343 K, and this peak shifts to lower $t_{polym}$ and
increases in magnitude with an increase in $T_{\text{polym}}$. It is important to note the simultaneous peak which appears in $\varepsilon''$ in Fig. 3.65 (B). Only the onset of the second peak, not the entire peak, is seen with the 323 K curve, since the experiment was ended prematurely.

An increase in $\varepsilon'$ during real-time measurements of polymerizing liquids has been observed in systems where phase separation is known to occur. A marked increase in $\varepsilon'$ prior to the step decrease has been observed in epoxy-amine mixtures with rubber composites such as butadiene acrylonitrile (ATBN) and its functionalized derivatives [Maistros et al. 1992, Wang et al. 1992] and by poly(ether imide) [Vinh-Tung et al. 1996] which induce phase separation. Wang et al. (1992) investigated the polymerization of DGEBA-diamino diphenyl methane with ATBN and found a concomitant increase in $\varepsilon'$ and $\varepsilon''$.

The marked increase in $\varepsilon'$ and $\varepsilon''$ from interfacial polarization in this study could be due to phase separation, and if so, then it can be said that the phase separation occurs in two stages; the first prior to gelation, and the second after it. Without the aid of microscopy, however, phase separation cannot be confirmed. It is sufficient to say that changes in the electrode/material interface from changes in the structure of the material increase permittivity and loss.
Figure 3.65 – (A) $\varepsilon'$ plotted against $t_{\text{polym}}$ of four POSS-DETA mixtures polymerized at different temperatures and measured at 1 kHz and (B) the corresponding $\varepsilon''$ plots.
Chapter 4: Resolution of the Residual Entropy on Heating and Cooling Through the Glass Region

4.1 Residual Entropy of Glasses

A crystalline material can be made into a glass when it is heated past its melting temperature, $T_m$, and subsequently supercooled. The material’s structure becomes frozen-in at the glass transition temperature, $T_g$, and its entropy decreases during the process. Calorimetric experiments have shown that the measured entropy change on cooling (or heating) a material from $T_m$ to absolute zero deviates with respect to the calculated value from the statistical equation [Bestul and Chang 1964, Chang and Bestul 1972]. This has been interpreted as a frozen-in or residual entropy, $S_{res}$. Residual entropy has also been observed for some disordered crystals, such as sodium sulfate hydrates [Ruben et al. 1960] and KOH-doped hexagonal ice [Tajima et al. 1982].

Classical thermodynamics predicts that as $T \rightarrow 0$ K, the number of accessible configurations of a material diminishes. Entropy of a perfect crystal becomes nil at absolute zero according to Boltzmann’s statistical equation (1876)

$$S = k_B \ln(\Omega) ,$$  \hspace{1cm} (4.1)

where $S$ in entropy (J/K), $k_B$ is Boltzmann’s constant ($= 1.38 \times 10^{-23}$ J/K), and $\Omega$ is the number of accessible configurations or the number of distinguishable configurations of a fixed energy state, which is equal to 1 at 0 K. Like a perfect crystal, the number of configurations of a glass is expected to equal 1 at absolute zero, and $S_{config}$ would be zero. Debates have surrounded the issue of whether or not $S_{res}$ of glasses is real. Kivelson and
Reiss (1999) state that $S_{\text{res}}$ is an artifact stemming from the inclusion of the irreversible glass transition process for which there is not any latent heat. The arguments of Kivelson and Reiss were dismissed by Goldstein (2008) who showed that the vanishing configurational entropy, $S_{\text{config}}$, from their proposed thought-experiment leads to a perpetual motion machine and a non-trivial violation of the second law of thermodynamics. Goldstein further points out that for those crystals that show a $S_{\text{res}}$, the temperature of kinetic freezing is greater than the temperature of disordering, and the path between the two temperatures is reversible.

Strictly speaking, calorimetric entropy can be measured only on reversible paths and the effect of irreversibility during the temperature range of glass formation can be estimated using the second law of thermodynamics. Bestul and Chang (1965) proposed using the limits of the measured entropy to resolve the errors in $S_{\text{res}}$. They point out that the integral of $(C_p/T)dT$ from heating measurements actually brackets the lower limit of the true entropy change, and cooling measurements bracket the upper limit. This implies that adiabatic calorimetry performed by supplying heat to a sample gives an upper limit to $S_{\text{res}}$. Using empirical $C_p$ data for the heating and cooling of $B_2O_3$ through its glass transition region, Bestul and Chang (1965) found that differences in the entropy values from the two paths was an order of magnitude less than the values themselves, for which they felt reflected the reality of $S_{\text{ref}}$. In the event that the measured $S$ on heating from 0 K through $T_g$ is comparable to that from cooling over the same $T$-range, the process may be regarded as meeting the classical thermodynamic criteria of reversibility [Goldstein 2008]. An attempt is made to resolve the issue of residual entropy by demonstrating that
this criterion is met for a variety of materials (metallic glasses, crystals melts, and polymers).

4.2 Data Analysis and Results

The \( C_p \) data of seven materials were taken from literature and analyzed for differences in the change in entropy from heating and cooling paths through the glass transition region. These glasses vary in molecular structure and in intermolecular interactions, three of which are hydrogen bonded materials, acetaminophen, nifedipine [Tombari et al. 2008a], and 2-ethyl-1-hexanol [Wang 2009], one molecular liquid with a large number of intramolecular degrees of freedom, triphenylolmethane triglycidyl epoxide (TPTGE) [Tombari et al. 2008b], one polymer, poly(vinyl acetate) (PVA) [Tombari et al. 2007], and two silica based Schott glasses [Fotheringham et al. 2009], one in the annealed state, for which Dr. U. Fotheringham provided published data. Molecular structures of acetaminophen, nifedipine, 2-ethyl-1-hexanol, TPTGE and PVA are shown in Fig. 4.1. Efforts to analyze at least one of the cured POSS-containing samples were prevented by cooling issues with the DSC.
Figure 4.1 – The molecular structures of (A) acetaminophen (B) nifedipine (C) 2-ethyl-1-hexanol and (D) triphenylolmethane triglycidyl ether and (E) vinyl acetate monomer.
$C_p$ plotted against $T$ and $\ln T$ for the seven samples are shown in Figs. 4.2 to 4.8. When a liquid is cooled through the glass region its enthalpy decreases, and the $C_p-T$ curve appears as a stretched sigmoid. When the glass is heated from its non-equilibrium state there is an initial decrease in enthalpy which is recovered during the glass region, and appears as an overshoot, or endothermic peak prior the equilibrium liquid state. These features and the temperature at which they occur are time-dependent and vary with heating and cooling rates $q_h$ and $q_c$. Shapes and features of the cooling and heating curves differ even when $q_c = q_h$, and such differences are most pronounced when $q_c > q_h$ [Moynihan et al. 1976].

