



Shouqi Shen

Thermo-mechanical and curing behaviour of
epoxy/dicarboxylic acid vitrimers

School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

PhD
Academic Year: 2019 - 2023

Supervisor: Alexandros A. Skordos
Associate Supervisors: David Ayre, Vijay Kumar Thakur
September 2023

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.



School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

PhD

Academic Year 2019 - 2023

Shouqi Shen

Thermo-mechanical and curing behaviour of
epoxy/dicarboxylic acid vitrimers

Supervisor: Alexandros A. Skordos
Associate Supervisor: David Ayre, Vijay Kumar Thakur
September 2023

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

ABSTRACT

This research delineates the complex relationships between the chemical evolution processes and the physical behaviour of vitrimeric materials, particularly focusing on the transesterification bond exchange mechanism. The curing behaviour, stress relaxation, and high-temperature viscoelastic behaviour of dicarboxylic acid -bisphenol A diglycidyl ether vitrimers are investigated, with respect to the influence of catalysts content and dicarboxylic acid chain length. The influence of catalyst concentration and dicarboxylic acid chain length on the glass transition temperature and bond exchange rate is significant. A notable finding is the substantial decrease in both activation energy from 120 to 74 kJ/mol and glass transition temperature from 36°C to 6°C as the carbon chain length increases from 6 to 14 carbons, due to enhanced monomer flexibility. The catalyst and dicarboxylic acid structure play a crucial role in polymerisation, significantly affecting the cure kinetics of the process and, consequently, material stability and processing. The cure kinetics of epoxy-dicarboxylic acid systems are described using a diffusion limitation modified autocatalytic model, showcasing an average 84% goodness of fit, highlighting its effectiveness in understanding these systems. The study investigates temperature-dependent thermomechanical properties and thermal degradation, revealing that the speed of formation and extent of crosslinks are influenced by temperature, which in turn affects thermomechanical properties, and also shows that mechanical properties increase at higher temperature, along with enhanced thermal stability as the length of the dicarboxylic acids increases. This study provides a robust foundation for future research endeavours, aiming to optimise vitrimer properties for diverse and efficient applications including advanced composites in aerospace and automotive sectors, self-healing materials, eco-friendly recyclable thermosets, and adaptable biomedical devices.

Keywords:

Vitrimer, Epoxy, Dicarboxylic acid, Curing, Kinetics Modelling, Transesterification, Stress Relaxation, Thermal Degradation, Rheology, Differential Scanning Calorimetry (DSC)

ACKNOWLEDGEMENTS

First and foremost, I would like to express my profound gratitude to my advisor, Dr. Alexandros A. Skordos. His unwavering academic guidance has been instrumental in shaping this research. Beyond the academic realm, Dr Skordos has been a beacon of personal and emotional support, especially during the challenging times of the pandemic. His friendship, understanding, and genuine concern have been a source of immense comfort.

I owe a special debt of gratitude to my second supervisor, Prof. Vijay Kumar Thakur, for opening the gates of PhD for me. His faith in my capabilities set me on this transformative journey. Additionally, I would like to thank Dr Ayre for his invaluable guidance and insights that have enriched my research.

The emotional hardships I faced during my PhD journey were at times overwhelming, but the unwavering support from my supervisors and mentors consistently stood by me, acting as guiding lights and pillars of strength. Their presence transformed many of my challenges into learning experiences, and for that, I am eternally grateful.

I extend my heartfelt thanks to the members of the Composite Material Centre, especially to our technician, James Hurly, for his invaluable assistance throughout my research journey. I'm also deeply grateful to my young, aspiring, and inspiring colleagues: Eva, Caghan, and Shaun. Their technical and academic support has been invaluable. Beyond our professional interactions, I cherish the moments of camaraderie, the chats, and the personal growth we've shared throughout my PhD journey.

On the sporting front, I want to express my immense gratitude to all the members of the Cranfield Ultimate Frisbee team. Each one of you has been amazing, both on and off the field. Special thanks to my boxing partner, Tom, and my tennis partner, Rodolphe. The time spent training and competing with you both has been invaluable. I'm also grateful for the friendships I've forged through sports, including with Finn and Aziz. These relationships have added a vibrant dimension to my PhD journey.

On a personal note, my deepest gratitude goes to my mum for her unwavering and unconditional support. My dad has been the foundation of my strength, guiding me through every challenge with his wisdom. I also want to express my heartfelt gratitude to my ex-partner, Ben. His love taught me the true essence of affection, becoming the soil for all the colours of my life. The journey was made all the more memorable with the amazing times I shared with my friends. To the group of close girls: Echo, Janice, Ray, and Ruifan, I am immensely proud to witness our growth as women in science. We have proven time and again that we are more than capable, breaking barriers and setting new standards. This sentiment is not just a feminist perspective but a testament to our resilience, determination, and capability. I also want to extend my gratitude to my male friends: Bert, Ju, and Shuang, for their camaraderie and support.

A special mention to Tracy and Teresa for their unwavering support during some of the most challenging times. I am also deeply grateful to my GP for their attentive care and support in ensuring my mental well-being throughout this journey.

Lastly, I would like to extend my gratitude to all those who directly or indirectly contributed to this thesis. Your support has made this journey both possible and deeply rewarding.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	ii
LIST OF FIGURES.....	vi
LIST OF TABLES	xiii
LIST OF EQUATIONS.....	xv
LIST OF ABBREVIATIONS	xvii
1 Introduction.....	1
1.1 Vitrimer Background and Applications	1
1.2 Objectives of the thesis.....	6
1.3 Structure of the thesis	7
2 Literature review.....	9
2.1 Epoxy dicarboxylic acid transesterification-based vitrimers	9
2.2 Vitrimer composites and their applications.....	12
2.2.1 Carbon nanoparticles based vitrimer composites.....	13
2.2.2 Fibre reinforced vitrimer composites	14
2.3 Tuning of the thermo-mechanical properties of vitrimers	16
2.3.1 Tuning of vitrimeric materials by changing the type and amount of catalyst.....	17
2.3.2 Modulating vitrimer properties through molecular structure.....	19
2.4 Curing of DGEBA with dicarboxylic acids	23
2.4.1 Curing kinetics of epoxy-dicarboxylic acid systems.....	26
2.5 Thermo-mechanical dynamics of vitrimeric polymers: catalysts, bond exchanges, and design implications	31
2.5.1 Thermo-mechanical properties: crosslinking and temperature effects	31
2.5.2 Employment of master curves for analysing the viscoelastic behaviour of vitrimers.....	33
2.5.3 Bond exchange induced relaxation	34
2.5.4 Frequency dependence of modulus and $\tan \delta$	35
2.6 Research gap	36
3 Material preparation and methodology	38
3.1 Materials and preparation	38
3.2 Characterisation methods	40
3.2.1 FTIR	40
3.2.2 Differential scanning calorimetry (DSC)	40
3.2.3 Cure kinetics modelling	42
3.2.4 Stress relaxation by Dynamic Mechanical Analysis (DMA)	45
3.2.5 Thermogravimetric analyses (TGA)	46
3.2.6 Rheological Measurements.....	46
4 Cure kinetics of epoxy- dicarboxylic acid vitrimers	48

4.1 DSC data analysis	48
4.2 Reproducibility of DSC data.....	48
4.2.1 Dynamic DSC results	50
4.2.2 Isothermal DSC results	62
4.2.3 Superposition of isothermal and dynamic cure kinetics data.....	65
4.3 Cure kinetics modelling of epoxy-dicarboxylic acid vitrimer systems	68
4.3.1 Application of Kissinger model	69
4.3.2 Application of isoconversional analysis	72
4.3.3 Cure kinetics model fitting and prediction.....	84
5 Influence of catalyst and dicarboxylic acid structure on transition of vitrimers	99
5.1 Influence of catalyst and dicarboxylic acid structure on the glass transition temperature on vitrimeric materials	99
5.2 Influence of catalyst and dicarboxylic acid structure on topological transition	106
5.2.1 Stress relaxation results	106
5.2.2 Influence of catalyst.....	108
5.2.3 The effect of monomer dicarboxylic acid structure on vitrimer relaxation.....	114
5.2.4 Relationship between catalyst concentration, activation energy and the kinetics coefficient of bond exchange.....	116
6 High temperature behaviour of dicarboxylic acid-epoxy vitrimers.....	121
6.1 Rheological behaviour	121
6.1.1 The development of vitrimer physical properties from uncured mixture	121
6.1.2 Multi-frequency oscillation rheological behaviour	129
6.2 Thermal degradation of vitrimeric materials	139
7 Limitation and general impact of the research.....	151
7.1 Limitations of the research.....	151
7.2 General impact of the research.....	152
8 Conclusions and recommendation for further work	153
8.1 Conclusions	153
8.2 Recommendation for further work.....	155
References	157
Appendix	185

LIST OF FIGURES

Figure 1.1: Schematic illustration of dynamic covalent bonds used in vitrimeric materials and their applications (Reprinted from Matter 5, (2022), Luo, J. <i>et al.</i> , Luo, J. <i>et al.</i> , Elastic vitrimers: Beyond thermoplastic and thermoset elastomers, 1391–1422., and Mater. Today 51, (2021), Zheng, J. <i>et al.</i> , Vitrimers: Current research trends and their emerging applications, 586–625., Copyright (2022), with permission from Elsevier) ^{6,7}	1
Figure 1.2: Illustration of topological rearrangements pathway for a) dissociative and b) associative covalent adaptable networks (CANs)	4
Figure 2.1: Schematic of blending TPU/vitrimer and the mechanism of copolymerization based on the bond exchange reactions (adapted with permission from {Chen, Z. <i>et al.</i> Flexible, Reconfigurable, and Self-Healing TPU/Vitrimer Polymer Blend with Copolymerization Triggered by Bond Exchange Reaction. ACS Appl. Mater. Interfaces 12, 8740–8750 (2020)} Copyright {2020} American Chemical Society)	12
Figure 2.2: Schematic of the self-healing of CNTs/xLCEs composite realised by the electrical reconnection of fractured carbon nanotubes and electro or photo-induced healing mechanism (adapted with permission from {Wang, H. <i>et al.</i> Electricity-Triggered Self-Healing of Conductive and Thermostable Vitrimer Enabled by Paving Aligned Carbon Nanotubes. ACS Appl. Mater. Interfaces 12, 14315–14322 (2020)} Copyright {2020} American Chemical Society)	13
Figure 2.3: Recycling of fibre-reinforced vitrimer-based composites. (a) A schematic view of the closed-loop recycling paradigm for carbon fibre reinforced composites ⁷⁰ (b) The morphology of crude and chemically recycled carbon fibres from was recycled from vanillin-based epoxy and isophoronediamine carbon fibre composites in 0.1 M HCl/ N,N-Dimethylformamide solution at 25 °C for 2 h, after then it was rinsed with dichloromethane ⁷⁵ (c) The recycling process of CFRCs is based on a dual disulphide vitrimer: embedding the carbon fibres in an epoxy matrix; dissolving the epoxy matrix at 90°C in 1 h; washing and drying the recovered carbon fibres; reusing the recycled carbon fibres to form new composites ⁷⁶ (adapted from Haochuan Zhang, Jingjing Cui, Guang Hu & Biao Zhang (2022) Recycling strategies for vitrimers, International Journal of Smart and Nano Materials, 13:3, 367-390 ⁷⁷)	16
Figure 2.4: Reaction and transesterification mechanism of dicarboxylic acid and diepoxy	18
Figure 2.5: The mediation of Zn ²⁺ in transesterification reactions	18
Figure 2.6: Curing mechanism of epoxy and carboxylic acids with base catalyst	25

Figure 2.7: Frequency independency of normalised storage and loss modulus over an elevated temperature range (adapted with permission from {Huagao Fang, Wujin Ye, Yunsheng Ding, and H. Henning Winter., Rheology of the Critical Transition State of an Epoxy Vitrimer, <i>Macromolecules</i> 2020 53 (12), 4855-4862}) Copyright {2021} American Chemical Society) ¹⁸⁹	36
Figure 4.1: Repeat DSC tests for C8Z1.....	49
Figure 4.2: Repeat DSC tests for C10Z1.....	50
Figure 4.3: DSC heat flow as a function of temperature for heating rates for C6Z1	50
Figure 4.4: DSC heat flow as a function of temperature for heating rates for C8Z1	51
Figure 4.5: DSC heat flow as a function of temperature for heating rates for C10Z1.....	51
Figure 4.6: DSC heat flow as a function of temperature for heating rates for C12Z1.....	52
Figure 4.7: DSC heat flow as a function of temperature for heating rates for C14	53
Figure 4.8: Average of the enthalpy for vitrimers. Error bars correspond to one standard deviation	55
Figure 4.9: Average of the molar enthalpy for vitrimers. Error bars correspond to one standard deviation	56
Figure 4.10: Curves of reaction degree and temperature at different heating rates for C6Z1 curing reactions	56
Figure 4.11: Curves of reaction degree and temperature at different heating rates for C8Z1 curing reactions	57
Figure 4.12: Curves of reaction degree and temperature at different heating rates for C10Z1 curing reactions	57
Figure 4.13: Curves of reaction degree and temperature at different heating rates for C12Z1 curing reactions	58
Figure 4.14: Curves of reaction degree and temperature at different heating rates for C14Z1 curing reactions	58
Figure 4.15: Curves of reaction rate and temperature for all formulations at heating rates of 2.5°C/min	59
Figure 4.16: Curves of reaction rate and temperature for all formulations at heating rates of 5°C/min	59
Figure 4.17: Curves of reaction rate and temperature for all formulations at heating rates of 10°C/min	60

Figure 4.18: Addition reaction of a carboxylic acid to an epoxy group.....	60
Figure 4.19: Transesterification converting monoesters into a glycol and a diester	61
Figure 4.20: schemes of etherification reaction and condensation polyesterification reaction	62
Figure 4.21: Isothermal enthalpy evolution of C6Z1	62
Figure 4.22: Isothermal enthalpy evolution of C8Z1	63
Figure 4.23: Isothermal enthalpy evolution of C10Z1	63
Figure 4.24: Isothermal enthalpy evolution of C12Z1	63
Figure 4.25: Isothermal enthalpy evolution of C14Z1	64
Figure 4.26: Superposition of dynamic and isothermal reaction rate versus degree of cure data of vitrimer C6Z1	65
Figure 4.27: Superposition of dynamic and isothermal reaction rate <i>versus</i> degree of cure data of vitrimer C8Z1	66
Figure 4.28: Superposition of dynamic and isothermal reaction rate <i>versus</i> degree of cure data of vitrimer C10Z1	66
Figure 4.29: Superposition of dynamic and isothermal reaction rate <i>versus</i> degree of cure data of vitrimer C12Z1	66
Figure 4.30: Superposition of dynamic and isothermal reaction rate <i>versus</i> degree of cure data of vitrimer C14Z1	67
Figure 4.31: Fitting curve for the apparent activation energy for vitrimers.....	71
Figure 4.32: Relationship between apparent activation energy obtained using the Kissinger model and dicarboxylic acid chain length.....	72
Figure 4.33: Plot corresponding to Starink method for vitrimer C6Z1 in the degree cure range of 0.05-0.95	75
Figure 4.34: Plot corresponding to Starink method for vitrimer C8Z1 in the degree cure range of 0.05-0.95	76
Figure 4.35: Plot corresponding to Starink method for vitrimer C10Z1 in the degree cure range of 0.05-0.95	76
Figure 4.36: Plot corresponding to Starink method for vitrimer C12Z1 in the degree cure range of 0.05-0.95	77
Figure 4.37: Plot corresponding to Starink method for vitrimer C14Z1 in the degree cure range of 0.05-0.95	77
Figure 4.38: Relationship between degree of cure and apparent activation energy obtained using Kissinger's model	81