The law of conservation of energy requires that,

$$H_{T_m}^{T_w} + \int_{T_m}^{T_w} C_{p,cool}dT = H_{T_m}^{T_w} - \int_{0}^{T_m} C_{p,heat}dT \tag{4.2}$$

where $H_{T_m}^{T_w}$ is the enthalpy of the liquid at $T_m$. When a sample is obtained by cooling to a temperature deep in the glassy state, $T_{glass}$, and subsequently heated without annealing, Eqn. 4.2 becomes,

$$\int_{T_{glass}}^{T_m} C_{p,cool}dT = -\int_{T_{glass}}^{T_m} C_{p,cool}dT \tag{4.3}$$

$$\Delta H_{cool} = \int_{T_{glass}}^{T_m} C_{p,cool}dT \quad \Delta H_{heat} = \int_{T_{glass}}^{T_m} C_{p,heat}dT \tag{4.4}$$

where $\Delta H_{cool}$ and $\Delta H_{heat}$ are the enthalpy change on the cooling and heating paths. The glass transition event is kinetic in nature, and the time-dependence of structural relaxation means that $C_p$ of a material while in the glass-liquid range depends upon the rate of temperature change and thus both $\Delta H_{cool}$ and $\Delta H_{heat}$ depend upon $q$. 

141
The entropy is determined from the $C_p d\ln T$ integral when the $C_p - T$ plots on the cooling and heating paths coincide. In the glass-liquid temperature range, the $C_p - T$ plots on the cooling and heating paths differ both in the shape and the temperature range. To maintain this distinction between the true entropy and that which is measured though the glass-liquid temperature range, the notation $\sigma$ is used for the $C_p d\ln T$ integral.

$$\Delta \sigma_{\text{cool}} = \int_{T_{\text{glass}}}^{T_{\text{cool}}} C_{p,\text{cool}} d\ln T ; \quad \Delta \sigma_{\text{heat}} = \int_{T_{\text{glass}}}^{T_{\text{heat}}} C_{p,\text{heat}} d\ln T \quad (4.5)$$

Unless the first law of thermodynamics is empirically verification, where $\Delta H_{\text{cool}}$ and $\Delta H_{\text{heat}}$ are equal within experimental errors, application of the Clausius limits and Eqn. 4.5 is compromised. The difference between the enthalpy determined by heating and cooling, and likewise with entropy, is computed as:

$$x_H = 100(\Delta H_{\text{cool}} - \Delta H_{\text{heat}})/\Delta H_{\text{cool}} \quad (4.6)$$

$$x_{\sigma} = 100(\Delta \sigma_{\text{cool}} - \Delta \sigma_{\text{heat}})/\Delta \sigma_{\text{cool}} \quad (4.7)$$

Differences in values arise from: (i) the inaccuracy of the original $C_p$ data, (ii) the procedure used for separating the $(dH/dT)_q$ curves of the cooling and heating paths in the DSC studies. (The two curves are obtained in a continuous cycle in which the heat flow signal of the DSC scan changes from positive to negative. The cooling curve is separated from the heating curve by first displacing it with respect to the other and then by graphical inversion.), (iii) digitization of the plots of data taken from the literature, save for the two Schott glasses [Fotheringham et al. 2009] for which the original data were available, (iv) the choice of $T_{\text{glass}}$ at which $C_p$ measured during cooling and heating may not be the same. (If the distribution of relaxation times is broad the $C_p - T$ plot would be
stretched out as $T_g$ is approached on the heating path. Since the $C_p - T$ plot on the cooling path would be even more stretched-out, a suitable value for $T_{glass}$ may not be determined with enough accuracy.), and from (v) the integration of $C_p dT$ whose accuracy is linked to the temperature step between two data points. The relative magnitude of errors from these sources is not known, but $C_p$ estimated from DSC measurements is usually accurate to within 1-2%. If errors from sources (iii) – (v) could be included, the estimated net errors would be close to $\pm 2\text{-}3\%$. A difference of 2% for $\Delta H_{cool}$ and $\Delta H_{heat}$ was chosen as the error tolerance in the analysis here.

Errors from (iv) can be minimized with a choice of a large temperature range – a low $T_{glass}$ and a high $T_{liq}$. However, since the range of interest is only that over which the transition occurs, it must be reduced as much as possible, and the temperatures at which heating and cooling curves coincide are the designated $T_{glass}$ and $T_{liq}$. These values, along with $\Delta H_{cool}$, $\Delta H_{heat}$, $\Delta \sigma_{cool}$, $\Delta \sigma_{heat}$, $x_H$ and $x_\sigma$ are listed in Table 4.1.
Table 4.1 - The cooling and heating rates \( q \), the temperature limits of integration \( T_{\text{glass}} \) and \( T_{\text{liq}} \), the \( C_p dT \) and \( C_p d\ln T \) integrals denoted as \( \Delta H \) and \( \Delta \sigma \) measured for cooling and for heating and the percentage difference between the respective integrals, \( x_H \) and \( x_\sigma \).

<table>
<thead>
<tr>
<th>Material ((q, \text{K/min}))</th>
<th>( T_{\text{glass}} ) K</th>
<th>( T_{\text{liq}} ) K</th>
<th>( \Delta H_{\text{cool}} ) kJ/mol</th>
<th>( \Delta H_{\text{heat}} ) kJ/mol</th>
<th>( x_H ) %</th>
<th>( \Delta \sigma_{\text{cool}} ) J/mol K</th>
<th>( \Delta \sigma_{\text{heat}} ) J/mol K</th>
<th>( x_\sigma ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen(^a) (0.333)</td>
<td>253</td>
<td>301</td>
<td>2.071</td>
<td>2.044</td>
<td>1.3</td>
<td>7.15</td>
<td>6.99</td>
<td>2.1</td>
</tr>
<tr>
<td>Nifedipine(^a) (0.333)</td>
<td>271</td>
<td>320</td>
<td>3.384</td>
<td>3.339</td>
<td>1.3</td>
<td>11.01</td>
<td>10.74</td>
<td>1.8</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol(^b) (20)</td>
<td>116</td>
<td>163</td>
<td>2.174</td>
<td>2.177</td>
<td>-0.1</td>
<td>14.51</td>
<td>14.42</td>
<td>0.6</td>
</tr>
<tr>
<td>TPTGE(^{a,c}) (1.0)</td>
<td>250</td>
<td>293</td>
<td>4.964</td>
<td>4.978</td>
<td>-0.3</td>
<td>17.93</td>
<td>17.79</td>
<td>0.7</td>
</tr>
<tr>
<td>Poly(vinyl acetate)(^d) (1.0)</td>
<td>281</td>
<td>314</td>
<td>9.26*</td>
<td>9.30*</td>
<td>-0.5</td>
<td>30.3*</td>
<td>30.2*</td>
<td>0.3</td>
</tr>
<tr>
<td>Schott glass K7(^e) 8(cool) 10(heat)</td>
<td>673</td>
<td>1000</td>
<td>58.0*</td>
<td>58.1*</td>
<td>-0.2</td>
<td>65.1*</td>
<td>65.5*</td>
<td>-0.7</td>
</tr>
<tr>
<td>Annealed-Schott glass Na-LaK12(^e) 8(cool) 10(heat)</td>
<td>270</td>
<td>1000</td>
<td>245.7*</td>
<td>253.8*</td>
<td>-3.3</td>
<td>243.0*</td>
<td>248.6*</td>
<td>-2.3</td>
</tr>
</tbody>
</table>

\(^a\) Tombari et al. 2008a; \(^b\) Wang 2009; \(^c\) Tombari et al. 2008b; \(^d\) Tombari et al. 2007; \(^e\) Fotheringham et al. 2009. Baseline for the integral was taken at the value of \( C_p \) at \( T_{\text{glass}} \) measured on heating. Integration was done from a baseline for \( C_p \) at \( T_{\text{glass}} \). *Units are J/g for enthalpy values and J/gK for entropy values. The values of \( \Delta H \) and \( \Delta \sigma \) are given to one more decimal place than would be significant considering the errors in the \( C_p - T \) data.
Figure 4.2 – (A) The plot of $C_p$ against $T$ for 2-ethyl-1-hexanol on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.3 – (A) The plot of $C_p$ against $T$ for poly(vinyl acetate) on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.
Figure 4.4 – (A) The plot of $C_p$ against $T$ for Schott Glass K7 on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.5 – The plot of $C_p$ against $T$ for Annealed Schott Glass – Na-LaK12 on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.
Figure 4.6 – (A) The plot of $C_p$ against $T$ for nifedipine on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.

Figure 4.7 – (A) The plot of $C_p$ against $T$ for TPTGE on the cooling path from liquid to glass and on the heating path from glass to liquid. (B) The corresponding plots of $C_p$ against $\ln T$. The temperatures $T_{\text{glass}}$ and $T_{\text{liq}}$ are marked. See Table 4.1 for details.
4.3 Discussion

The difference in enthalpy from heating and cooling paths, $\Delta H$, for six of the seven samples is less than the tolerance limit of 2% for the summation of errors (i)-(v). Therefore, because Eqn. 4.3 is experimentally verified, application of the Clausius limits is valid. Only the annealed Schott Glass, Na-LaK12, does not meet this criterion, as the absolute value of $\Delta H$ is 3.3 %. Complications may arise from the occurrence of spontaneous relaxations in glasses before being heated. If $C_p$ was on the cooling path to $T \rightarrow 0$ K and then heated to a $T_{liq}$, $\Delta H_{cool}$ and $\Delta H_{heat}$ would be equal, regardless of differences in $q_h$ and $q_c$. But if the sample were cooled to a $T_{glass}$ much higher than 0 K and the structure relaxed during the time interval between the end of cooling and beginning of heating there would be a decrease in enthalpy, $\Delta H_{relax}$. Upon heating this enthalpy loss...
would be recovered, amounting to an extra evolution and causing $C_p dT$ to be larger. If $\Delta H_{relax}$ is sufficiently high, it would be recovered in the endothermic overshoot of $C_p$ before the liquid state is reached, yielding a $\Delta H_{heat}$ greater than $\Delta H_{cool}$ and $x_H$ would be negative. This might have occurred for the annealed Schott Glass Na-LaK12, whose thermal history is unknown.

The real change in entropy measured is not well approximated by the $C_p d\ln T$ curves, but instead provides a bracket for the true value. By application of the second law of thermodynamics, Bestul and Chang (1965) derived the limits for $S_{res}$ as

$$S^T_{l_m} - \int_0^{T_m} C_{p,heat} d\ln T \geq S_{res} \geq S^T_{l_m} + \int_0^{T_m} C_{p,cool} d\ln T , \quad (4.8)$$

where $S^T_{l_m}$ is entropy of melting the disordered crystal at $T_m$. The limits of $S_{res}$ are determined by adding $S^T_{l_m}$ to the $C_p d\ln T$ integral for a supercooled liquid from near 0 K to $T_m$, and likewise for the heating path which provides the upper bracket of the real $S_{res}$. Expressing the integral in Eqn. 4.8 in its parts gives

$$\int_0^{T_m} C_p d\ln T = \int_0^{T_{high}} C_p d\ln T + \int_{T_{high}}^{T_m} C_p d\ln T + \int_{T_m}^{T_{low}} C_p d\ln T . \quad (4.9)$$

Since $S^T_{l_m}$ is unique for a material, and recognizing that the first and last integrals on the RHS of Eqn. 4.9 are identical for the cooling and heating paths, the values of $\Delta \sigma_{cool}$ and $\Delta \sigma_{heat}$ would suffice for bracketing $S_{res}$ and thus serve as the Clausius limits, and therefore Eqn. 4.9 condenses to
\[ \Delta \sigma_{\text{heat}} \geq S_{\text{res}} \geq \Delta \sigma_{\text{cool}}. \] (4.10)