Figure 4.39: Relationship between degree of cure and apparent activation energy obtained using Flynn–Wall–Ozawa’s model	81
Figure 4.40: Relationship between degree of cure and apparent activation energy obtained using Starink’s model	82
Figure 4.41: The relationship between the pre-exponential factor and dicarboxylic acid length	85
Figure 4.42: Comparison of autocatalytic cure kinetics model and experimental data for C6Z1 under dynamic conditions	88
Figure 4.43: Comparison of autocatalytic cure kinetics model and experimental data for C6Z1 under isothermal conditions	88
Figure 4.44: Comparison of autocatalytic cure kinetics model and experimental data for C8Z1 under dynamic conditions	89
Figure 4.45: Comparison of autocatalytic cure kinetics model and experimental data for C8Z1 under isothermal conditions	89
Figure 4.46: Comparison of autocatalytic cure kinetics model and experimental data for C10Z1 under dynamic conditions	90
Figure 4.47: Comparison of autocatalytic cure kinetics model and experimental data for C10Z1 under isothermal conditions	90
Figure 4.48: Comparison of autocatalytic cure kinetics model and experimental data for C12Z1 under dynamic conditions	91
Figure 4.49: Comparison of autocatalytic cure kinetics model and experimental data for C12Z1 under isothermal conditions	91
Figure 4.50: Comparison of autocatalytic cure kinetics model and experimental data for C14Z1 under dynamic conditions	93
Figure 4.51: Comparison of autocatalytic cure kinetics model and experimental data for C14Z1 under isothermal conditions	93
Figure 5.1: DSC scans for glass transition measurements for C6	100
Figure 5.2: DSC scans for glass transition measurements for C8	101
Figure 5.3: DSC scans for glass transition measurements for C10	101
Figure 5.4: DSC scans for glass transition measurements for C12	101
Figure 5.5: DSC scans for glass transition measurements for C14	102
Figure 5.6: The relationship between catalyst content and glass transition temperature	102
Figure 5.7: FTIR spectra of the cured and uncured vitrimer material for formulation C10 and the enlarged details of change in peak intensity in three	

zones with interest: (a), hydroxyl group in 3700-3100 cm^{-1} ; (b), ester group in 1800-1650 cm^{-1} ; and (c), epoxy group in 990-880 cm^{-1}	103
Figure 5.8: The relationship between dicarboxylic acid carbon number and glass transition temperature	105
Figure 5.9: The overall trend of dicarboxylic acid carbon number and glass transition temperature	105
Figure 5.10: The stress relaxation behaviour of the crosslinked vitrimer C6Z5 at different temperatures from DMA analysis.....	106
Figure 5.11: Vitrimer C6 stress relaxation at 230°C from DMA analysis	109
Figure 5.12: Vitrimer C8 stress relaxation at 230°C from DMA analysis	109
Figure 5.13: Vitrimer C10 stress relaxation at 230°C from DMA analysis	109
Figure 5.14: Vitrimer C12 stress relaxation at 180°C from DMA analysis	110
Figure 5.15: Vitrimer C14 stress relaxation at 180°C from DMA analysis	110
Figure 5.16: Dependence of the relaxation time on temperature of vitrimer C6	112
Figure 5.17: Dependence of the relaxation time on temperature of vitrimer C8	112
Figure 5.18: Dependence of the relaxation time on temperature of vitrimer C10	112
Figure 5.19: Dependence of the relaxation time on temperature of vitrimer C12	113
Figure 5.20: Dependence of the relaxation time on temperature of vitrimer C14	113
Figure 5.21: Topological transition temperature as function of catalyst content	113
Figure 5.22: Topology freezing temperature of all formulations.....	116
Figure 5.23: Activation energy as a function of chain length	117
Figure 5.24: Topology freezing temperature as a function of chain length	117
Figure 6.1: The dynamic thermal mechanical development of vitrimer C6Z5 .	122
Figure 6.2: Temperature-dependent mechanical behaviour of cured C6Z5 ...	123
Figure 6.3: Evolution of storage modulus during C6Z5 vitrimer curing at different temperatures	124
Figure 6.4: Temperature-dependent mechanical behaviour of C6Z5 cured at different temperatures.....	126

Figure 6.5: Complex modulus of the materials cured under different temperatures after being elevated to 250°C	128
Figure 6.6: The change of modulus of C10Z5 regarding temperature	129
Figure 6.7: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z1 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	131
Figure 6.8: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z2.5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	133
Figure 6.9: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	133
Figure 6.10: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z1 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	134
Figure 6.11: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z2.5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	134
Figure 6.12: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	135
Figure 6.13: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C6Z1 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	135
Figure 6.14: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C6Z2.5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	136
Figure 6.15: Rheological heating scan from 50°C to 230°C with lines for constant frequency converging at a significant temperature for C6Z5 amplified with three functions: (a)G'/G*, (b)G''/G* and (c)Tan δ	136
Figure 6.16: Thermal degradation of vitrimers containing 1% catalyst in terms of weight loss	140
Figure 6.17: Thermal degradation of vitrimers containing 2.5% catalyst in terms of weight loss	141
Figure 6.18: Thermal degradation of vitrimers containing 2.5% catalyst in terms of weight loss	141
Figure 6.19: Rate of the thermal degradation vs. temperature curves of vitrimers containing 1% catalyst	142

Figure 6.20: Rate of the thermal degradation vs. temperature curves of vitrimers containing 2.5% catalyst	142
Figure 6.21: Rate of the thermal degradation vs. temperature curves of vitrimers containing 5% catalyst	143
Figure 6.22: Rate of the thermal degradation vs. temperature curves of vitrimer C6	143
Figure 6.23: Rate of the thermal degradation vs. temperature curves of vitrimer C8	144
Figure 6.24: Rate of the thermal degradation vs. temperature curves of vitrimer C10	144
Figure 6.25: Rate of the thermal degradation vs. temperature curves of vitrimer C12	144
Figure 6.26: Rate of the thermal degradation vs. temperature curves of vitrimer C14	145
Figure 6.27: Scheme of intramolecular β -hydrogen scission process	145
Figure 6.28: (a) Temperature for 5% weight loss of vitrimers, (b) Temperature for 10% weight loss of vitrimers	147
Figure A.1: FTIR spectra of adipic acid	185
Figure A.2: FTIR spectra of suberic acid	185
Figure A.3: FTIR spectra of sebacic acid	186
Figure A.4: FTIR spectra of zinc acetylacetonate	186

LIST OF TABLES

Table 2.1: Common kinetic models used for the chemical kinetics of thermoset cure	28
Table 2.2: Methods for apparent activation calculation	28
Table 3.1: Chemical structure and information of the ingredients for vitrimer... 39	
Table 3.2: Composition of the vitrimeric materials.....	39
Table 3.3: Adopted activation energy for cure kinetic model from Kissinger's method.....	44
Table 3.4: Temperatures for the DMA relaxation test on all the formulations ...	45
Table 4.1: The recorded enthalpy and difference for two sets of dynamic tests for material C8Z1 and C10Z1	49
Table 4.2: Curing data obtained from the dynamic DSC thermograms recorded at 2.5,5,10°C/min heating rate for all formulations.....	53
Table 4.3: Isothermal enthalpy for all vitrimeric materials.....	64
Table 4.4: Superposition data for vitrimers	67
Table 4.5: Curing kinetic parameters, pre-exponential factor and the goodness of the fitting obtained from dynamic DSC runs of all five vitrimer formulations at different heating rate.....	71
Table 4.6: Values of the parameters for three integral isoconversional methods	73
Table 4.7: Activation energy obtained from three isoconversional methods with degree of cure from 0.05-0.95	79
Table 4.8: Comparison of the apparent activation energy at the peak of the reaction obtained from Kissinger's model and three different isoconversional methods.....	83
Table 4.9: Calculated vales of αM and αp^∞ for all vitrimers for three heating rates from isoconversional for kinetic model determination.	84
Table 4.10: Curing kinetic parameters for the autocatalytic model of vitrimers	85
Table 4.11: The comparison between the degree of cure for the isothermal tests compared to their dynamic test and the degree of cure when diffusion limitation was effective for all vitrimeric materials	86
Table 4.12: MSR, RMSR and R^2 values of the autocatalytic model for all the vitrimer formulations	94
Table 5.1: Measured glass transition temperature (°C) for vitrimer	99

Table 5.2: Intercepts and slopes for the Arrhenius fitting for the vitrimer formulations	108
Table 5.3: Topological transition temperatures for all formulations	111
Table 5.4: Influence of increasing methylene groups in dicarboxylic acid chains on bond exchange rate	114
Table 5.5: Estimated relaxation time for all vitrimer formulations at their T_g ..	118
Table 6.1: Modulus at temperature of 160°C, 170°C and 180°C	126
Table 6.2: The parameters of the linear relationship illustrated in Figure 6.5 .	128
Table 6.3: The temperature required for rheological relaxation	137
Table 6.4: Transition temperature for vitrimers <i>via</i> stress relaxation and rheological experiment.....	138
Table 6.5: 5% and 10% weight loss temperature for all vitrimeric materials...	148

LIST OF EQUATIONS

(2-1).....	27
(2-2).....	27
(2-3).....	28
(2-4).....	28
(2-5).....	28
(2-6).....	29
(2-7).....	29
(2-8).....	29
(2-9).....	29
(2-10).....	30
(2-11).....	33
(2-12).....	34
(3-1).....	42
(3-2).....	42
(3-3).....	42
(3-4).....	42
(3-5).....	42
(3-6).....	43
(3-7).....	43
(3-8).....	43
(3-9).....	44
(3-10).....	44
(3-11).....	44
(3-12).....	44
(3-13).....	45
(3-14).....	46
(4-1).....	69
(4-2).....	69

(4-3).....	69
(4-4).....	70
(4-5).....	70
(4-6).....	70
(4-7).....	70
(4-8).....	73
(4-9).....	73
(4-10).....	73
(4-11).....	73
(4-12).....	74
(4-13).....	74
(4-14).....	74
(4-15).....	84
(4-16).....	84
(5-1).....	106
(5-2).....	107
(5-3).....	107
(5-4).....	107
(5-5).....	110

LIST OF ABBREVIATIONS

T_g	Glass Transition Temperature
T_v	Vitrification Temperature (Topology freezing temperature)
ACAT	Aniline Trimer
AFD	Aminophenyldisulphide
AIE	Aggregation-Induced Emission
ATR-IR	Attenuated Total Reflection Infrared Spectroscopy
BADGE	Bisphenol A Diglycidyl Ether
CANs	Dynamic Covalent Adaptable Networks
CF	Carbon Fibre
CFRCs	Carbon Fibre Reinforced Composites
CPPA	Carboxyphenyl Phthalamic Acid
DA	Diels-Alder
DEA	Dielectric Analysis
DGEBA	Diglycidyl Ether Of Bisphenol-A
DGEVA	Diglycidyl Ether Of Vanillyl Alcohol
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
ELO	Epoxidized Linseed Oil
ESO	epoxidized soybean oil
FTIR	Fourier Transform Infrared Spectroscopy
FWO	Flynn-Wall-Ozawa
IHR	Inhomogeneous Rouse
KAS	Kissinger-Akahira-Sunose
MNR	Macromolecular Network Rearrangement
MSE	Mean Square Error
NGP	Neighbouring Group Participation
NMR	Nuclear Magnetic Resonance
PBT	Polybutylene Terephthalate
PDI	Polydispersity Index
PDMS	Polydimethylsiloxane
PPh	Triphenylphosphine
RMSE	Root Mean Square Error

SAOS	Small-Amplitude Oscillatory Shear
SSR	Simplified Sticky Rouse
TBD	Triazabicyclodecene
TGA	Thermogravimetric Analysis
TPU	Polyurethane
t-TSP	time–temperature superposition
WLF	Williams–Landel–Ferry
xLCEs	Exchangeable Liquid Crystalline Elastomer
Zn(acac) ₂	Zinc Acetylacetonate

1 Introduction

1.1 Vitrimer Background and Applications

Historically, polymers have been divided into thermoplastics and thermosets according to the existence of covalently crosslinks. Such exclusive boundary was clear until the introduction of adaptable covalent crosslinks. The dynamic nature of associative bond exchange endows robust thermosets with mouldability and recyclability, which are traditionally associated with thermoplastic polymers. Since Leibler's team first introduced this new class of polymers and coined the term vitrimer¹, the unique characteristics of these material have received broad attention with increasing number of relevant research outputs^{2,3,4,5}.

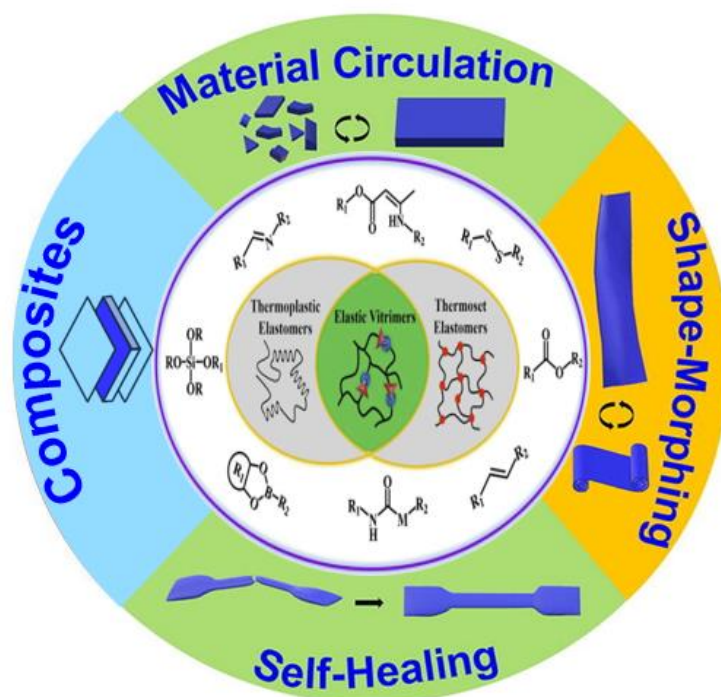


Figure 1.1: Schematic illustration of dynamic covalent bonds used in vitrimeric materials and their applications (Reprinted from Matter 5, (2022), Luo, J. *et al.*, Luo, J. *et al.*, Elastic vitrimers: Beyond thermoplastic and thermoset elastomers, 1391–1422., and Mater. Today 51, (2021), Zheng, J. *et al.*, Vitrimers: Current research trends and their emerging applications, 586–625., Copyright (2022), with permission from Elsevier)^{6,7}

Thermosetting polymers are characterised by their high mechanical, thermal, and chemical stability due to their intrinsic internal cross-links⁸. Excellent properties and weight to strength ratio make thermosetting polymeric materials indispensable in numerous industries such as coatings, adhesives, biomedical materials, and as matrix in structural composites with applications in aircraft and wind turbines⁹. Once set, the permanent crosslinked structure restricts segmental diffusion and chain movement, which makes thermosets excellent at maintaining their shape. When heated above their glass transition temperature (T_g), thermosets soften but do not flow. On the other hand, this behaviour also results in poor malleability, reprocessability and recyclability¹⁰. These characteristics have limited their applications in many areas, whilst the rapid market growth of the disposable, irreparable and unsustainable thermosetting matrix composites material has caused great environment concerns¹¹.

Thermoplastics are linear or branched polymer chains associated by intermolecular forces, which have temperature dependent viscosity behaviour¹². Over a certain temperature - glass transition temperature and melting point for semi-crystalline thermoplastics - macromolecular chains have enough energy to flow, become more fluid and can be easily manipulated. The chains lose mobility and solidify again upon cooling. Because of this temperature dependent behaviour, thermoplastics are ideal for successive processing and widely used for products with customised shape and dimensions¹³. Compared to thermosets, most thermoplastics are relatively chemically unstable as they can be dissolved easily when exposed to an appropriate solvent¹⁴.

Dynamic covalent adaptable networks (CANs) are crosslinked macromolecular networks, wherein the covalent links within the polymer can be dynamically exchanged *via* a chemical reaction¹⁵. CANs can achieve structure rearrangement and stress relaxation through bond exchange in response to external stimulus such as light or heat. Introducing CANs based on thermally reversible chemical reactions endues reversibility in thermosetting materials as part of their thermal response, repairability, reprocessability and recyclability while still maintaining their advantageous mechanical behaviour¹⁶.

There are two basic consecutive reaction steps in the process of reversible addition bond exchange to achieve stepwise macromolecular network rearrangement (MNR): discrete bond breaking and bond forming. Depending on the bond cleavage and forming sequence during the course of bond exchange, there are two straightforward pathways: (i) separation/addition (bond breaking and bond reforming), *i.e.*, dissociative pathway and (ii) the reverse process of addition/separation (bond forming and bond breaking) *i.e.*, associative pathway. CANs can be classified accordingly into dissociative CANs and associative CANs¹⁷ with the sequence of molecular activities playing a fundamental role in the difference in mechanical behaviour around the transition.