The purpose of this analysis is to investigate the reality of \( S_{\text{res}} \) by showing whether or not the \( C_p-T \) path through the glass transition can be considered an almost reversible process, even though in actuality it never is. If \( \Delta \sigma_{\text{cool}} \) and \( \Delta \sigma_{\text{heat}} \) are exactly equal, the difference between the Clausius limits would be zero and would represent the true value of \( S_{\text{res}} \). From the values in Table 4.1, the argument in favour of thermodynamic reversibility is valid on the condition that \( \Delta \sigma_{\text{cool}} \) and \( \Delta \sigma_{\text{heat}} \) differ by no more than experimental errors (± 2%). The only material in which this criterion has not been met is the Na-LaK12 Schott Glass, where errors arising from relaxation have already been discussed. For the remainder of the materials, the non-reversibility of the \( C_p \) path on cooling and heating has a negligible effect on the \( C_p d \ln T \) integrals. In discussing the difference between \( \Delta \sigma_{\text{cool}} \) and \( \Delta \sigma_{\text{heat}} \), Bestul and Chang (1965) claim that the method is validated when the magnitude of this difference is an order less than \( S_{\text{res}} \). For the samples studied here, all the entropy values exceed 7 (J/K per unit mass or mole) and the maximum difference of \( \Delta \sigma_{\text{cool}} \) and \( \Delta \sigma_{\text{heat}} \) is 0.25 J/mol K, which is still an order of magnitude less than the entropy values. The true \( S_{\text{res}} \) is therefore more likely to be described by the upper limit from Eqn. 4.10.

The reality of \( S_{\text{res}} \) has also been investigated by comparison of fictive temperatures estimated from the same \( C_p \) data. Aji and Johari (2010) demonstrated that the fictive temperatures from \( C_p d \ln T \) and \( C_p d T \) of two metallic glasses and a basalt composition glass are close enough in value to state that \( S_{\text{res}} \) is not an artifact from differences between heating and cooling paths through the liquid-glass region.
(1976) discussed Bestul and Chang’s analysis in connection with errors in determining the difference between the entropies of a quenched and annealed glass. He provided a model calculation for different heating and cooling rates by using a single relaxation time for enthalpy relaxation, and showed that the errors due to irreversibility in heating and cooling at constant rates were minimized when the rates are equal.

The residual entropy obtained by a variety of methods for many glasses of different chemical nature has been found to range between 3.7 – 44 J/(mol K) [Johari 2000]. \( S_{\text{res}} \) determined calorimetrically at absolute zero is comparable to the excess entropy which decreases to a critical value at \( T_g \) in supercooled liquids [Bestul and Chang 1964]. Bestul and Chang (1964) claim this excess value to be universal, around 3.3 J per degree per ‘bead’, and described this bead as being analogous to a repeating segment of a polymer.

The notion that \( S_{\text{conf}} \) of glass is zero is based upon the experience that over a reasonable time scale, a glass does not show structural fluctuations of the type that occur in a liquid. It is therefore argued that the term \( \Omega \) in the Boltzmann equation be taken as equal to 1 for a glass. One of the principal issues associated with the entropy problem is the definition of \( \Omega \), which itself is subject to debate. Goldstein (2008) argues in favour of the definition of potentially accessible states, as opposed to the number of configurations accessed during an observation, by showing that for 1 mole of a crystal composed of atoms A and B to pass through \( 10^{23} \) microstates every \( 10^{-6} \) seconds would take astronomical amounts of time over billions of years.
Chapter 5 : Conclusion

The main conclusions from this thesis can be summarized in three parts.

(i) The following effects on the polymerization of DGEBA-amine mixtures by POSS were observed from calorimetry measurements:

- Enthalpy of polymerization decreased with increasing amounts of POSS.
- Rate of polymerization increased with small amounts of POSS, but then progressively decreased with further increase. POSS-only mixtures polymerized slower than DGEBA-only mixtures.
- The maximum extent of isothermal polymerization for the mixtures increased with the amount of substituent POSS.
- Rate of post-polymerization initially increased with small amounts of POSS but then decreased with further increase of substituent.

The initial increase in rate of polymerization with low amounts of POSS was discussed in terms of the diffusion-controlled mechanism and heterogeneity. The presence of POSS causes diffusion-control to occur sooner, and the viscosity estimated by the Stokes-Einstein relation decouples sooner as well. Despite the earlier onset of decoupling, it was rationalized that the 2% POSS – DGEBA-DETA mixture must maintain a higher diffusion coefficient for the reaction to polymerize faster than the DGEBA-DETA reaction. Additionally, the cause of the increase in polymerization rate was hypothesized based on the possibility of an increase in autocatalytic activity due to the higher density of epoxides from the POSS molecules.
(ii) POSS was found to have the following effects on the dielectric relaxation behaviour:

- Conductivity at the onset of polymerization and $t_{gel}$ increased with POSS.

- The relaxation time distribution parameter, $\beta$, decreased slightly by about 0.02 – 0.04 from the neat mixtures to the 10 % POSS mixtures according to an analysis of the isochrones using the KWW formalism.

- The relaxation time distribution parameter, $\beta$, decreased slightly with polymerization time according to the analysis of the spectra using the KWW formalism.

- A dipolar relaxation peak was not observed for mixtures containing more than 20 % POSS.