During a dissociative bond-breaking process, one crosslink cleaves into two individual segments with reactive moieties, which can diffuse through the network before encountering a complementary reactive end to form a new bond at another location (Figure 1.2 a). Consequently, bond dissociation allows chains to flow even in highly crosslinked networks, which results in a decrease of crosslinking density at the microscopic level and a sharp drop in viscosity at macroscopic level associated with rapid topology chain rearrangement. A well-studied dissociative bond exchange mechanism is the thermally reversible Diels-Alder (DA) cycloaddition reaction, in which the bond breaking and reforming rate between furan and maleimide bonds increases with temperature¹⁸. The Diels-Alder reaction is exothermic (5-10 J/mol) which makes the chemical equilibrium shift towards the endothermic side upon heating and results in reduction of total network connectivity. Moreover, as the polymer chains fragmentation process does not require association of functional groups, there is a temporary intermediate de-crosslinked state. Extensive loss of network connectivity results in an exponential viscosity drop with an increase in temperature. Theoretically, all dissociated networks should be able to fully recombine upon subsequent cooling and accomplish repeatable thermal processing of the material. However, in reality, dissociative CANs show reduced crosslinking density after thermal processing due to two main reasons: (i) the pathway for pairing ends reformation can be hindered by chain arrangement or solidification of the material and; (ii) loss of reactivity due to chain transfer, termination and crosslink degradation¹⁹.

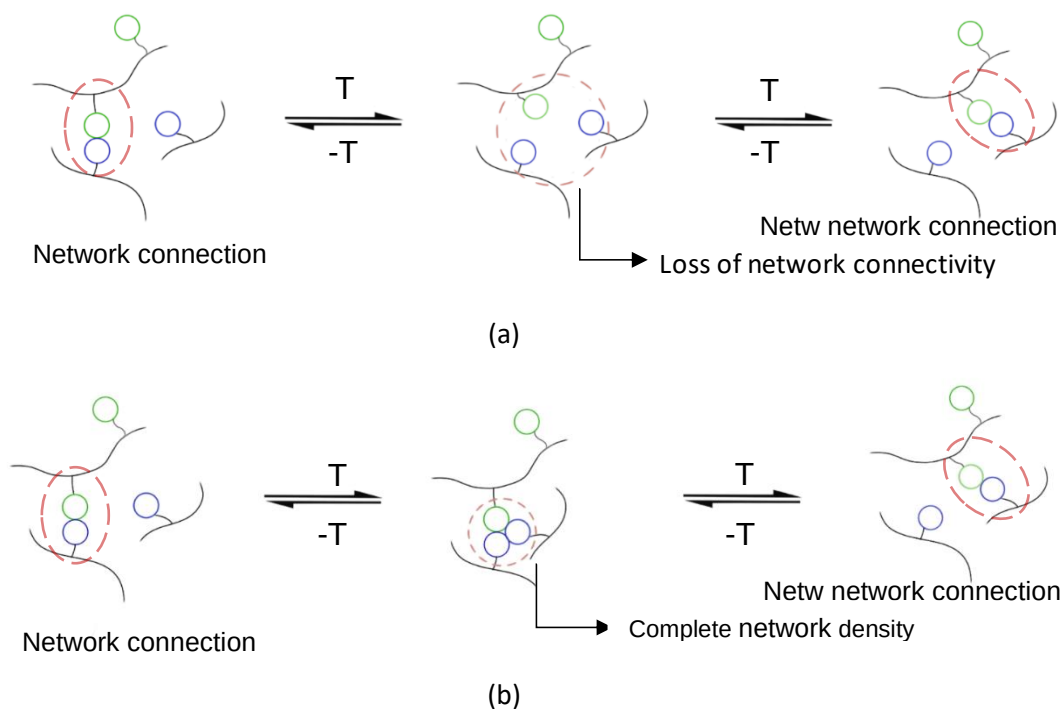


Figure 1.2: Illustration of topological rearrangements pathway for a) dissociative and b) associative covalent adaptable networks (CANs)

In a polymer network that undergoes an associative stepwise MNR (Figure 1.2 b) the rearrangement pathway involves the prior association of two polymer chains, resulting in a new covalent network bond, followed by an elimination step to create a new reactive end. Compared to dissociative CANs, the reversed addition/separation process achieves associative CANs with fixed crosslinking density yet rapid fluctuations in network topology. The retention of constant crosslink density is also a key factor in maintaining the material integrity at high temperature or in the presence of a solvent. The first reported attempt of associative CANs was reported by Scott *et al.*²⁰ using a photo-induced radical reaction of allyl sulphides to introduce plasticity in the crosslinked structure. Radicals are employed through photo-cleavage of residual photo-initiator in the polymer matrix to facilitate fragment diffusion and chain transfer of midchain functional groups *via* addition-fragmentation. However, later reports of CANs using photo-mediated free radical chain transfer mechanisms, such as trithiocarbonate²¹ and thiuram disulphide²², showed that despite the initial ability for topology rearrangement, the extent of structure adaptability, active life span

and repeatability of radical based CANs are largely limited due to the inevitable nature of radical termination. The idea of a thermally induced silica-like malleable material was presented in 2011 by Leibler *et al.*¹. The rapid topology rearrangement of the network was obtained *via* catalyst-controlled bond exchange of transesterification reaction in an dicarboxylic acid/epoxy system. Such temperature dependent CANs were named vitrimers because they share distinctive characteristics of vitreous silica.

Vitrimer technology has seen significant advancements, especially in understanding the dynamics of covalent adaptable networks (CANs) and the potential applications of various dynamic covalent linkages. Among the studies focusing on tuning material behaviour based on system composition, most have primarily reported the incorporation of exchangeable mechanisms and the implementation of the vitrimer concept in new materials. The properties of the final product often derive from the intrinsic chemistry of the monomers and the exchangeable bonds. Efforts to modify the behaviour of these materials have been relatively direct, with common methods including changing the type or concentration of catalysts used for bond exchange or introducing inorganic fillers to alter the mechanical behaviour of the product, such as its flow and toughness.

In recent years, transesterification-based vitrimer technology has emerged as a pivotal option in the field, offering a versatile platform for the development of resilient and adaptable materials. Complementing this, other dynamic covalent linkages, such as boronic ester, dioxaborolane metathesis, and sulphide containing reversible exchange, have been rigorously explored for their potential in pioneering self-healing materials and groundbreaking biomedical applications^{23,24,25}. Imine-based exchange, which is the product of condensation reactions between aldehydes and amines, has found significant applications in the formation of hydrogels and state-of-the-art drug-delivery systems^{26,27}. Moreover, the transamination process, a reversible amination and deamination catalysed by protic sources, has unveiled its potential in optimising vitrimer systems²⁸. Adding to this innovation, the transalkylation of triazolium salts, characterised by the *N*-alkylation of polymerised poly(1,2,3-triazole)s, has

broadened the scope of vitrimeric materials, suggesting a wider spectrum of applications and emphasising the necessity for a deeper understanding of vitrimer chemistry^{29,30}.

Vitrimers, with their unique blend of thermoset robustness and thermoplastic adaptability, have garnered significant attention in the realm of material science. Their potential to revolutionise industries, from aerospace to biomedical applications, hinges on their recyclability, malleability, and self-healing properties. These materials, which can be reprocessed without compromising their inherent strength, offer a sustainable alternative to conventional polymers, addressing the pressing environmental concerns associated with disposable and non-recyclable materials. The increasing demand for high-performance materials that can be tailored for specific applications underscores the need for a deeper understanding of vitrimer chemistry. While the foundational principles and potential applications of vitrimers are well established, there remains a significant gap when it comes to manipulating their properties at the molecular level. The ability to fine tune vitrimers, both in terms of their mechanical properties and their reactivity, could unlock a plethora of novel applications, ranging from adaptive coatings³¹ to smart biomedical devices³².

1.2 Objectives of the thesis

This research delves into the intricate relationship between dicarboxylic acid structures and the role of zinc acetylacetonate ($\text{Zn}(\text{acac})_2$) catalyst in epoxy-dicarboxylic acid based vitrimers, aiming to enhance the understanding of their combined impact on material properties and performance. This aim is addressed through the following objectives:

- Synthesis of epoxy-dicarboxylic acid based vitrimer material with various dicarboxylic acids and catalyst content to create a diverse set of materials for comprehensive evaluation.
- Characterisation of the cure behaviour of the vitrimer formulations using thermal and rheological analysis.
- Development of cure kinetics models for the vitrimer formulations and assessment of the effect of dicarboxylic acid chain length on kinetics.

- Assessment of the influence of vitrimer formulation parameters (dicarboxylic acid chain length and catalyst content) on glass transition temperature.
- Assessment of the influence of vitrimer formulation parameters (dicarboxylic acid chain length and catalyst content) on topological transition temperature.
- Establishment of the link between pre-polymer structure and transesterification catalyst content and the stress relaxation behaviour of vitrimers.
- Assessment of the high temperature behaviour of epoxy-dicarboxylic acid vitrimers with respect to development of modulus and thermal degradation.

1.3 Structure of the thesis

The thesis is organised in 8 chapters. Chapter 1 introduces the topic and motivation of the research and outlines the aim and objectives. Chapter 2 presents comprehensive surveys of the literature on the topics of epoxy-dicarboxylic acid vitrimers and their applications, control and tailoring of thermo-mechanical attributes of vitrimers and cure analysis and modelling of epoxy-dicarboxylic acid systems and concludes with a statement of the identified research gap. Chapter 3 provides details of the chemicals and procedures employed for material preparation and characterisation and described the methods used for modelling of the kinetics. Chapters 4-6 report the main body of the results and associated analysis and discussion of this work. Chapter 4 presents the experimental results from the cure analysis of epoxy-dicarboxylic acid formulation and the development of cure kinetics models based on isoconversional analysis as well as on a phenomenological autocatalytic model incorporating diffusion effects. Chapter 5 presents the outcomes of the investigation of the influence of dicarboxylic acid chain length and catalyst content on the glass transition temperature and topological transition temperature of the vitrimer formulations. Chapter 6 reports the results from the investigates of the evolution of vitrimer mechanical properties throughout the curing process as well

as the high temperature behaviour of cure vitrimers including effects on modulus development and thermal decomposition and their link with formulation parameters. Chapter 7 provides a summarising discussion of the findings from Chapters 4-7, identifies limitations and describes general areas of impact of the research work. Chapter 8 provides a list of conclusions from the research and a brief presentation of future work areas.

List of publications from this thesis includes the following papers:

1. Influence of Acid Structure on Topological and Glass Transitions of Dicarboxylic Acid-Epoxy Vitrimers. Under reviewing (ACS Macromolecules)
2. Cure Kinetics and Modelling of Dicarboxylic Acid-Epoxy Vitrimers. In preparation (Intended journals: ACS Macromolecules, RSC Polymer Chemistry, RSC Soft Matter)
3. High Temperature Behaviour of Dicarboxylic Acid-Epoxy Vitrimers. In preparation (Intended journals: ACS Macromolecules, Elsevier Polymer, Wiley Polymers for Advanced Technologies)

Conferences and seminars:

- 1 International Composites Summit 2023 [Milton Keynes, Sep 2023]
Attended this premier UK event focused on the latest advancements in composite materials, bringing together industry leaders and innovators.
- 2 Manufacturing 2075 – 2020, [Cranfield, Dec 2019], Participated in this global forum discussing long-term manufacturing challenges, exploring future research directions, and anticipating industry needs.

2 Literature review

The advent of transesterification-based vitrimers signifies a major shift in the landscape of polymer science. Their combination of reprocessability, stability, and adaptability positions them as a potential future solution for sustainable materials. As research in this domain continues to grow, it is anticipated that new applications and innovations will emerge, further solidifying the importance of vitrimers in modern material science.

2.1 Epoxy dicarboxylic acid transesterification-based vitrimers

Epoxy resins, characterised by their reactive polymers and prepolymers containing epoxide groups, have garnered significant attention due to their superior mechanical properties, outstanding thermal and chemical resistance, and strong adhesion to a myriad of substrates. Historically, these intrinsic characteristics have facilitated their broad application across various industries. They have been employed as adhesives in a structural engineering context, capitalising on their robust bonding capabilities³³. Their role as protective coatings for metals has been pivotal, offering enhanced corrosion resistance and durability³³. In the aerospace and automotive sectors, they have been of fundamental importance as matrix materials in composites³⁴, and their insulating properties have been harnessed in electrical systems for laminates and encapsulations³⁵. A notable representative of epoxy resins is bisphenol A diglycidyl ether (BADGE) or diglycidyl ether of bisphenol A (DGEBA): a staple in epoxy formulations¹⁹ currently dominates and takes up 90% of the global conventional epoxy resin market with annual production over 2 million tons worldwide³⁶ which is synthesised from bisphenol A and epichlorohydrin. Its versatility, ease of use, and potential for modification have solidified its position as a leading epoxy resin. Its applications span industries, from electronics to construction, underlining its adaptability³³. Cured products of DGEBA are recognised for their mechanical strength, resistance to chemicals, and high thermal stability³⁴.

Among the myriad crosslinkers available for epoxy systems, carboxylic acids have emerged as a pivotal class, distinguishing themselves from other crosslinkers in terms of their unique reactivity and performance attributes. Their role in epoxy thermoset technology is not only foundational but also transformative, offering a distinct set of advantages over other curing agents. Carboxylic acids, especially organic variants, have emerged as crucial curing agents in epoxy thermoset technology^{37,38,39}. Their nucleophilicity, which is moderate compared to nitrogen-containing agents, ensures that homogeneous mixtures of epoxy resins and carboxylic acid hardeners exhibit extended pot-life, often lasting several months at room temperature⁴⁰. However, for practical applications, catalysis is essential to achieve a viable reaction rate^{41,42}. The introduction of a catalyst can dramatically reduce pot-life, from months to a few days. Innovative approaches to achieve latent curing formulations include the use of thermo- or photo-generated catalysts. These catalysts remain dormant under standard storage conditions but activate under specific stimuli, such as elevated temperatures or UV exposure^{43,44,45}. Base-catalysed reactions are typically favoured, as they minimise the initiation of competing epoxy homopolymerisation⁴¹. Carboxylic acid functional polyester resins, commonly employed as hardeners, yield materials with exceptional corrosion resistance and adhesion, making them ideal for powder coatings⁴⁶. Formulations based on fatty acids combined with epoxy monomers have proven suitable for varnishes and coatings, with the resultant esters providing superior adhesion, flexibility, and water resistance⁴⁷.

The early 2010s witnessed a significant shift in polymer science with the integration of dynamic bond exchange capability, epitomised by epoxy dicarboxylic acid transesterification, with traditional thermosetting materials¹. This integration expanded the scope of vitrimer research and emphasised the importance of understanding the nuances of epoxy dicarboxylic acid transesterification. The hallmark behaviour of epoxy-dicarboxylic acid vitrimers arises from two pivotal processes: the polymerisation of multi-functional carboxylic acids with epoxy and the catalyst-facilitated bond exchange reaction. An optimal stoichiometric balance between epoxy and dicarboxylic acid groups

ensures a sufficient presence of both ester and hydroxyl groups, facilitating rapid bond exchange. Given the broad applicability of epoxy resins, their vitrimer counterparts hold promise in protective coatings and structural applications⁴⁸. Notably, Pripol® 1040, a blend of di- and tri-carboxylic fatty acids combined with DGEBA, has been the focus of multiple studies on vitrimers^{49,50,51,52}. However, a common limitation is the relatively low glass transition temperature of these systems, influenced by factors like backbone rigidity, reactant functionality, stoichiometry, and cure profile⁵³. To cater to high-temperature aerospace applications, molecular modifications are necessary. For instance, a vitrimer synthesised from triepoxy derived from renewable lignin-sourced vanillin and guaiacol with an anhydride exhibited glass transition temperatures exceeding 180°C when dry⁵⁴. Beyond the direct crosslinking of epoxy with dicarboxylic acids, transesterification vitrimer chemistry has been extended to modify thermoplastics, preserving their inherent reshapeability and weldability. For poly(butylene terephthalate) (PBT), two strategies have been proposed: one involving extrusion and injection processing conditions that promote hydroxyl group degradation⁵⁵, and another introducing triol glycerol, leading to alcoholised PBT chains⁵⁶. The kinetics can be modulated by selecting appropriate catalysts, PBT precursors, and crosslinkers. This tunability in rheological behaviour aids in optimising processing conditions⁵⁵. Additionally, dynamic crosslinks can enhance melt yield strength, benefiting processes like blow moulding and sheet extrusion⁵⁷. Tran *et al.* proposed a strategy to reduce hydrolysis in epoxy/dicarboxylic acid vitrimers using mini-emulsion polymerisation⁵⁸. Han and Xu introduced a DGEBA-citric acid network doped with varying poly(methyl methacrylate) constituents, producing a polymer-polymer composite⁵⁹. Furthermore, maximising the tunability of vitrimeric materials in terms of thermomechanical properties is crucial for diverse material performance requirements. Achieving such tunability often requires blending two compatible transesterification-based vitrimers⁶⁰. This blending approach can also be employed to synthesise polymer blends by covalently cross-linking thermosetting vitrimers with commodity thermoplastics, such as polyurethane (TPU)⁶¹. Figure 2.1 illustrates the mechanical blending procedures and the principal mechanism

of copolymerization based on the bond exchange reactions (BERs) between the ester and the hydroxyl functional groups.

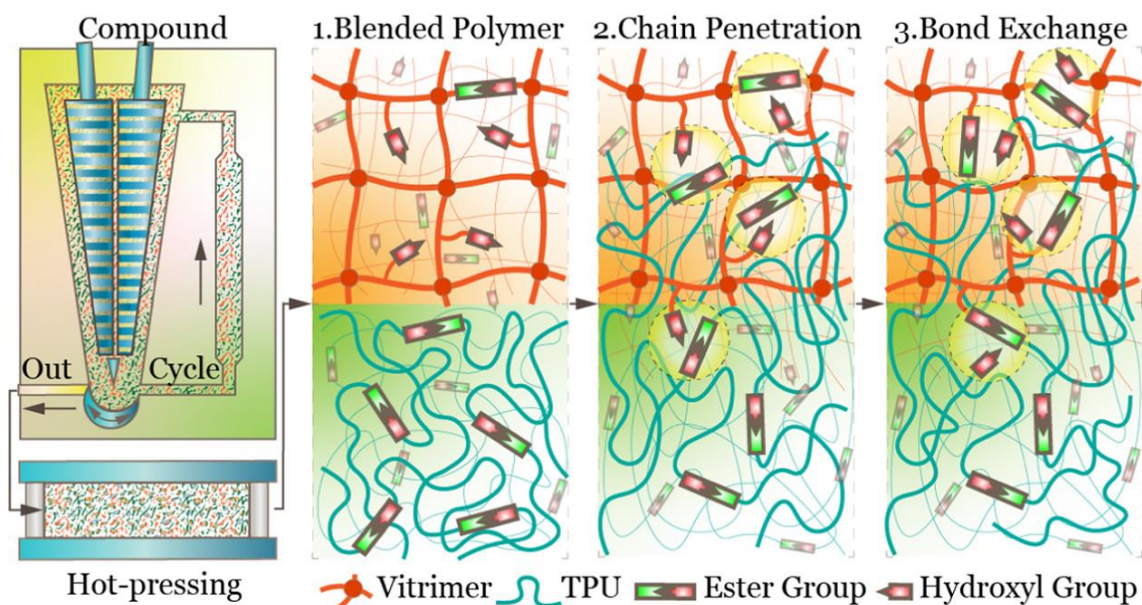


Figure 2.1: Schematic of blending TPU/vitrimer and the mechanism of copolymerization based on the bond exchange reactions (adapted with permission from {Chen, Z. *et al.*

Flexible, Reconfigurable, and Self-Healing TPU/Vitrimer Polymer Blend with Copolymerization Triggered by Bond Exchange Reaction. *ACS Appl. Mater. Interfaces* 12, 8740–8750 (2020)} Copyright {2020} American Chemical Society)

2.2 Vitrimer composites and their applications

Vitrimer composites represent a transformative advancement in the realm of material science, distinguishing themselves significantly from traditional thermosetting composites. While traditional thermosets are known for their rigidity and irreversibility once cured, vitrimers bring unparalleled adaptability, resilience, and multifunctionality to the table. This adaptability allows for post-cure shape changes, recyclability, and self-healing properties, which are largely absent in conventional thermosets. By integrating various components, from carbon-based materials to fibres, vitrimer composites are poised to redefine the boundaries of traditional materials. They usher in a new era of sustainable, efficient, and versatile applications, addressing many of the limitations and environmental concerns associated with traditional thermosetting composites.

2.2.1 Carbon nanoparticles based vitrimer composites

Incorporating carbon particles, especially carbon nanotubes (CNTs) and graphene, into vitrimers introduces multifunctionality, with a marked increase in electrical conductivity. Achieving optimal conductivity often necessitates high filler loadings which can lead to aggregation. Vitrimers with a mere 0.25 wt.% CNTs demonstrated a significant conductivity boost, reaching levels of $1.5 \times 10^{-2} \text{ S/m}^{62}$. Graphene, in its various forms, provides another conductivity enhancement avenue, with certain vitrimers containing graphene achieving conductivity levels of up to 160 S/m^{63} . Beyond conductivity, these carbon-enhanced vitrimers exhibit multi-stimuli responsiveness, and can react to stimuli like light, electricity, and heat. Among these, the photothermal behaviour of CNTs stands out and has the greatest influence on improving the adaptability and versatility of vitrimers. The localised heating benefits fast and efficient welding for CNT infused vitrimers. Efficient welding can be achieved after 30 seconds of light with power density of 0.82 Wcm^2 which is equivalent to 10 minutes of direct heating at 180°C^{64} .

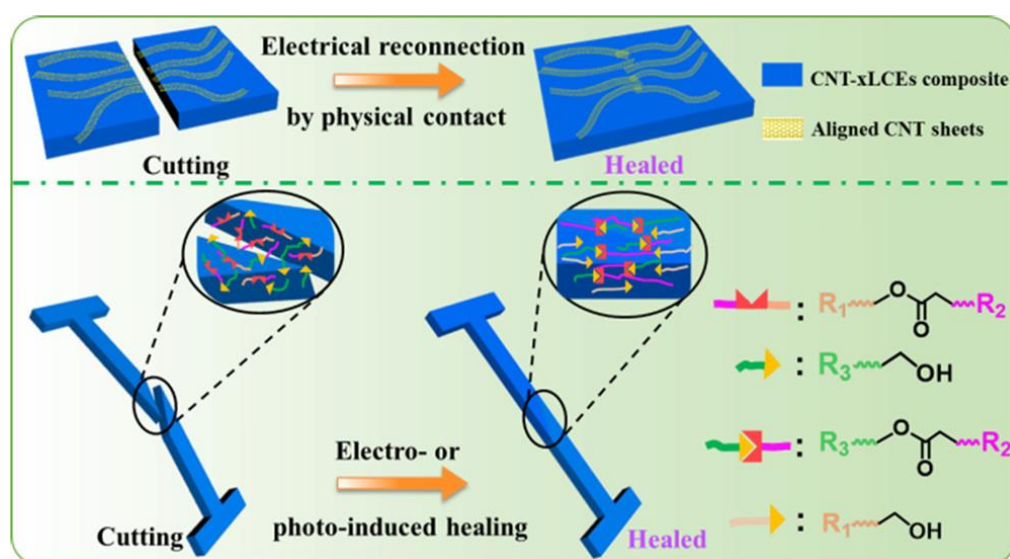


Figure 2.2: Schematic of the self-healing of CNTs/xLCEs composite realised by the electrical reconnection of fractured carbon nanotubes and electro or photo-induced healing mechanism (adapted with permission from {Wang, H. *et al.* Electricity-Triggered Self-Healing of Conductive and Thermostable Vitrimer Enabled by Paving Aligned Carbon Nanotubes. *ACS Appl. Mater. Interfaces* 12, 14315–14322 (2020)})

Copyright {2020} American Chemical Society)

Research conducted by Y Zhang *et al.*⁶⁵ highlighted the potential of a dual-responsive bond exchange process, depicted in Figure 2.2, developing a film that possesses self-healing, thermal stability, and electrical conductivity properties. This was achieved by arranging carbon nanotubes in alignment on the surface of an exchangeable liquid crystalline elastomer (xLCE) composite film, which has the ability to undergo healing through the application of both electrical currents and light. Apart from the carbon-based fillers, ACAT (aniline trimer)⁶⁶ and polydopamine⁶⁷ have also been used successfully to achieve photoheating when embedded in vitrimers. This multifaceted responsiveness, combined with the exploration into bio-based materials, highlights the expansive potential of nanocarbon/vitrimer composites in cutting-edge applications.

2.2.2 Fibre reinforced vitrimer composites

Owing to the excellent stiffness and strength-to-weight ratio, fibre reinforced composites (FRCs) are exceptional materials that are widely adopted for advanced structural applications. Carbon fibres and glass fibres are the most commonly used reinforcement materials for FRCs in both primary and secondary structures with applications in civil infrastructure, aerospace, wind turbines and high performance automotive⁶⁸. Thermosetting and thermoplastics can both be utilised as FRCs matrices. Typically, thermosets are the main matrix for FRCs, because of their thermomechanical, chemical and creep stability as well as their processability compared with thermoplastics. At the moment, epoxy resins are the primary matrix choice for FRCs because of their outstanding thermal and chemical resistance, dimensional and mechanical stability and excellent processability. However, thermoplastics have superior thermo-formability, recyclability, and impact resistance. When employing thermosets as the matrix because of the crosslinked structure and permanent bonds, recycling of the composite materials is extremely difficult. The flexibility and processability of vitrimers make an ideal matrix material to address the two major issues regarding the safety and sustainability of structural composites:

- Avoiding catastrophic failure by monitoring and repairing of internal failure. Monitoring inner failure of FRCs has been reported using multiple non-

destructive inspection techniques including X-ray, ultrasonic and electromagnetic testing. One of the limitations with these techniques is that they are not suitable or cost-effective for real-time monitoring. To address this problem, self-sensing agents such as continuous carbon fibres have been utilised⁶⁹.

- Recycling of various products in the manufacturing process. Examples of full recycling for both fibre and vitrimer matrix part of carbon fibre reinforced composites (CFRCs) have been successfully demonstrated that the reclaimed carbon fibres keep their integrity and exhibit very high recovery of modulus and strength compared to the original fibres, 95% and 97% respectively as reported by Yu *et al.*⁷⁰ and 96% and 95.6% by Wang *et al.*⁷¹. A relevant new approach for CFRPs recycling is by replacing the sizing agent on the surface of carbon fibres with polymers containing exchangeable bonds such as acetal metathesis⁷² and transacetalisation⁷³.

Dynamic covalent bonds in vitrimers offer avenues for recycling beyond just thermal methods. Specifically, these bonds can be cleaved using appropriate solvents, enabling the recycling of thermosets as illustrated in Figure 2.3. However, the degradation behaviour and mechanism vary across different vitrimer systems, necessitating the selection of a tailored recycling method for optimal efficiency. For instance, Schiff base vitrimers undergo hydrolysis in a mildly acidic environment, with the rate of degradation influenced by factors such as acidity, solvent type, and the solvent-to-water ratio⁷¹. Meanwhile, amine/epoxy thermosets containing disulphides can be completely dissolved using thiol solvents like 2-mercaptoethanol⁷⁴.

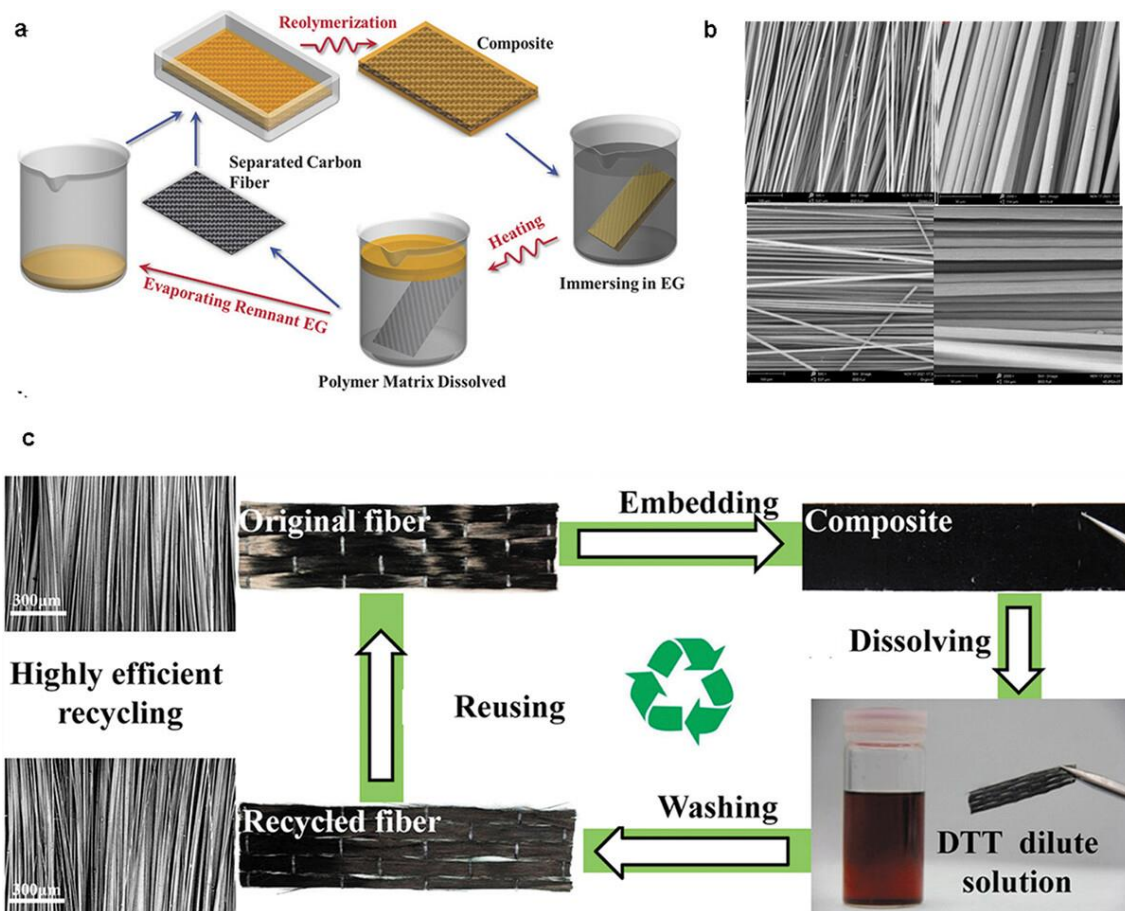


Figure 2.3: Recycling of fibre-reinforced vitrimer-based composites. (a) A schematic view of the closed-loop recycling paradigm for carbon fibre reinforced composites⁷⁰ (b) The morphology of crude and chemically recycled carbon fibres from was recycled from vanillin-based epoxy and isophoronediamine carbon fibre composites in 0.1 M HCl/ N,N-Dimethylformamide solution at 25 °C for 2 h, after then it was rinsed with dichloromethane⁷⁵ (c) The recycling process of CFRCs is based on a dual disulphide vitrimer: embedding the carbon fibres in an epoxy matrix; dissolving the epoxy matrix at 90°C in 1 h; washing and drying the recovered carbon fibres; reusing the recycled carbon fibres to form new composites⁷⁶ (adapted from Haochuan Zhang, Jingjing Cui, Guang Hu & Biao Zhang (2022) Recycling strategies for vitrimers, International Journal of Smart and Nano Materials, 13:3, 367-390⁷⁷)

2.3 Tuning of the thermo-mechanical properties of vitrimers

Beyond the distinct bond exchange characteristics inherent in various vitrimers, several factors influence vitrimer properties significantly and are crucial for material design. This section offers an exploration of vitrimer design, emphasising

the impact of catalysts, molecular structure, and stoichiometry on vitrimer behaviour and attributes.