Several features were observed in the POSS-only mixtures that are uncharacteristic of changes in the dipolar response of a thermosetting liquid. The structure of the materials changed such that $\varepsilon'$ increased with polymerization time prior to the step decrease caused by dipolar relaxation. For polymerization with DETA and EDA this appeared as a peak, and as a broad but shallow increase with HA. An analysis using an expression for interfacial polarization contributions to $\varepsilon'$ showed that the impedance of interfacial polarization, $z_0$, changed according to the material’s structure. The isothermal cure of POSS-DETA was investigated at temperatures ranging 298 K to 363 K, where the uncharacteristic features were observed at temperatures of 323 K and greater. In addition to the pre-gelation increase in $\varepsilon'$, a simultaneous increase in $\varepsilon'$ and $\varepsilon''$ was also observed closer to the vitrification stage of polymerization. Again, the increase was attributed to an increase in $z_0$. 
(iii) An analysis of heat capacity data for seven materials showed that the change between the upper and lower limits differed by no more than 2%. This showed that although the thermodynamic path through the glass transition temperature range is irreversible, this irreversibility has a negligibly small effect on determining the entropy. Although the Clausius inequality relation is violated, the violation does not have a significant effect on the residual entropy of glasses.
Appendix

Appendix A – Turret-Type Heat Flux DSC

The relation of heat capacity of a sample and reference to heat flow from a non-steady state process is approximated to a first order by

\[ C_s \frac{dT_s}{dt} = \phi_{FS} - \phi_s \]  \hspace{1cm} (A.1)

\[ C_R \frac{dT_R}{dt} = \phi_{FR} \]  \hspace{1cm} (A.2)

where \( C_s \) and \( T_s \) are the heat capacity and temperature of the sample, \( \phi_s \) is the heat flow rate from the sample caused by a physical or chemical change (\( \phi_s \) is negative for exothermic process), and \( \phi_{FS} \) is the heat flow rate between the furnace and sample. \( C_R \) and \( T_R \) are the heat capacity and temperature of the reference, and \( \phi_{FR} \) is the heat flow rate between the furnace and the reference. Taking the temperature difference of the sample and reference, \( \Delta T = T_s - T_R \), and substituting it into A.1 gives

\[ C_s \left( \frac{dT_R}{dt} + \frac{d\Delta T}{dt} \right) = \phi_{FS} - \phi_s \]  \hspace{1cm} (A.3)

Taking the difference of \( \phi_{FR} \) and \( \phi_{FS} \) gives,

\[ \phi_{FS} - \phi_{FR} = (C_s - C_R) \frac{dT_R}{dt} + C_s \frac{d\Delta T}{dt} + \phi_s \]  \hspace{1cm} (A.4)
The heat flow rates $\phi_{FR}$ and $\phi_{FS}$ are inversely proportional to the global heat resistances, and are proportional to the temperature difference of the respective paths from furnace to sample or furnace to reference. Assuming thermal symmetry, these resistances can be assumed equal, and will be denoted as $R$. Equation A.4 can be re-written as

$$\phi_s = -\left( \frac{\Delta T}{R} + (C_s - C_R) \frac{dT_R}{dt} + C_s \frac{d\Delta T}{dt} \right).$$  \hspace{1cm} (A.5)

The first term in Eqn. A.5 relates the heat absorbed or released by the sample to the temperature difference between the reference and sample. The second term takes asymmetry in the measuring system into account by the difference in heat capacities of the sample and reference, and the third term measures contributions from thermal inertia. An analogy of the charging/discharging of a capacitor, of capacity $C$, to a thermodynamic system, where a time constant $\tau$ can similarly be defined for the heat flow rates: $\tau = C_s R$. $R$ is the effective thermal resistance to the charging or discharging of the “capacitor” to changes in $\Delta T$. Since the reference is always in steady state, $dT_R/dt = q$, Eqn. A.5 can be rewritten as

$$\phi_s(t) = -\left( \frac{\Delta T(t)}{R} + q(C_s - C_R) + \frac{\tau}{R} \frac{d\Delta T}{dt} \right).$$  \hspace{1cm} (A.6)

The delayed response in temperature of the sample means that $\phi_s$ cannot be proportional to $\Delta T$. Furthermore, $R$ is temperature dependent and must be determined by calibration. Higher order approximations take into account the distance and thermal resistance between the temperature measurement locations and the sample/reference.
\[ T_{MS} = T_s - \tau_2 \frac{dT_{MS}}{dt} \]  
(A.7 A)

\[ T_{MR} = T_R - \tau_2 \frac{dT_{MR}}{dt} \]  
(A.7 B)

where \( T_{Mi} \) is the temperature of the measurement point for either the reference or sample. \( \tau_2 \) is the characteristic time constant for the temperature relaxation between the sample and measurement point, and is assumed equal for both sides. By knowing the temperature at the measurement point, the true \( T_s \) and \( T_R \) can be known, and this is used in the Tzero\textsuperscript{TM} technology that the Q100 operates on. Substituting Eqn. A.7 into Eqn. A.6 yields

\[
\phi_s(t) = -\frac{1}{R} \left( \Delta T + q R (C_s - C_R) + \tau \frac{d\Delta T_m}{dt} + \tau_2 \frac{d^2\Delta T_m}{dt^2} \right), 
\]  
(A.8)

where \( T_m \) is equal to \( T_s - T_R \). A more thorough description of the theory behind the DSC can be found in a monograph by Höhne \textit{et al.}
Appendix B - Dielectric Spectroscopy

### B.1. Background and Theory

The application of a voltage across two parallel electrodes separated by a narrow gap generates an electric field, $E_o [\text{V/m}]$. If a non-conducting material, a dielectric, fills the volume of the gap, the field causes (i) electron clouds to be displaced with respect to their atomic nuclei and (ii) polar molecules, or polar segments of a molecule, to orientate in the direction of the field. The polarization of a material, $P [\text{C/m}^2]$, is a measure of charge build up on the electrode surface (per unit area) as a consequence of these electrical density changes in response to the field. At the instant the field is applied, the electrons are first displaced relative to their nuclei, and this is described by $P_o$, the instantaneous polarization. The polarization from angular and crankshaft rotations of dipole segments is defined by $P_r$. The total time-dependent polarization is described as,

$$ P(t) = P_o + (P_r - P_o)(1 \phi(t)) $$

where $\phi(t)$ is a function which describes the approach of $P$ towards equilibrium at a time, $t$, after the field has been removed. It is called the relaxation function [McCrum et al. 1967]. Gauss’ law states that the divergence of $E$ is proportional to the density of charges, $\rho$, which is the sum of free and atomically-bound charges,

$$ \nabla \cdot E = \frac{\rho}{\varepsilon_o} $$

\[(B1.2)\]
where $\varepsilon_0$ is the dielectric permittivity of a vacuum and is equal to 8.8541 pF/m. The density of bound charges is equal to the negative of the divergence of $P$. Therefore, the density of free electrons, $\rho_f$, is described as,

$$\rho_f = \varepsilon_0 \nabla \vec{E} + \nabla \vec{P}. \quad \text{(B1.3)}$$

The charge density of free electrons on the electrode is described by the electric displacement field, $D$ [C/m$^2$],

$$\vec{D}(t) = \varepsilon_0 \vec{E}_0 + \vec{P}(t). \quad \text{(B1.4)}$$

The polarization of a homogenous and isotropic dielectric is proportional to $E_0$.