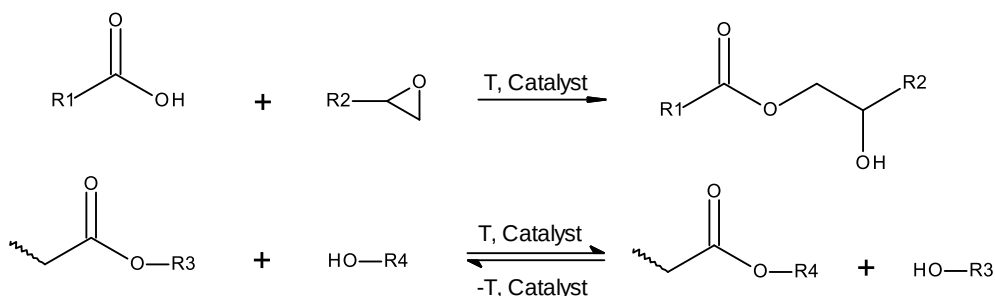
2.3.1 Tuning of vitrimeric materials by changing the type and amount of catalyst

The dynamic behaviour of vitrimers depends on the bond exchange reactions, permitting the material to adapt and reconfigure under specific conditions, such as thermal stimuli. There are two predominant strategies to modulate the exchange rates of dynamic reactions, pivotal for the conceptualisation of adaptive molecular systems:

- External catalysis: this approach activates robust covalent bonds *via* external agents, such as potent Lewis's acids or bases. It is a versatile strategy, with exemplars like acid-promoted catalytic transesterification.
- Internal catalysis: this sophisticated approach embeds both robust covalent bonds and intrinsic catalytic functionality within a molecule. The internal activation can engender marked acceleration in exchange rates. This concept includes: (a) immobilised catalysts: incorporation of established catalysts within a molecule; (b) proximity-induced or emergent catalysis: adjacent groups which amplify reactivity *via* stabilisation of transition states.

Transesterification is the interchanging process of ester groups transformed into one another through free hydroxyl groups⁷⁸ as illustrated in Figure 2.4. The exchange reactions of transesterification are so slow that they in most cases require the assistance of external catalysis, sometimes in high loadings. The temperature range for physical property change to occur in vitrimers can be tuned by either the chemical composition or the types and concentration of catalysts employed in the system. For the same concentration, more efficient catalysts with lower activation energy yield faster reconfiguration, lower viscosity at the same temperature and result in a lower topology freezing temperature⁷⁹. The most widely employed catalysts for transesterification reactions are organometallic complexes (organic tin or zinc salts) or bases such as triazabicyclodecene (TBD) and triphenylphosphine (PPh₃). The activation energy for triazobicyclodecene

(TBD), zinc acetylacetonate ($\text{Zn}(\text{acac})_2$), zinc(II)acetate ($\text{Zn}(\text{OAc})_2$) and triphenylphosphine (PPh_3) are 106, 104, 86, and 43 kJ/mol respectively^{80,16}. In terms of the impact of the amount of catalyst, it has been shown that an increase of the catalyst concentration does not affect the activation energy y but lowers vitrification temperature (T_v).



Where $\text{R1}, \text{R2}, \text{R3}, \text{R4}$ = polyester chain

Figure 2.4: Reaction and transesterification mechanism of dicarboxylic acid and diepoxy

Owing to its exceptional thermal stability, $\text{Zn}(\text{acac})_2$ and related zinc-based organometallic catalysts have emerged as the benchmark for transesterification chemistry, as evidenced by numerous studies^{1,81,82,83,84,85}. Zinc-based catalysts are environmentally friendly^{86,87,88,89} and catalyse transesterification even at a very low concentration. During catalysed transesterification of epoxy-dicarboxylic acid systems, Zn^{2+} acts as a catalyst by activating ester carbonyl, stabilising alkoxide groups and bringing them close to each other. Zn^{2+} is structurally attached to the vitrimer network, so that each Zn^{2+} is tetracoordinated with four oxygen atom ligands; two of them being alkoxide groups in a tetrahedral geometry as illustrated in Figure 2.5⁹⁰.

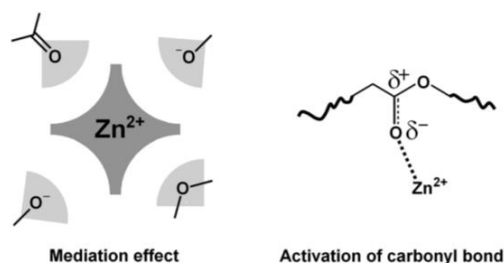


Figure 2.5: The mediation of Zn^{2+} in transesterification reactions

Brønsted acids have also been studied for their efficacy as catalyst used for transesterification: Bates *et al.* demonstrated that Brønsted acids activate transesterification at significantly lower temperatures compared to their Lewis acid counterparts⁹¹. Contrary to the behaviour of tin-based catalysts, Brønsted acids exhibit an inverse trend; stronger acids relax faster but possess higher activation energies⁹¹.

Exchange reactions, such as transesterification, which are fundamental to vitrimer behaviour, inherently exhibit slow kinetics, often necessitating high catalyst loadings. However, the introduction of catalysts can introduce challenges related to material ageing and potential leaching^{92,93}, issues that are particularly concerning for applications in sensitive areas like materials applied in the food industry or the health sector. In a groundbreaking study in 2015, Guan *et al.* introduced the concept of neighbouring group participation (NGP) to vitrimers⁹⁴, a principle well-established in organic chemistry but novel to vitrimer research. Materials crosslinked with difunctional dioxaborolane and equipped with adjacent amino groups exhibit faster relaxation compared to counterparts without such groups⁹⁵. The potential of leveraging internal catalysis, or internal activation, combined with NGP to optimise Covalent Adaptable Networks (CANs) has been the subject of recent reviews^{96,97}. Several functional groups have been identified as efficacious for NGP, including phthalate monoesters⁹⁸ and benzenesulfonic acid groups⁹⁹. These groups alter the transesterification mechanism, facilitating bond exchange. Inductive activation effects have been observed in materials like Meldrum's acids in polydimethylsiloxane (PDMS)¹⁰⁰ and polyimine vitrimers¹⁰¹. In the context of transesterification vitrimers, malonates¹⁰² have been employed to expedite the exchange reaction. Notably, owing to its pronounced electronegativity, fluorine exhibits significant potential in bond exchange activation. The carbonyl group in fluorinated esters, owing to its heightened electrophilicity¹⁰³, readily undergoes hydrolysis and nucleophilic attacks^{104,105}.

2.3.2 Modulating vitrimer properties through molecular structure

Beyond the modification of catalysts and the nature of exchangeable bonds, the intrinsic molecular structure of the polymer chain offers another avenue for tuning

vitriimer properties. This approach can be dissected into three primary pathways: changing the structure of the monomers, controlling the density of the exchangeable bonds and adjusting the chemical balance of the reactants.

2.3.2.1 Influence of molecular weight and polydispersity on vitriimer design

Molecular weight is instrumental in shaping the physical characteristics of vitrimers. An elevated molecular weight is typically associated with increased viscosity, which in turn affects the processability of vitrimers¹⁰⁶. Furthermore, greater molecular weight often leads to enhanced chain entanglement, resulting in improved mechanical properties, higher glass transition (T_g) and melting temperatures (T_m)^{107,108}, and augmented thermal stability^{109,110}. Research from the mid-1990s established a correlation between material toughness and molecular weight^{111,112}. Complementing molecular weight, the polydispersity index (PDI) characterises the molecular weight distribution within a polymer. Vitriimer samples with a narrow molecular weight distribution (low PDI) tend to display uniform material properties. In contrast, a wider distribution might modulate viscosity and potentially enhance toughness, due to the synergistic effects of low and high molecular weight chains. While initial studies centred on the foundational relationship between molecular weight and polymer properties, contemporary research delves deeper. A study by Helms *et al.* revealed that T_g decreases with the rising molecular weight of flexible linear segments but increases with that of rigid segments¹¹³. This behaviour underscores the dual influence of bond exchange thermodynamics/kinetics and polymer chain mobility within the network. To achieve a higher molecular weight in vitriimer design, strategies such as employing sterically shielded catalysts like phosphine sulfonate palladium or inhibiting associative chain transfer with specific copolymers, like boronic-ester, have been proposed¹¹⁴.

2.3.2.2 Chain flexibility role vitriimer behaviour

Helms *et al.* reported that T_g decreases with increasing molecular weight of the flexible linear segments, but increases with increasing molecular weight of the rigid segments, because the reconfigurability of vitrimers is affected not only by

the thermodynamics/kinetics of bond exchange at a given network density, but also by the mobility of the polymer chains within the network¹¹³. The flexibility of polymer chains, governed by factors like chemical structure, side group incorporation, and backbone rigidity, has a profound impact on vitrimer properties. Vitrimer systems characterised by increased chain flexibility tend to have faster bond exchange rates in dynamic covalent networks, as the chains can more efficiently align for bond exchanges. Such flexibility also modulates the vitrimer mechanical attributes, with more flexible chains yielding materials with enhanced elasticity and a diminished modulus. On the thermal front, chain flexibility depending on the rotation or torsion of skeletal bonds can influence the T_g ¹¹⁵; heightened flexibility might reduce the T_g , making the material more pliable at room temperature. To modulate chain rigidity in vitrimers, a prevalent strategy involves the integration of rigid structures, such as aromatic rings¹¹⁶, cyclic structure¹¹³ into the monomer. In contrast, introducing flexibility in the main chain of the monomers or the crosslinkers such as polyethylene¹¹⁷ poly(propylene glycol) segments¹¹⁸ and linear aliphatic chains including polyesters¹¹⁹, long methylene bridge¹²⁰ and polydimethylsiloxane¹²¹ in the monomer reduces the T_g . Incorporation of bulky groups that can hinder the rotation around the polymer backbone either in the backbone or as substitute groups¹²² increases rigidity but potentially slows down bond exchange rate. Also, the incorporation of branches affects the mechanical properties of vitrimers¹²³ and materials with large amount of branching exhibit lower mechanical properties. For example, most of branched diamine-containing vitrimers exhibit tensile strengths no more than 10 MPa^{124,125,126,127}.

Although vitrimers are typically amorphous, introducing segments that can crystallise might enhance rigidity. On the other hand, the dynamic nature of vitrimer enables the crystallisation of dense ethylene that would typically not crystallise^{128,107}. Integration of inorganic fillers with vitrimer inhibits both crosslinking and the dynamic bond exchange processes. This results in lower glass transition and topology freeze temperature^{129,130}. Introduction of functional groups capable of hydrogen bonding in vitrimer systems is a promising pathway to increase their rigidity while potentially offering additional dynamic interactions

to provide the materials with higher mechanical strength, improved creep resistance^{131,132} whilst promoting self-healing¹³³.

2.3.2.3 Crosslinking density: architectural significance and implications in vitrimer properties

Crosslinking density is a fundamental architectural characteristic of vitrimer matrices, representing the number of crosslinking junctures per unit volume in the polymer network. This metric critically influences the spatial organisation and interconnectedness of polymer chains within the matrix. Materials characterised by a high crosslinking density typically manifest increased rigidity and brittleness. This heightened rigidity stems from the limited mobility of individual polymer chains, leading to a more constrained network structure. In contrast, vitrimers with a reduced crosslinking density exhibit enhanced elasticity and ductility. This is attributed to the fewer crosslinking junctures, which grant polymer chains greater mobility and flexibility¹³⁴. Crosslinking density also profoundly impacts interaction with solvents. Matrices with a dense crosslinking network resist swelling in the presence of solvents, a phenomenon rooted in the restricted movement of the polymer chains, which curtails their capacity to absorb solvent molecules.

From a thermal standpoint, an augmented crosslinking density elevates the vitrimer glass transition temperature (T_g). The reason behind this is the restricted segmental motion of polymer chains due to the increased crosslinking junctures, necessitating a higher thermal input to transition from a glassy to a rubbery state. The dynamic nature of vitrimers presents a complex interplay with crosslinking density. Steric hindrance, resulting from densely packed chains, can potentially obstruct the bond exchange, a quintessential feature of vitrimers. However, empirical studies have yielded mixed results. For instance, certain research indicates faster relaxation times in less crosslinked materials^{135,136}, while others observed an accelerated bond exchange with increased crosslink density^{30,137}. Such discrepancies might arise from variations in the concentration and proximity of bond-reactive exchangeable groups concurrent with changes in crosslink density. Notably, Hayashi *et al.* reported enhanced relaxation in trans-

esterification-based vitrimers with higher crosslinking, without altering the concentration of reactive groups¹³⁸. This behaviour is attributed to the predominance of unstable, entropically perturbed segments in densely crosslinked networks.

The multifaceted relationship between crosslinking density and vitrimer properties necessitates a comprehensive approach in vitrimer design. It is imperative to strike a balance between dynamic covalent processability and the overarching material properties to harness the full potential of vitrimers.

2.3.2.4 Influence of stoichiometry of reactive functions within vitrimer matrices

The stoichiometry of reactive functions within vitrimer matrices is crucial for their properties and performance. Understanding of covalent exchange factors is essential for creating low creep and highly processable vitrimer elastomers. The proximity and availability of reactive centres or crosslinks play a significant role in vitrimer design. Stoichiometry can greatly impact vitrimer properties, especially in the context of epoxy ester vitrimers. Although networks formed under exact stoichiometric conditions have simpler reactivity profiles⁴⁷, most vitrimers require off-stoichiometry conditions for faster exchange^{139,140}. Increasing the concentration of reactive groups can enhance exchange reactions but may also alter the overall polymer properties. For instance, a greater concentration of reactive hydroxyl groups can lead to faster stress relaxation but may also result in increased swelling and reduced stability¹⁴¹. Designing vitrimers requires a balance between chemical reactivity and the desired material properties for specific applications.

2.4 Curing of DGEBA with dicarboxylic acids

Diglycidyl ether of bisphenol-A (DGEBA) as a main precursor for epoxy resins, has historically been used in curing with carboxylic acids, especially their organic derivatives. This curing process has been a focal point of research, given its implications for optimising industrial manufacturing cycles¹⁴². Understanding and application of curing kinetics can enhance final product quality and streamline process development¹⁴³. Furthermore, kinetics models can be instrumental in

shortening the curing cycle and, when integrated with heat transfer and chemorheological models, can mitigate internal stress in composites during production, thereby enhancing the end product attributes^{144,145,146,147}.

Over the years, substantial progress has been made in understanding the kinetics of epoxy-dicarboxylic acid curing, with numerous studies shedding light on the molecular mechanisms and factors governing the cure rate^{7,8}. Molecular-level understanding of the curing process¹⁵⁰. Yet, a holistic grasp of the kinetics, especially concerning innovative epoxy and dicarboxylic acid formulations and diverse environmental conditions, remains elusive.

The esterification of epoxy resins with carboxylic acids is a complex process, riddled with potential side reactions. At its core, the reaction involves the epoxide ring of the epoxy resin undergoing a ring-opening reaction, mediated by carboxylic acid. The interaction between the epoxide groups and carboxylic acids results in the formation of slower-reacting ester linkages, often necessitating accelerators for efficiency. Base-catalysed conditions are typically favoured over acid catalysis to mitigate competing epoxy homopolymerisation⁴¹.

A detailed examination of the base-catalysed polymerisation of epoxy with dicarboxylic acids (as depicted in Figure 2.6) reveals the following sequence: In the presence of a base catalyst, such as imidazole or tertiary amine, the carboxylic acid undergoes deprotonation to produce a carboxylate anion¹⁵¹. This anion then initiates a nucleophilic attack on the epoxy group electrophilic carbon, leading to epoxide ring-opening. The intermediate alkoxide ion undergoes rearrangement to yield a β -hydroxy ester linkage, signifying the esterification completion. Concurrently, the protonated base transfers a proton to the negatively charged oxygen of the epoxide ring, converting it into a hydroxyl group. This series of reactions results in a three-dimensional network, imparting the cured epoxy with its characteristic strength³⁵. The formation of β -hydroxy esters under stoichiometric conditions is pivotal for transesterification^{79,83}. The dicarboxylic acid choice and its concentration intricately influence the curing speed, the cured epoxy properties, and the material suitability for specific applications³⁴. Notable base catalysts include imidazoles^{152,153,154}, tertiary

amines^{155,156}, phosphonium bromide¹⁵⁷, and certain metal salts^{1,79,83}. The reaction efficiency and selectivity hinge on several factors, including the base catalyst type, the reactants stoichiometric ratio, and the reaction temperature¹⁵¹. In a system with 1:1 stoichiometric ratio of the epoxy and dicarboxylic acid functional groups, typically only addition esterification proceeds in the initial stage in a base-catalysed system. Further reactions - etherification, condensation esterification, and disproportionation are consecutive and become operative only after the dicarboxylic acid or epoxide has been consumed¹⁵⁸, but deviations can alter product distributions. Elevated temperatures can accelerate the reaction, but potential degradation risks must be managed. Side reactions, such as etherification or epoxy homopolymerisation, may be manifested under specific conditions, emphasising the need to fine-tune reaction conditions and catalyst selection in this intricate esterification process.