$$\vec{P} = (1 + \chi) \varepsilon_0 \vec{E} = \varepsilon \varepsilon_0 \vec{E}. \quad \text{(B1.5)}$$

where $\chi$ is the susceptibility, a dimensionless constant that describes the degree of polarization. $\varepsilon$ is the relative permittivity of the material, which can be expressed in terms of $\phi(t)$ by

$$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)(1 - \phi(t)). \quad \text{(B1.6)}$$

(static permittivity: $\varepsilon_\infty = \varepsilon (t \to 0)$ or $\omega \to 0$)

(limiting high permittivity: $\varepsilon_\infty = \varepsilon (t \to \infty)$ or $\omega \to \infty$)

When the electric field changes incrementally, the Boltzmann superposition principle [Boltzmann 1876, Hopkinson 1877, Curie 1888] is used to describe the change in displacement. The charge displacement becomes equal to the sum of displacements $dD(t)$ from each incremental change in the field, $dE(t)$ of each step applied at the previous time, $\mu$, when $\mu < t$. 

159
\[
\frac{D(t)}{\varepsilon_0} = \int_{-\infty}^{t} \frac{\partial E(\mu)}{\partial \mu} \varepsilon(t - \mu) \, d\mu
\]  \hspace{1cm} (B1.7)

Substituting \( a = t - \mu \) and integrating B1.7 by parts gives

\[
\frac{D(t)}{\varepsilon_0} = \varepsilon_\infty E(t) + \int_{0}^{\infty} E(t - a) \frac{\partial \varepsilon(a)}{\partial a} \, da .
\]  \hspace{1cm} (B1.8)

Substituting B1.6 into the above equation gives

\[
\frac{D(t)}{\varepsilon_0} = \varepsilon_\infty E(t) + (\varepsilon_\infty - \varepsilon') \int_{0}^{\infty} E(t - a) \left( -\frac{\partial \phi(a)}{\partial a} \right) \, da .
\]  \hspace{1cm} (B1.9)

When the field is applied periodically, the dynamic \( E \) and \( D \) are expressed as,

\[
E^* = E_o \exp (i\omega t)
\]  \hspace{1cm} (B1.10)

\[
D^* = D_o \exp (i(\omega t - \delta))
\]  \hspace{1cm} (B1.11)

where \( t \) is the time of measurement and \( E_o \) and \( D_o \) are the amplitude constants of the respective fields. \( i \) is the square root of \(-1\), \( \omega \) is the angular frequency \((= 2\pi f)\) and \( \delta \) is equal to \( \pi/2 - \phi \), the phase delay angle between the complex current and admittance.

Since \( E^* \) and \( D^* \) are related by B1.5, the complex dielectric permittivity is given by,

\[
\varepsilon^* = \left( \frac{D_o}{\varepsilon_o E_o} \right) (\cos(\delta) - i\sin(\delta))
\]  \hspace{1cm} (B1.12)

\[
\varepsilon^* = \varepsilon' - i\varepsilon'' .
\]  \hspace{1cm} (B1.13)

The real component of the complex permittivity, \( \varepsilon' \), is called as the dielectric permittivity, while the imaginary component, \( \varepsilon'' \), is the dielectric loss. The loss to permittivity ratio is
\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'}, \quad (B1.14) \]

where \( \delta \) is the angle of phase delay of polarization in response to the electric field. \( \varepsilon', \varepsilon'' \) and \( \tan \delta \) are unitless. The frequency dependence of the dielectric permittivity is obtained by combining (B1.9), (B1.10), and (B1.12) to give the expression of complex permittivity from dipolar orientation;

\[ \varepsilon^* = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \exp(-i\omega t) \left( -\frac{d\phi}{dt} \right) dt. \quad (B1.15) \]

The integral expression on the right side of B1.15 is equal to the one-sided Laplacian transformation of the change in relaxation. This integral is also equal to a parameter termed the normalized complex permittivity, \( N^* \), which is equivalent to the two expressions below,

\[ \int_0^\infty \exp(-i\omega t) \left( -\frac{d\phi}{dt} \right) dt = \Im \left( -\frac{d\phi}{dt} \right) \quad (B1.16) \]

\[ N^* = \frac{\varepsilon^* - \varepsilon_\infty}{(\varepsilon_s - \varepsilon_\infty)}. \quad (B1.17) \]

**B.2. Theory and Analysis of Dielectric Relaxation Processes**

After an electric field has been removed from a material that exhibits elastic behaviour, the structure will spontaneously return to its more stable, randomized arrangement. In other words, a time-dependent property such as \( P(t) \) returns to equilibrium. The time required for the value of such a property to decrease by a factor of \( e^{-1} \) is called the relaxation time. The exponential relaxation function, \( \phi(t) \), for a material
that exhibits a single relaxation time, \( \tau_o \), is given by the equation [Debye 1929, Fröhlich 1958]:

\[
\phi(t) = \exp\left(-\frac{t}{\tau_o}\right)
\]

(B2.1)

where \( t \) is the time after the removal of the field or mechanical stress. The complex permittivity is then related to \( \tau \) by combining the previous two equations to give,

\[
\frac{\varepsilon^* - \varepsilon_\infty}{(\varepsilon_\infty - \varepsilon_0)} = \frac{1}{1 + i\omega\tau_o}.
\]

(B2.2)

This equation is applicable for a limited number of cases, as few materials actually exhibit a single relaxation time (Debye behavior). Some examples include dilute solutions of polar molecules in a non-polar solvent and substances at high temperatures. For most amorphous materials, the nonexponential relaxation decay behaviour has been interpreted in terms of a superposition of exponential relaxation functions of the form (although there is more than one interpretation):

\[
\phi(t) = \int_0^\infty \exp\left(-\frac{t}{\tau}\right) g(\tau) d\tau
\]

(B2.3)

and

\[
\int_0^\infty g(\tau) d\tau = 1,
\]

(B2.4)

where \( g(\tau) \) is the normal relaxation time distribution function. This approach leads to a distribution of relaxation times [Lindsey and Patterson 1980, Davidson and Cole 1951] Evaluation of \( g(\tau) \) has been attempted by empirically means, and the two most accepted
formalisms are that of Cole-Davidson [Davidson and Cole 1951] and Kohlrausch-Williams-Watt (KWW) [Kohlrausch 1854, Williams and Watts 1970]. A comparison of the two can be found in a paper by Lindsey and Patterson (1980). The KWW formalism is given as

$$\phi = \phi_0 [\exp(-t/\tau)\beta]$$, \hspace{1cm} (B2.5)

where $\tau$ is the characteristic relaxation time. $\beta$ is a parameter that is interpreted as a measure of the distribution of relaxation times ($0 < \beta \leq 1$). For $\beta = 1$, Eqn. B2.5 collapses to the Debye expression. In the frequency domain of a material that decays according to Eqn. B2.5, an asymmetrical broadening of $\varepsilon'$ and $\varepsilon''$ spectra with a half width greater than 1.14 decades occurs. A plot of $\varepsilon''$ vs. $\varepsilon'$ of a material exhibiting Debye behaviour yields a semi-circle, where $\omega \tau = 1$ at the peak of the circle. A skewed arc is observed for most dynamic materials. The characteristic relaxation time $\tau_o$ is related to the average relaxation time, $\langle \tau \rangle$, through the gamma function, $\Gamma$, by

$$\langle \tau \rangle = \frac{\tau_o \Gamma \left( \frac{1}{\beta} \right)}{\beta}.$$ \hspace{1cm} (B2.6)

Returning to B1.17, the normalized complex permittivity is the sum of its real and imaginary components, which are computed from empirical photon correlation, mechanical or dielectric data by,

$$N'(\omega \tau) = \frac{\varepsilon' - \varepsilon_c}{\varepsilon_s - \varepsilon_c}$$ \hspace{1cm} (B2.7a)

$$N''(\omega \tau) = \frac{\varepsilon''}{\varepsilon_s - \varepsilon_c}.$$ \hspace{1cm} (B2.7b)
Theoretical values of \( N'' \) and \( N' \) pairs have been generated based on stable distribution function theory [Moynihan et al. 1973, Dishon et al. 1985] for \( 0.1 < \beta < 0.7 \) and \( 10^3 < \omega \tau_o < 10^4 \), numerically evaluated using the following expressions:

\[
N' = z \pi V_\beta(z) - 1 \tag{B2.8a}
\]
\[
N'' = z \pi Q_\beta(z) \tag{B2.8b}
\]

where \( z = \omega \tau_o \) and \( V_\beta \) and \( Q_\beta \) are defined as,

\[
V_\beta = \frac{1}{\pi} \int_0^\infty \exp(-u^\beta)\sin(zu)du \tag{B2.9a}
\]
\[
Q_\beta = \frac{1}{\pi} \int_0^\infty \exp(-u^\beta)\cos(zu)du \tag{B2.9b}
\]

where \( u \) is a variable for integration. Relaxation of experimental data is assessed using the KWW formalism by comparison with the theoretical \( N'' \) and \( N' \), whereby \( \beta \) is determined from a best fit of the two data sets.

**B.3. Dielectric Spectroscopy in a Parallel Circuit**

A sinusoidal voltage applied across parallel plates at a frequency of \( \omega \) is equal to

\[
V = V_o \sin(\omega t). \tag{B3.1}
\]

The response in the current is also sinusoidal but may be delayed by an angle \( \phi \),

\[
I = I_o \sin(\omega t + \phi). \tag{B3.2}
\]
The complex resistance is referred to as impedance, $Z^*$, and is equal to the inverse of a property known as admittance, $Y^*$ ($Z^* = 1/Y^*$). $Y^*$ is equal to the ratio of $I$ to $V$, which yields,

$$Y^*(\omega) = (I_o/V_o)\cos(\varphi) + i(I_o/V_o)\sin(\varphi), \quad (B3.3)$$

where $i$ is the square root of $-1$. For an equivalent circuit of a capacitor and resistor in parallel,

$$Y^*(\omega) = 1/R_p(\omega) + i\omega C_p(\omega), \quad (B3.4)$$

where $R_p(\omega)$ and $C_p(\omega)$ are resistance and capacitance of the dielectric, respectively.

Capacitance is measured as

$$C_p = \varepsilon_r \varepsilon_o \frac{A}{d} \quad (B3.5)$$

where $A$ is the total surface area of both electrodes, $\varepsilon_r$ is the dielectric constant of the material, and $d$ is the distance between the electrodes. The relative permittivity, $\varepsilon'$, and loss, $\varepsilon''$, are then calculated from the capacitance, $C_p$, and conductance, $G_p$, measurements by

$$\varepsilon' = \frac{C_p}{C_o} \quad (B3.6)$$

$$\varepsilon'' = \frac{G_p}{\omega C_o} \quad (B3.7)$$

where $C_o$ is the capacitance of air, given by

$$C_o = \frac{\varepsilon_o A}{d} \quad (B3.8)$$
Appendix C – General Calculations and Additional Experiment Data

C.1. Integration of DSC \( \frac{dH}{dt} \) \( _T \) and \( \frac{dH}{dT} \) \( _q \) curves

The heat of reaction for the ramp and isothermally cured samples were calculated by integrating the area underneath the exothermic curve. The baseline of the ramp cure plot \( \frac{dH}{dT} \) \( _q \) was taken from the onset of the peak to as far into the plateau region as possible, as shown in Fig. C2. The baseline of the isothermal plot, \( \frac{dH}{dt} \) \( _T \), was taken as a horizontal line, just above the plateau level in Fig.C2-A. Integrating the post-cure curve required a rough estimation of an appropriate baseline. In some cases, the pre-glass region portion of the curve could be extrapolated to the plateau region Fig.C2-B. Otherwise the baseline was fitted based on the tangents of the pre-glass and plateau regions as shown in Fig.C2-C.