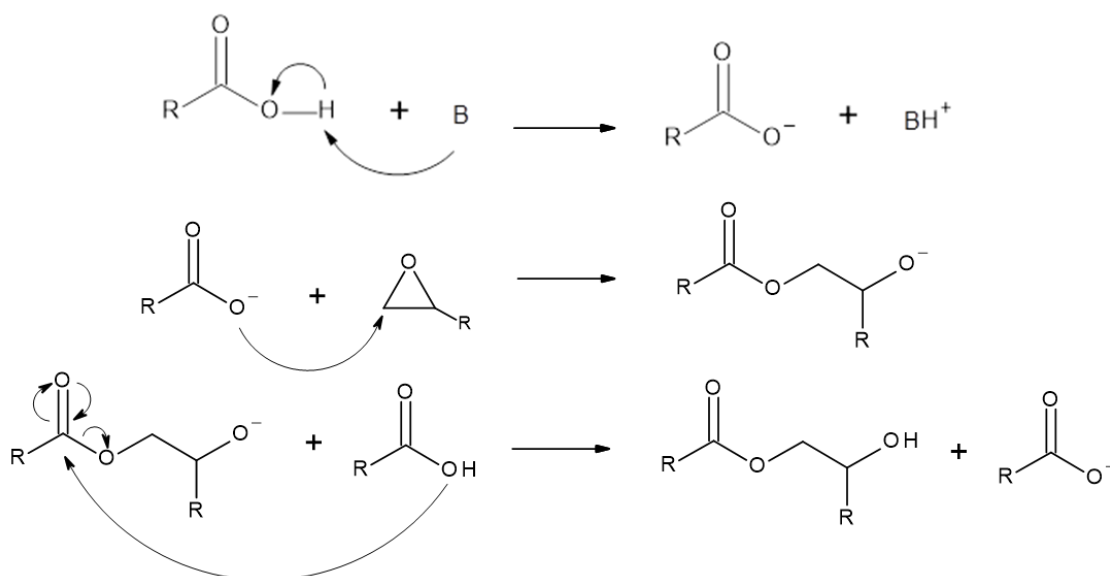


Figure 2.6: Curing mechanism of epoxy and carboxylic acids with base catalyst

Among the diverse techniques employed for cure kinetics investigations, Differential Scanning Calorimetry (DSC) stands out as the most prevalent. DSC examines the heat flow dynamics as samples undergo thermal variations or remain isothermal. The exothermic heat emanating during the curing phase of thermosetting resins¹⁵⁹ can be investigated under variable time-temperature conditions. The data obtained allows determining the degree of cure, reaction

enthalpy, and an array of kinetics parameters including activation energies and reaction orders¹⁶⁰. A specialised variant, isothermal DSC¹⁶¹, where the reaction heat flow is monitored at a fixed temperature, offers unique kinetics study advantages. This methodology excels in pinpointing specific reactions, sidestepping the convolution of overlapping reactions seen in non-isothermal DSC. Its prowess extends to the analysis of slow reactions, unravelling reaction mechanisms, and ensuring reproducibility. Furthermore, it holds significant relevance for real-world scenarios, mirroring predominantly isothermal conditions in applications like resin curing in manufacturing¹⁶². Other instrumental techniques include Thermogravimetric Analysis (TGA), which evaluates weight loss in relation to temperature or time, offering insights into thermal stability and degradation nuances^{163,164}. Dynamic Mechanical Analysis (DMA) gauges a mechanical attributes dynamically, illuminating aspects like the glass transition temperature and crosslink density¹⁶⁵. Fourier Transform Infrared Spectroscopy (FTIR) tracks vibrational spectra alterations during curing, facilitating the assessment of reaction rates and extents¹⁶⁶. Dielectric Analysis (DEA) is adept at *in-situ* curing monitoring, especially vital for thicker sections¹⁶⁷. Rheometers, used in rheological measurements, are pivotal for understanding viscosity variations, elucidating gelation and vitrification phenomena¹⁶⁸. Nuclear Magnetic Resonance (NMR) offers a molecular-level view, focusing on dynamics, mobility, and chemical transformations during curing¹⁶⁹. Each method provides different types of information, and often a combination of techniques is used to get a comprehensive understanding of the curing process. The choice of method depends on the material being studied, the specific information desired, and the conditions under which the material is processed.

2.4.1 Curing kinetics of epoxy-dicarboxylic acid systems

As with traditional thermosetting polymers, understanding the kinetics of vitrimers is crucial for optimising their properties and processing conditions. However, contrary to the extensively researched cure kinetics of traditional thermosetting epoxies, the kinetics mechanisms of vitrimers emphasise bond-exchange-induced relaxation. This relaxation is explored more comprehensively and in

greater depth than the cure reaction kinetics associated with reactant curing. Typically, the former is assessed using mechanical techniques such as stress relaxation or creep¹⁷⁰, implemented through rheological¹⁷¹ or thermomechanical means. In contrast, the study of curing and crosslinking formation predominantly relies on detecting heat energy changes *via* Differential Scanning Calorimetry (DSC). The methodologies employed to study the kinetics of these innovative materials are not new. Established kinetic analysis techniques, originally devised for traditional thermosetting systems, have been adapted for vitrimers.

The curing kinetics of thermoset polymers is defined as Equation (2-1)

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2-1)$$

where α is the degree of curing reaction, and $f(\alpha)$ is a function related to the type of kinetic model. $k(T)$ is the rate constant re, which follows an Arrhenius dependence on temperature:

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad (2-2)$$

where E_a is the activation energy, A the pre-exponential factor, T the temperature and R is the universal gas constant. Here the apparent activation energy (E_a), the pre-exponential factor (A), and the reaction mechanism $f(\alpha)$, form the kinetics triplet, offering a comprehensive view of the factors governing the rate and mechanism of a reaction. Accurate determination of the kinetics triplet is crucial for optimising reaction conditions in various industrial and laboratory settings¹⁷².

For vitrimer cure kinetics research, phenomenological models are predominantly employed. Their primary appeal lies in their foundation on empirical observations, circumventing the need to delve deeply into the intrinsic chemical mechanisms governing the reactions. These models are primarily based on the observed relationship between variables, such as temperature, time, and degree of cure. They are often used when a general description of the curing process is sufficient, and the detailed reaction mechanisms are not required. The most common phenomenological models are listed in Table 2.1.

Table 2.1: Common kinetic models used for the chemical kinetics of thermoset cure

Model	Equation
nth order	$f(\alpha) = k(T)(1 - \alpha)^n$ (2-3)
Autocatalytic	$f(\alpha) = k(T)\alpha^m(1 - \alpha)^n$ (2-4)
Kamal-Sourour	$f(\alpha) = [k_1(T) + Kk_2(T)\alpha^m](1 - \alpha)^n$ (2-5)

Here m and n are the reaction orders. In the context of epoxy-dicarboxylic acid curing kinetics, the mechanism is predominantly autocatalytic, a characteristic attributed to the formation of hydroxyl groups during the reaction^{173,174,175}. This curing reaction is typically monitored using DSC at varying heating rates.

To calculate E_a , various equations have been suggested grounded on the temperature integral approximation. The traditional Kissinger method, which employs non-isothermal experiments, posits that the reaction rate reaches its zenith at the peak temperature¹⁷⁶. A notable challenge in model-fitting approaches is the kinetics compensation effect¹⁴², becoming especially pronounced in dynamic settings. To address the oversimplification of reaction mechanisms, isoconversional methods emerged. These allow the estimation of activation energy based on conversion, acknowledging its fluctuation, a feature particularly useful for intricate materials like polymers¹⁶⁰. These techniques hinge on parameters like the experiment heating rate β and the temperature corresponding to the cure degree T_α during the curing process. The Flynn-Wall-Ozawa method¹⁷⁷ has been built upon Kissinger-Akahira-Sunose (KAS)¹⁷⁸ model, which is better suited for non-isothermal scenarios. By the 1990s, Starink's model¹⁷⁹ offered a holistic view, encompassing both the reaction model and the conversion rate. The detailed models mentioned are listed in Table 2.2.

Table 2.2: Methods for apparent activation calculation

Methods	Equation
---------	----------

Kissinger	$\ln\left(\frac{\beta}{T_{\alpha}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_{\alpha}} \quad (2-6)$
Flynn-Wall-Ozawa (FWO)	$\ln(\beta) = C - 1.052 \frac{E_a}{RT_{\alpha}} \quad (2-7)$
Kissinger-Akahira-Sunose (KAS)	$\ln\left(\frac{\beta}{T_{\alpha}^2}\right) = C - 1.00 \frac{E_a}{RT_{\alpha}} \quad (2-8)$
Starink	$\ln\left(\frac{\beta}{T_{\alpha}^{1.92}}\right) = C - 1.08 \frac{E_a}{RT_{\alpha}} \quad (2-9)$

In recent years, the field of epoxy and dicarboxylic acid vitrimers has witnessed significant advancements, particularly in understanding their kinetics behaviours. The curing reaction of an epoxy resin is an exothermic reaction and the heat generated during the process is proportional to the number of consumed reactive groups¹⁶⁰.

In the application of isoconversional methods, there is an initial decline in the activation energy from the start of the cure, suggesting a shift in the reaction mechanism from non-catalytic to autocatalytic, influenced by the rising concentration of hydroxyl groups. The average apparent activation energy decreases from initial values of 94 and 100 $\text{kJ} \cdot \text{mol}^{-1}$ to 71 and 76 $\text{kJ} \cdot \text{mol}^{-1}$ when sebacic acid and DGEBA react with 10% and 20% epoxidised soybean oil (ESO) respectively, up until the reaction achieves 25% completion¹⁸⁰. As the degree of reaction further increases, the activation energy of the reaction increases slowly in the range of 50–100 $\text{kJ} \cdot \text{mol}^{-1}$ when $\alpha < 0.7$ due to the counterbalance of autocatalysis and increasing molecular weight. However, because mobility limitations continue to increase as molecular chains grow and crosslinking density increases, the reaction starts to shift from chemical to diffusion control resulting in the activation energy of the reaction rising sharply for $\alpha > 0.7$ ¹⁸¹.

The kinetics studies confirm that the structure of monomers plays a pivotal role in determining the parameters of epoxy-carboxylic acid curing reactions. Numerous studies have identified a single exothermic peak associated with this

curing reaction, with the reaction peak temperatures ranging from 115 to 200°C, contingent upon the reactivity of the involved components¹⁸². For instance, the incorporation of sulphur in the β position of the carboxylic group augments the acidity of the carboxylic acid, thereby enhancing the reactivity of the acid proton towards the epoxy group¹⁸³. A comprehensive study examining the impact of elongating the chain length of linear α,ω -dicarboxylic acids revealed a rise in peak reaction temperature and a decline in total enthalpy for dicarboxylic acids with extended chain lengths¹⁸⁴. This phenomenon can be attributed to the increased likelihood of polymeric or oligomeric chain entanglement, which amplifies steric hindrance during the curing reaction, subsequently diminishing curing reactivity¹⁸⁴. In scenarios involving the curing of epoxidised linseed oil (ELO) with succinic acid, a relatively shorter chain, there is a heightened pre-exponential factor, resulting from enhanced transport and collision efficacy with the epoxy group¹⁸⁵. Another noteworthy investigation delved into the curing reactions between DGEBA and two variants of amidodicarboxylic acids¹⁸⁶. This study underscored the multifaceted nature of curing processes, which often transpire in sequential stages. Notably, the DGEBA/CPPA (4-carboxyphenyl phthalamic acid) system has an elevated apparent activation energy, stemming from the CPPA inherently rigid structure.

Snijkers *et al.* introduced an approach that leverages thermo-mechanical data from rheological tests, employing the Arrhenius equation¹⁸⁷:

$$t_{gel} = K^* e^{\frac{E_{a,rx}}{RT}} \quad (2-10)$$

with K^* being a pre-exponential constant, $E_{a,rx}$ the activation energy of the reaction. In this method, gelation times are plotted against varying cure temperatures to deduce the reaction activation energy. A subsequent study, based on this principle and conducted on vanillin-based epoxy vitrimers, highlighted distinct differences in activation energies for crosslinking¹⁸⁸. This was determined by plotting gel time against inverse temperature and bond exchange using the Kissinger model. The resulting apparent activation energy values are 69 and 63 $\text{kJ} \cdot \text{mol}^{-1}$ for vitrimers composed of diglycidyl ether of vanillyl alcohol

(DGEVA)/cystamine and DGEBA/4-aminophenyldisulphide (4AFD), respectively. Notably, the activation energy values derived from the Kissinger model follow a similar trend, albeit with slightly lower values, at 46 and 53 $\text{kJ} \cdot \text{mol}^{-1}$ ¹⁸⁸.

2.5 Thermo-mechanical dynamics of vitrimeric polymers: catalysts, bond exchanges, and design implications

Vitrimeric polymers are characterised by their unique adaptability, which is attributed to thermally induced bond exchange reactions. This adaptability emphasises the importance of understanding their mechanical properties in relation to temperature changes. Research on transesterification-based vitrimers offers profound insights into their thermo-mechanical attributes. Specifically, under certain conditions, these polymers demonstrate variations in their effective modulus, for a fact critical for real-world applications. Delving into the thermo-mechanical properties of vitrimers facilitates predictions about their behaviour under diverse conditions, an understanding that is indispensable for refining manufacturing processes and ensuring the consistent fabrication of materials that meet desired specifications.

What sets vitrimer polymers apart is their dual behaviour, displaying characteristics of both thermosets and thermoplastics. This duality accentuates their distinctiveness and highlights the need to understand their thermo-mechanical behaviour, especially for devising efficient recycling methodologies that promote sustainability. Furthermore, a comprehensive understanding of vitrimer thermo-mechanical properties can catalyse the development of advanced materials, leading to innovations in various sectors, including manufacturing and cutting-edge biomedical applications.

2.5.1 Thermo-mechanical properties: crosslinking and temperature effects

The thermo-mechanical characteristics of vitrimers predominantly stem from two key processes: the formation of crosslinks during curing and the alterations in bond exchange reactions across varying temperatures. The following sections delve into the impact of temperature on mechanical attributes, the utilisation of

master curves to understand viscoelastic behaviour, the relaxation induced by bond exchange, and vitrimer distinct frequency-independent modulus behaviour.

2.5.1.1 Crosslinking state during the cure

During vitrimer crosslinking, the modulus typically increases as dynamic covalent bonds form between polymer chains, creating a three-dimensional network. This network facilitates bond exchange reactions, allowing the material to reconfigure its structure without net bond breaking. Factors such as the degree of crosslinking, the type of crosslinking agent, and vitrimer molecular weight influence the extent of modulus increase. Unlike traditional crosslinked polymers, vitrimers can avoid becoming overly brittle with increased crosslinking due to their dynamic bond exchange mechanism. For the uncured mixture, the loss modulus dominates the early stage of isothermal crosslinking before the storage modulus takes over, indicating the system transformation from a viscous stage to a gel then to a highly elastic solid stage. However, after the rapid increase, both storage and loss modulus continue to grow with time but at a much slower rate indicating a slow development of crosslinks. During the curing process crosslink density or the degree of cure is related to the curing temperature and time. Higher curing temperature leads to a faster reaction and shorter time to reach the plateau of the modulus. To reach the fully crosslinked structure through achieving the exchange equilibrium a long period of time is required. In the case of epoxy and fatty acid vitrimer, when cured at 130°C the increase of modulus continues for 38 hours¹⁸⁹. As the modulus is related to the state of the crosslinking, insufficient annealing time would result in a lower mechanical property. For example, in the DGEBA and sebacic acid vitrimer incorporated with linear alkylamine as side chains are polymerised at 120°C for 3 h followed by isothermal at 160°C for 6 h to allow transesterification equilibrium. For example, an additional 21 hours of annealing at 100°C results in more physical crosslinks which leads to a higher elastic modulus of 170 kPa compared to 80 kPa at 90°C and 120 kPa to 50 kPa at 160°C¹⁹⁰.