C.2. Conversion of \( \Delta H_{rxn} \) from units of J/g to J/(mol compound)

Assume basis of 1 mol amine, \( n_{amine} = 1 \), \( m_{amine} = MW_{amine} \times 1 \) mol. Therefore, the number of moles of amine proton is:

\[
\begin{align*}
n_{nH} &= f_{amine} \times n_{amine} = f \text{ (subscript amine can be dropped)} \quad (C2.1)
\end{align*}
\]

Therefore, total moles of epoxides in a stoichiometric mixture, \( n_{epoxide} = f \). A certain fraction, \( X \), of epoxides comes from DGEBA, balance POSS. The mass of DGEBA and POSS,

\[
\begin{align*}
m_{DGEBA} &= EEW_{DGEBA} \times f \times X \\
m_{POSS} &= EEW_{POSS} \times f \times (1-X) \quad (C2.3)
\end{align*}
\]

Total mass of bulk mixture

\[
m_{mixture} [g] = f \left( X \ EEW_{DGEBA} + (1-X) \ EEW_{POSS} \right) + MW_{amine} \quad (C2.4)
\]

Enthalpy of reaction is now converted to units of Joule per mole epoxide (or proton)

\[
\Delta H_{rxn} [J/(mol epoxide)] = (\Delta H_{rxn} [J/g] \times m_{mixture} [g]) / f \text{ [mol epoxide]} \quad (C2.5)
\]
Figure C1 – Example of integration for typical ramp cure plot.

Figure C2 – (A) Isothermal cure plot \( \frac{dH}{dt} \) vs curing time) with baseline. (B) Post-cure plot \( \frac{dH}{dT} \) vs. \( T \) with an easily definable baseline. (C) Post-cure plot \( \frac{dH}{dT} \) vs. \( T \) with an approximated baseline.
C.3. De-convolution of DGEBA-IPDA \((dH/dT)_q\) curves

MATLAB program PeakFit – programmed by Tom O’Haver

DGEBA-IPDA \((dH/dT)_q\) curves showing a peak and shoulder were deconvoluted as to assess the effect of heating rate, \(q\), and, stoichiometry on the distance between the two peaks. The ‘window range’ parameter was varied so that the large peak (peak 1) fit as close to the experimental data as possible. The parameters could be changed in a manner such that two small peaks were obtained, but whose sum fit the experimental well. Such curves were regarded as an incorrect.

Table C1 – DGEBA-IPDA peak temperatures, \(T_p\), rounded to the nearest whole number. Subscript \(m\) denotes value obtained directly from the plot, while \(d\) denotes value obtained by deconvolution.

<table>
<thead>
<tr>
<th>(q) (K/min)</th>
<th>(r = 1.25)</th>
<th>(r = 1.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{P1, m})</td>
<td>(T_{P1, d})</td>
<td>(T_{P2, d})</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>386</td>
<td>382</td>
</tr>
<tr>
<td>20</td>
<td>402</td>
<td>399</td>
</tr>
<tr>
<td>30</td>
<td>411</td>
<td>458</td>
</tr>
</tbody>
</table>

Table C.2 – DGEBA-POSS-IPDA peak temperatures, \(T_p\), rounded to the nearest whole number. Subscript \(m\) denotes value obtained directly from the plot, while \(d\) denotes value obtained by deconvolution.

<table>
<thead>
<tr>
<th>(q) (K/min)</th>
<th>(x_{\text{POSS}} = 5.6%)</th>
<th>(x_{\text{POSS}} = 15.2%)</th>
<th>(x_{\text{POSS}} = 35%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{P1, m})</td>
<td>(T_{P1, d})</td>
<td>(T_{P2, d})</td>
<td>(T_{P1, m})</td>
</tr>
<tr>
<td>5</td>
<td>373</td>
<td>370</td>
<td>404</td>
</tr>
<tr>
<td>10</td>
<td>388</td>
<td>385</td>
<td>425</td>
</tr>
<tr>
<td>20</td>
<td>403</td>
<td>403</td>
<td>446</td>
</tr>
<tr>
<td>30</td>
<td>413</td>
<td>413</td>
<td>459</td>
</tr>
</tbody>
</table>
C.4. \((dH/\text{d}t)_T\) curves of DGEBA-DETA & POSS-DETA polymerized at different \(T_{\text{polym}}\)

![Graph showing \((dH/\text{d}t)_T\) curves for DGEBA-DETA and POSS-DETA at different temperatures.](image)

Figure C3 - Isothermal curing of DGEBA-DETA and POSS-DETA at 323, 333 and 343 K.

C.3. \(E_\alpha(\alpha)\) of DGEBA-IPDA and POSS-IPDA using isoconversional method.

<table>
<thead>
<tr>
<th></th>
<th>(E_\alpha(\alpha = 0.2)) [kJ/mol]</th>
<th>(E_\alpha(\alpha = 0.4)) [kJ/mol]</th>
<th>(E_\alpha(\alpha = 0.6)) [kJ/mol]</th>
<th>(E_\alpha(\alpha = 0.8)) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>55.3</td>
<td>56.4</td>
<td>57.2</td>
<td>56.3</td>
</tr>
<tr>
<td>POSS</td>
<td>59.2</td>
<td>57.1</td>
<td>55.2</td>
<td>54.0</td>
</tr>
</tbody>
</table>
Appendix D – Calibration and Experiment Problems

D.1 Thermocouple equation

\[ T \ (°C) = d_0 + d_1 E + d_2 E^2 + d_3 E^3 + \ldots + d_n E^n \]  

(D.1)

Coefficients (for \( 400 > T > 0 \) °C):
- \( d_0 = 0 \)
- \( d_1 = 2.5928 \times 10^1 \)
- \( d_2 = -7.602961 \times 10^{-1} \)
- \( d_3 = -4.637791 \times 10^{-2} \)
- \( d_4 = 2.165394 \times 10^{-3} \)
- \( d_5 = 6.048144 \times 10^{-5} \)
- \( d_6 = -7.293422 \times 10^{-7} \)


D.2 Experiment Problems

At one point during the course of the DSC studies, periodic fluctuations began to appear in the TA Q100 heat flow measurements. An example is shown in Fig. D1. After consulting tech-support and performing a series of diagnostic experiments, the source of these fluctuations was from a mis-alignment of the metal lid that sits on top the furnace. The lid had to be shaved down and realigned.

Figure D1 – Screen shot of a heat flow measurement with periodic fluctuations.
References