2.5.1.2 Change of mechanical properties due to temperature changes

Upon exposure to a heating gradient, the cured vitrimer is noted to undergo a swift decline in storage modulus around its glass transition temperature⁶⁰, akin to thermosets. For instance, the rheological behaviour of an epoxy-thiol-acrylate dual curing system demonstrates a notable decrease in values as the material is heated across its glass transition temperature range from 30 to 60°C¹⁹¹. The tuneable thermo-mechanical properties of vitrimer blends can be achieved by adjusting the compositions of the base vitrimers, offering a flexible and eco-friendly approach to recycling thermoset waste for practical engineering applications.

2.5.2 Employment of master curves for analysing the viscoelastic behaviour of vitrimers

Master curves have been employed in the study of vitrimer thermos-mechanical behaviour to facilitate the efficient extrapolation of long-term material behaviour from short-term data using time–temperature superposition (t-TSP) of the dynamic response of the material to the frequency scans at different temperatures. This allows the extrapolation of the vitrimer behaviour over extended periods, based on short-term experimental data. This is particularly valuable in predicting the durability and longevity of vitrimer-based materials. The t-TSP of vitrimers is usually achieved by a shift factors (α_T) from Williams–Landel–Ferry (WLF) equation:

$$\log(\alpha_T) = \frac{-C_1 \cdot (T - T_{ref})}{C_2 + T - T_{ref}} \quad (2-11)$$

Here C_1 , C_2 are the WLF-parameters at lower temperature where the temperature dependence of relaxation or viscosity cannot be adequately described by a simple Arrhenius relationship and an Arrhenius equation at elevated temperatures where the temperature dependence is dominated by the activation energy.

The microscopic dynamics structure–viscoelasticity relationships of bond exchanging reactions have been investigated by computational models like a

hybrid molecular dynamics and Monte Carlo simulation¹⁹², or a sticky Rouse model (simplified sticky Rouse (SSR) and the inhomogeneous Rouse (IHR))¹²¹. These models enable insights into molecular dynamics and relaxation mechanisms, such as network strand relaxation and crosslink exchange. Moreover, they serve as a standardised benchmark for comparing various vitrimer formulations and other polymers, aiding in material selection and design. By capturing phase transitions and providing a temperature-independent analysis, master curves streamline the study of vitrimers, promoting cost-effective and time-efficient research while guiding the tailoring of vitrimers for specific applications. In a recent study based on the Kramer's thermally activated dynamics of bond exchange reactions exchange rate was expressed as¹⁹³:

$$\beta = \omega_0 e^{-W_0/k_B T} \quad (2-12)$$

where β represents the vitrimer chain exchange rate as the reciprocal of the duration time τ_x of a bond formed by an unattached end group, ω_0 is the intrinsic frequency of the vibration of the group, W_0 the potential barrier separating the bonded from the unbonded state, and k_B is a constant depending on the molecular weight of the chain. The Arrhenius thermal activation energy expressed as the slope of the curves of the logarithm of exchange rate β versus $\beta 1/T$, shows a dramatic change near the glass transition¹⁹⁴.

2.5.3 Bond exchange induced relaxation

Bond exchange reactions play a pivotal role in the relaxation behaviour of vitrimers. The relaxation behaviour of epoxy-dicarboxylic acid transesterification-based vitrimers reveals two factors contributing to relaxation: structural and bond exchange reaction-induced. The proportion of the contribution of these two mechanisms can vary based on the catalyst content and the speed of the external stimuli. Higher catalyst levels and slower heating can increase the ratio of bond exchange reactions in stress relaxation in single frequency stress relaxation¹⁹⁵.

In the case of compressive thermo-mechanical analysis under a constant force the materials start to decrease in dimension under compression at the point at which the effect of the bond exchange induces softening which exceeds the

structural relaxation induced expansion with increasing temperature. The dimensional change in this case is related to the bond exchange reactions which induces stress relaxation and endows the material the ability to flow like a thermoplastic and also causes decrease in modulus¹⁹⁶. Under constant stress creep test, the topology transition temperature is defined as the point at which the material starts to lose its effective modulus¹⁹⁷. There are few advantages of this method compared to the more widely used stress relaxation method as it requires a smaller sample, the time needed for the test is reduced, and the thermal expansion rate can also be measured at the same time. However, the results provided from this method are heating rate and force dependent.

2.5.4 Frequency dependence of modulus and $\tan \delta$

During the curing of crosslinked polymers at the gel point the formation of an infinite network implies that pathways span the entire system¹⁹⁸. This interconnected structure results in a unique equilibrium between the viscous and elastic components of the system. Both these components exhibit a similar sensitivity to frequency changes, leading to frequency independence of the loss tangent¹⁹⁹. The independence of the frequency on the $\tan \delta$ is also observed at the gel point in polymer networks with exchangeable bonds (Diels-Alder)¹⁸.

In addition to the gel point, the frequency independence of viscoelastic properties is also present at higher temperatures after the material is crosslinked. During a frequency sweep tests for an epoxy-acid vitrimer under varied temperature, as shown in Figure 2.7, the influence of frequency on the normalised storage and loss modulus becomes negligible at an elevated temperature transition period, indicating a change in material properties¹⁸⁹.

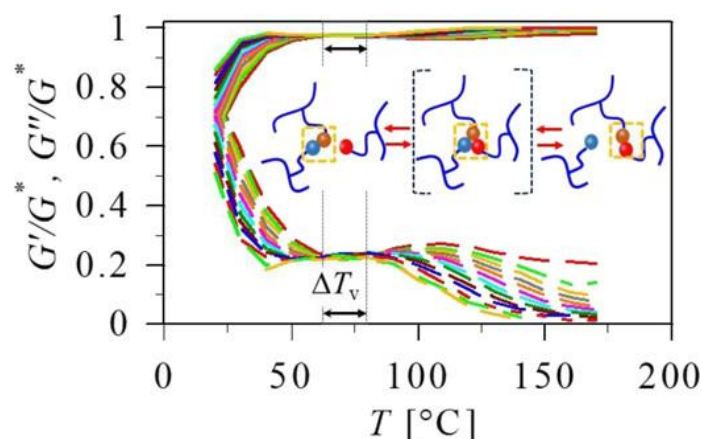


Figure 2.7: Frequency independency of normalised storage and loss modulus over an elevated temperature range (adapted with permission from {Huagao Fang, Wujin Ye, Yunsheng Ding, and H. Henning Winter., Rheology of the Critical Transition State of an Epoxy Vitrimer, *Macromolecules* 2020 53 (12), 4855-4862}) Copyright {2021} American Chemical Society)¹⁸⁹

A prevailing theory posits that during a rheological temperature ramp, the unification of the modulus can be attributed to two distinct relaxation mechanisms: structural relaxation and relaxation induced by bond exchange reactions. Following the transitional phase, the impact of bond exchange becomes more dominant than that of structural relaxation. To prove it, studies on the factors influencing the rate of bond exchange and their affection on this transition in terms of the onset temperature of frequency independence, its range, and the subsequent temperature and frequency response post-transition ought to be conducted. However, no studies have been conducted to explore this relationship in detail yet.

2.6 Research gap

There remains a discernible gap in the systematic study of the curing behaviour, kinetics, and modelling of DGEBA when combined with carboxylic acids of varying linear chain lengths. The influence of chain length on the curing kinetics and its subsequent impact on the thermal, mechanical, and rheological properties of the resulting polymers is not well understood. Catalytic control, which involves altering the type and concentration of catalysts, predominantly affects the activation energy of reactions, thereby modifying the temperature-dependent

viscosity behaviour. Yet, it does not significantly alter other material properties. An illustrative example is that vitrimers doped with various catalysts at different concentration levels often exhibit unchanged glass transition temperatures²⁰⁰. A knowledge gap exists regarding the connection between the chemical structure of monomers and the ensuing properties. The evolution of vitrimers' mechanical properties throughout the curing process is predominantly undocumented. A deeper insight is imperative to understand the complex interplay between the curing temperature, duration, and the subsequent crosslinking density and elastic state of the materials. The link between thermo-mechanical behaviour and temperature-dependent bond exchange behaviour is unexplored, necessitating further exploration in this domain. In light of these gaps, this study embarks on a comprehensive investigation of vitrimeric materials, grounded in the controlled design of the monomers. The aim is to unveil the nuanced influences of chemical structures on material properties. This not only provides a deeper comprehension of vitrimer chemistry but also underscores the pivotal role of monomer design in tailoring material properties for specific applications.

3 Material preparation and methodology

3.1 Materials and preparation

D.E.R.TM 332 was used as a high purity diepoxy (DGEBA) monomer. The carboxylic acids, tetradecanedioic acid, dodecanedioic acid, sebacic acid, suberic acid, and adipic acid were selected to study the effect of dicarboxylic acid structure on the epoxy-dicarboxylic acid vitrimer. $\text{Zn}(\text{acac})_2$ is a well-applied transesterification catalyst for epoxy-dicarboxylic acid based vitrimers. The chemical structure and detailed information of all chemicals are summarised in Table 3.1 and in Appendix Fig A.4 to A.7. All the chemical compounds were purchased from Merck Life Science UK Limited.

To make resin plates, dicarboxylic acid crystals were finely ground using a pestle and mortar to powder to ensure homogenous dispersion of dicarboxylic acid in epoxy during later mixing. Dicarboxylic acids and epoxy were weighted to ensure a stoichiometric amount (m/m) of epoxy and carboxylic acid groups. For each carboxylic acid and epoxy composition, three different levels of $\text{Zn}(\text{acac})_2$ catalysts were added resulting in total in 15 different vitrimer formulations. All three components (epoxy, carboxylic acid, catalyst) were added into a beaker and hand mixed into a homogenous liquid, followed by the degassing in a vacuum oven at 90°C for 1 hour to eliminate air bubbles caused by mixing before the casting of the sample plates. Then the mixture was carefully poured into a rubber-sealed glass mould. For the crosslinking to occur the mixture was heated to 160°C and left to cure for 2 hours. For all material the ratio of functional groups of epoxy to carboxylic acid was 1:1. The three levels of catalysts were 1 mol%, 2.5 mol%, and 5 mol%. For naming of formulations, the total number of carbons in the carboxylic acid chain was used after letter C to signify the carboxylic acid followed by letter Z and the content of catalyst. For example, formulation C6Z2.5 is made of adipic acid ($\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$) and uses 2.5 mol% of $\text{Zn}(\text{acac})_2$ catalyst. Table 3.2 lists the formulation and the associated material codes.

Table 3.1: Chemical structure and information of the ingredients for vitrimer

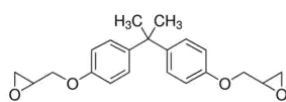
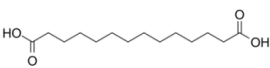
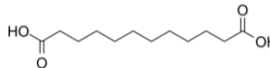
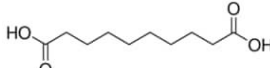
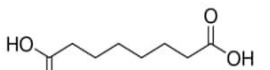
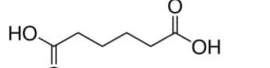
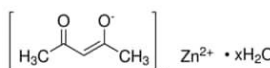
Compound(synonyms)	Chemical structure	Formula	Molecular weight (g/mol)	Number of methylene groups	CAS-No.
Bisphenol diglycidyl ether (D. E. R.™ 332)		$C_{21}H_{24}O_4$	340.4	N/A	1675-54-3
Tetradecanedioic acid (1,14-Tetradecanedioic acid)		$C_{14}H_{26}O_4$	258.35	12	821-38-5
Dodecanedioic acid (1,12-Dodecanedioic acid)		$C_{12}H_{22}O_4$	230.30	10	693-23-2
Sebacic acid (1,10-Decanedioic acid)		$C_{10}H_{18}O_4$	202.25	8	111-20-6
Suberic acid (1,8-Octanedioic acid)		$C_8H_{14}O_4$	174.19	6	505-48-6
Adipic acid (1,6-hexanedioic acid)		$C_6H_{10}O_4$	146.14	4	124-04-9
Zinc acetylacetonate hydrate		$C_{10}H_{14}O_4$ Zn $\cdot xH_2O$	263.61	N/A	1085-03-47-5

Table 3.2: Composition of the vitrimeric materials

Material code	Zn(acac) ₂ content (%mol)	Acid type	Epoxy
C6Z1	1.0	Adipic acid (C ₆ H ₁₀ O ₄)	DGEBA
C6Z2.5	2.5		
C6Z5	5.0		
C8Z1	1.0	Suberic acid (C ₈ H ₁₄ O ₄)	DGEBA
C8Z2.5	2.5		
C8Z5	5.0		
C10Z1	1.0	Sebacic acid	DGEBA

C10Z2.5	2.5	(C ₁₀ H ₁₈ O ₄)	
C10Z5	5.0		
C12Z1	1.0	Dodecanedioic acid (C ₁₂ H ₂₂ O ₄)	DGEBA
C12Z2.5	2.5		
C12Z5	5.0		
C14Z1	1.0	Tetradecanedioic acid (C ₁₄ H ₂₆ O ₄)	DGEBA
C14Z2.5	2.5		
C14Z5	5.0		

3.2 Characterisation methods

3.2.1 FTIR

Attenuated total reflection infrared spectroscopy (ATR-IR) was performed using a Thermo Scientific Nicolet™ iS™10 FT-IR spectrometer with Thermo Scientific Nicolet iZ™ 10 Auxiliary Experiment Module. The IR data of DGEBA, catalyst, all the carboxylic acids, and mixtures before and after curing were collected. Monitoring was performed through the integration of absorbance for a total of 50 scans over well-defined intervals. The wavelength range analysed was 800-2000 cm⁻¹. To confirm the state of the materials the change of intensity of peaks (δ_{COC} at 910 cm⁻¹, $\nu_{\text{C=O}}$ carboxylic acid at 1710 cm⁻¹, $\nu_{\text{C=O}}$ ester at 1730 cm⁻¹ and ν_{OH} at 3450 cm⁻¹) was observed.

3.2.2 Differential scanning calorimetry (DSC)

DSC experiments were conducted with TA Discovery DSC 250. DSC was used for analysis of the cure kinetics as well as measurements of the glass transition temperature of the formulations.

To determine the glass transition temperature, approximately 5 mg of sample was initially excised from the cured vitrimer plates. This sample was then placed in a hermetic aluminium pan, which was subsequently sealed with a compatible aluminium lid using a Tzero press. Similarly, a reference pan was prepared using the same type of hermetic aluminium pan and sealed with a corresponding aluminium lid. The prepared sample and reference pans were then transferred onto the DSC cell. Subsequently, both the sample and reference were exposed to a constant flow of nitrogen at a rate of 50 ml/min in a closed heating chamber while being subjected to a heating rate of 2°C/min within the temperature range

of -10 to 60°C. The glass transition temperature was determined as the temperature corresponding to the inflection point of the heat flow curve, as analysed using the TA instrument Trios software. All tests were conducted in triplicate to ensure accuracy and reproducibility. To investigate the curing behaviour of the vitrimers, approximately 5 mg of each sample was extracted from the mixed sample mixture before curing and subsequently placed in individual hermetic aluminium pans. These pans were sealed with precision using hermetic aluminium lids applied with a Tzero press. Similarly, a reference sample was prepared in a hermetic aluminium pan and sealed with a corresponding precision lid. The heat flow measurements were conducted under both dynamic and isothermal conditions. All tests were performed within a closed heating chamber, ensuring a constant flow of nitrogen at a rate of 50 ml/min for consistent environmental conditions. The cure characterisation was carried out for formulations containing 1% catalyst namely C6Z1, C8Z1, C10Z1 and C14Z1. For all dynamic tests a suitable starting temperature of 160°C was selected to ensure the melting of the carboxylic acid does not interfere with the experiment. The melting of the carboxylic acid and reaction. Prior to undergoing the dynamic heating programme, the samples were initially stabilised at a temperature of 40°C before being heated to 160°C at a vigorous heating rate of 50°C aiming to minimise both the effect of the shadowing of the reaction peak due to carboxylic acid melting and any crosslinking occurring during the ramp. Subsequently, they were subjected to a prescribed heating rate. until reaching a final temperature of 320°C. the rates used were of 2.5°C/min, 5°C/min, and 10°C/min. Isothermal DSC experiments were carried out at 160°C, 170°C, 180°C. The temperature was raised to the isothermal curing temperature at a heating rate of 50°C/min to minimise crosslinking before the start of the test. The heat flow curves were subsequently analysed using the software TA instrument Trios. Integrations were carried out using a linear baseline for dynamic experiments and a linear baseline horizontal from the end of the test for isothermal tests. The reaction rate was computed based on the assumption of proportionality between reaction rate and heat flow using:

$$\frac{d\alpha}{dt} = \frac{dH}{dt} \frac{1}{\Delta H_{total}} \quad (3-1)$$

where $\frac{d\alpha}{dt}$ represents the reaction rate, $\frac{dH}{dt}$ is the heat flow over the baseline and ΔH_{total} is the peak area of the reaction, i.e., the total enthalpy.

3.2.3 Cure kinetics modelling

The kinetics models of thermosetting resins can be categorised into two main types: (1) nth order models and (2) autocatalytic models. This distinction arises from the presence of two distinct categories of crosslinking reactions, characterised by whether the maximum reaction rate occurs at zero conversion or at a finite conversion value. The nth order model is represented as follows:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3-2)$$

This equation assumes a constant value of the reaction order n , independent of temperature and conversion, and predicts a linear relationship between $\ln\left(\frac{d\alpha}{dt}\right)$ and $\ln(1 - \alpha)$. One notable feature of this model is the prediction of a maximum reaction rate at zero conversion under isothermal conditions.

When the reaction rate reaches a maximum at an intermediate time during an isothermal experiment reaction is best described as autocatalytic reaction which can be expressed as:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}}(1 - \alpha)^n \alpha^m \quad (3-3)$$

The Malek method was used²⁰¹ to select an appropriate model. This method utilises two functions, $y(\alpha)$ and $z(\alpha)$ and defined as:

$$y(\alpha) = \frac{d\alpha}{dt} e^x \quad (3-4)$$

$$z(\alpha) = \pi(x) \frac{d\alpha}{dt} \frac{T}{\beta} \quad (3-5)$$

Here $x = E_a/RT$, $\pi(x) = \int \frac{E_a}{RT} dT$ which can be approximated by²⁰²:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (3-6)$$

The calculated values of $y(\alpha)$ and $z(\alpha)$ are normalised to [0,1] interval. The corresponding conversion degree for the maximum of $y(\alpha)$ and $z(\alpha)$ are denoted as α_M and α_p^∞ . The value of isoconversional E_a used is obtained from Starink method. To calculate α_p^∞ and α_M , both the fixed activation energy and the isoconversional E_a values are taken into consideration.

The shape of the $y(\alpha)$ function and the combination α_p^∞ and α_M play a crucial role in determining the most appropriate kinetics model choice. According to the Malek method, when $\alpha_p^\infty \neq 0.632$ and $0 < \alpha_M < \alpha_p^\infty$, the empirical Sestak-Berggren model Eq.(3-7) proves to be the most suitable kinetics model for analysing thermal data.

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3-7)$$

A transition from chemical kinetics to diffusion control is incorporated in the cure kinetics model by adopting an expression formulated by Cole *et al.*²⁰³ and Hubert *et al.*²⁰⁴ The model is represented as follows:

$$\frac{d\alpha}{dt} = \frac{A e^{-\frac{E_a}{RT}} \alpha^m(1 - \alpha)^n}{1 + e^{[C(\alpha - (\alpha_{c0} + \alpha_{CT}T))]} \quad (3-8)$$

In this equation, C represents the diffusion constant, α_{c0} represents the critical degree of cure at $T = 0K$, and α_{CT} represents a constant that accounts for the increase in the critical resin degree of cure with temperature. This modified kinetics model incorporates the influence of diffusion due to proximity to vitrification. As the reaction progresses and approaches α_c at a specific temperature, the cure rate experiences a notable deceleration, indicating a shift towards diffusion control. For the models the activation energy of the reaction E_a used are obtained using Kissinger's model:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (3-9)$$

where β is the heating rate of the dynamic DSC test, A is a pre-exponential factor, R is ideal gas constant, T_p is the temperature of the peak reaction. E_a is obtained as the inverse of the slope for the curve when plotting $\ln\left(\frac{\beta}{T_p^2}\right)$ against $\frac{1}{RT_p}$. And the value of which is listed in Table 3.3.

Table 3.3: Adopted activation energy for cure kinetic model from Kissinger's method

Materials	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
$E_a(kJ/mol)$	120.7	87.5	86.8	74.0	80.6

3.2.3.1 Estimation approaches of the goodness of the fitted model to experimental data

To assess the accuracy of these models, the mean square error (MSE):

$$MSE = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n} \quad (3-10)$$

and root mean square error (RMSE):

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad (3-11)$$

are utilised as measures of the prediction error between y_i (the observed value) and $\hat{y}_i$ -predicted value. The goodness of the fit is estimated using the coefficient of determination (R^2):

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y})^2} \quad (3-12)$$

which represents the correlation of the experimental data and the fitted model. Here $\bar{y}$ is the mean value of the data. The minimisation of error in fitting was carried out using the Generalised Reduced Gradient Nonlinear Optimisation method implemented in Solver of Microsoft Excel.

3.2.4 Stress relaxation by Dynamic Mechanical Analysis (DMA)

The stress relaxation of all 15 vitrimeric materials was measured using a TA instrument DMA Q800 to analyse the effect of the chemical structure of the polymer chain repeating unit on the overall ability of the material to maintain or adapt to the applied strain. The experiments were conducted on rectangular samples with size of 2 mm ×40 mm ×10 mm under stress relaxation mode with single cantilever geometry on. The strain was set at 2.5%. Testing was carried under at least three different temperatures to study the temperature dependence of the bond exchange reaction. The temperatures used for each material is listed in Table 3.4.

Table 3.4: Temperatures for the DMA relaxation test on all the formulations

Material	Temperature (°C)
C6Z1	210, 230, 250
C6Z2.5	210, 230, 250
C6Z5	200, 210, 230
C8Z1	210, 230, 250
C8Z2.5	210, 230, 250
C8Z5	180, 200, 230
C10Z1	200, 230, 250
C10Z2.5	210, 240, 250
C10Z5	180, 200, 230
C12Z1	180, 200, 220
C12Z2.5	140, 160, 180
C12Z5	140, 160, 180
C14Z1	180, 200, 220
C14Z2.5	140, 160, 180
C14Z5	140, 160, 180

The topological transition temperature (T_v) was determined by extrapolating Arrhenius curves of the relaxation time (τ^*)

$$\ln \tau^* = \ln \tau_0 + \left(\frac{E_{ar}}{RT} \right) \quad (3-13)$$

where E_{ar} is the activation energy for transesterification bond exchange, R is the ideal gas constant, T is the temperature in Kelvin, and τ_0 is a pre-exponential

factor¹⁰⁰. The relaxation time for each test was determined by fitting an exponential decay:

$$\frac{G}{G_0} = e^{-\frac{t}{\tau^*}} \quad (3-14)$$

where G is the bending modulus at time t , G_0 is the bending modulus at the beginning of the relaxation. The bond exchange rate of vitrimers is greatly affected by the kind and content of the added catalysts in the catalyst-assisted systems. The amount of catalyst added only alters the pre-exponential factor of the reaction and not the activation energy. To increase the robustness of the activation energy estimation instead of using three points for one formulation composition, a collective of nine points were utilised. In this case, the formulations made of the same carboxylic acid and epoxy share the same E_{ar} but different probability of collisions. The resulting activation energy and topology freezing temperatures were compared to that obtained from the set of three relaxations for each individual material to assess the value of this analysis.

3.2.5 Thermogravimetric analyses (TGA)

TGA tests were performed on the TA Q500. Approximately 5 to 10 mg of each sample was initially excised from the cured vitrimer plates before being transferred onto a platinum sample pan with an attached hook and placed on the autosampler. All the tests were conducted in a closed heating chamber with a constant flow of nitrogen at a rate of 50 ml/min. The samples were subjected to a heating from 25°C to 600°C with the ramp speed of 10°C/min under nitrogen flow of 60 ml/min. For each material the test was repeated at least three times to minimise experimental error. The 5 and 10% weight loss points were recorded for evaluation of the material thermal stability.

3.2.6 Rheological Measurements

Rheological measurements were conducted using the TA Instruments HR20 rheometer rotational rheometer with a 25 mm parallel plate geometry on. For curing evaluations, the uncured material mixture was placed between two parallel stainless steel plates. During the curing process, rheological properties were

tracked while maintaining a constant gap between the top and bottom plates. The oscillation was set at 0.1% strain and 1 Hz frequency. The temperature profile involved initial heating to 30°C, followed by ramping up to the curing temperature (160°C, 170°C, and 180°C) at a rate of 10°C/min. This was followed by a 2-hour isothermal period at the respective temperature. Subsequently, a heat-cool ramp was executed with a compression force of 10 N. The materials were heated from their curing temperatures to 260°C and then cooled to 70°C, with heating and cooling rates set at 5°C and 3°C, respectively.

Small Amplitude Oscillatory Shear (SAOS) tests were also carried out using the HR20 rheometer. The samples for the test were cut from the cured material plates using a cutting knife to the shape of approximate disk shapes with a diameter of 25mm. The tests are conducted with 25mm parallel stainless steel plates. The tests involved isothermal steps at regular temperature intervals. During heating scans, the temperature was incremented in 10°C steps from 50°C to 270°C, followed by stepwise cooling to 50°C in increments of 10°C. At each temperature step, a SAOS frequency sweep was conducted ranging from 0.01 to 100 rad/s with three points per decade. Throughout the multifrequency sweep, a compression force of 2.0 N was applied to all materials, with a consistent strain of 0.1%.

4 Cure kinetics of epoxy- dicarboxylic acid vitrimers

The curing process of epoxy is of paramount importance in tailoring the material mechanical, thermal, and chemical properties to suit specific applications and in optimising the production process to achieve reduced time and costs. In the context of this study, the curing process plays a critical role in the development of a crosslinked network for vitrimers, imparting them with exceptional physical properties. Investigating the variations in curing profiles resulting from slight differences in the chemical structure of the dicarboxylic acid component offers a valuable opportunity to gain deeper insights into the epoxy-dicarboxylic acid system. This understanding serves as a valuable reference for future advancements and developments in the field.

4.1 DSC data analysis

Differential Scanning Calorimetry (DSC) serves as a robust and indispensable tool in the investigation of the curing process. DSC allows for the real-time monitoring of the exothermic or endothermic heat flow linked to curing reactions, yielding valuable insights into the kinetics and temperature range of the curing phenomenon. In this study, the thermal profile of the vitrimeric materials curing was examined through a combination of dynamic and isothermal DSC experiments, leveraging the comprehensive capabilities of this versatile technique.

4.2 Reproducibility of DSC data

First of all, the consistency of the results is verified by comparing enthalpies, demonstrating a difference of 1.7% and 1.0% between two sets of identical dynamic tests for materials C8Z1 and C10Z1, respectively, as outlined in Table 4.1., Figure 4.1 and Figure 4.2 depict the variation in total enthalpy for C8Z1 and C10Z1 across temperatures for the tests. Remarkably, the dynamic enthalpies for tests conducted at 5°C/min and 10°C/min show substantial agreement throughout the entire temperature range, with minor deviations at the onset of the reaction for C8Z1 at 10°C/min and C10Z1 at both heating rates. Despite these, the curves overlap, exhibiting significant coordination for the majority of the curing

process Serving as a pivotal insight into the entire DSC data, the observed consistency and minimal deviations in the enthalpy comparisons not only affirm the reliability of the DSC data but also bolster the confidence in conducting further comprehensive analysis based on them, ensuring the robustness of subsequent findings and conclusions.

Table 4.1: The recorded enthalpy and difference for two sets of dynamic tests for material C8Z1 and C10Z1

Material	Heating rate (°C/min)	ΔH (J/g) Run 1	ΔH (J/g) Run 2	Difference
C8Z1	10	222	219	1.4%
	5	246	251	2.0%
	Average	234	235	1.7%
C10Z1	10	137	137	0.0%
	5	154	157	1.9%
	Average	145.5	147	1.0%

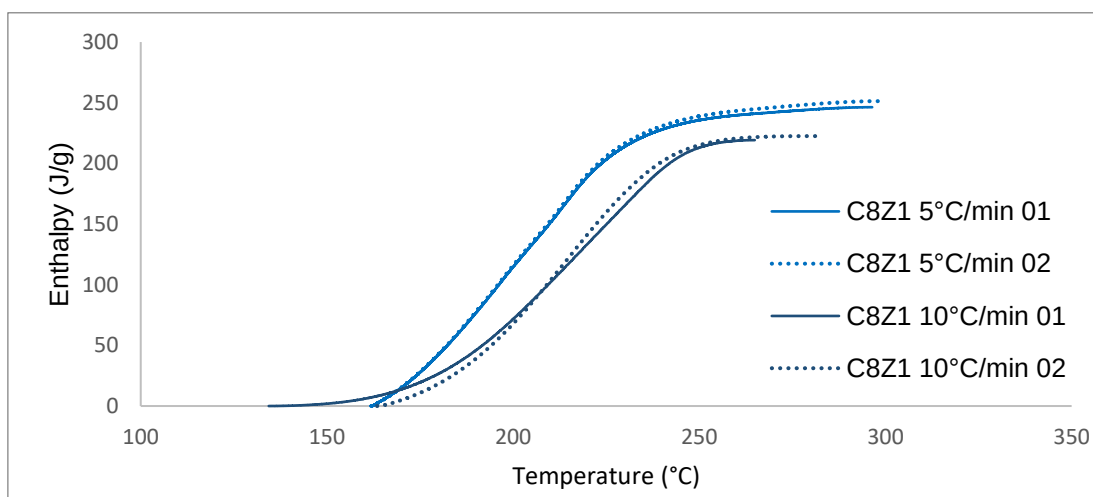


Figure 4.1: Repeat DSC tests for C8Z1

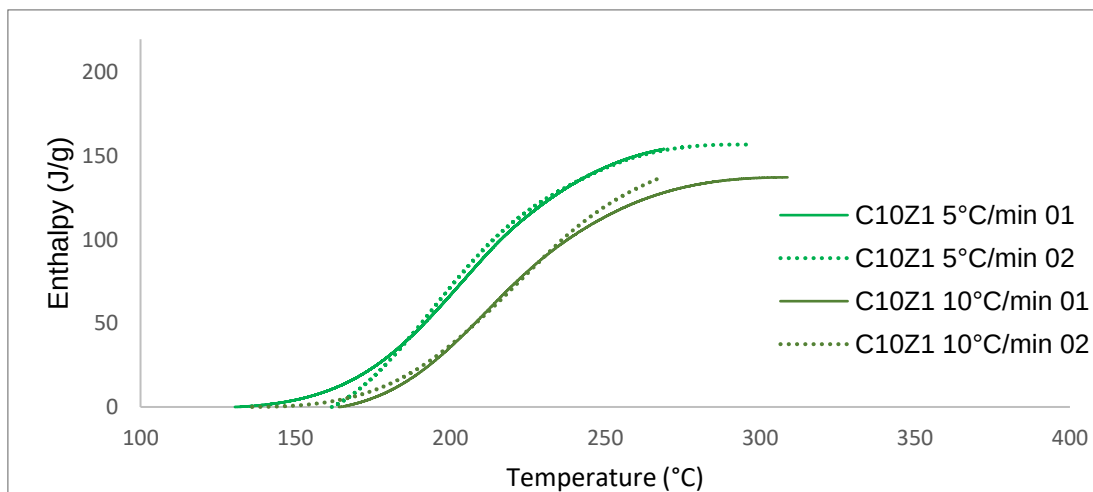


Figure 4.2: Repeat DSC tests for C10Z1

4.2.1 Dynamic DSC results

Figure 4.3- Figure 4.7 present the measured heat flow data for all the formulations at different temperatures under non-isothermal curing conditions. The reactions of all the materials primarily exhibit single-peak curves, occurring at temperatures ranging from 180-230°C. The heat flow peaks for C6Z1 (vitriimer made of adipic acid- $\text{C}_6\text{H}_{10}\text{O}_4$ and 1% $\text{Zn}(\text{acac})_2$) appear at a lower temperature range of 165-245 °C, than those observed for C8Z1, C12Z1, and C14Z1, for which the peaks end at around 265°C. For C10Z1, the peaks end at even higher temperatures, specifically at 265°C, 285°C, and 305°C for heating rates of 2.5°C/min, 5°C/min, and 10°C/min respectively (Figure 4.5).

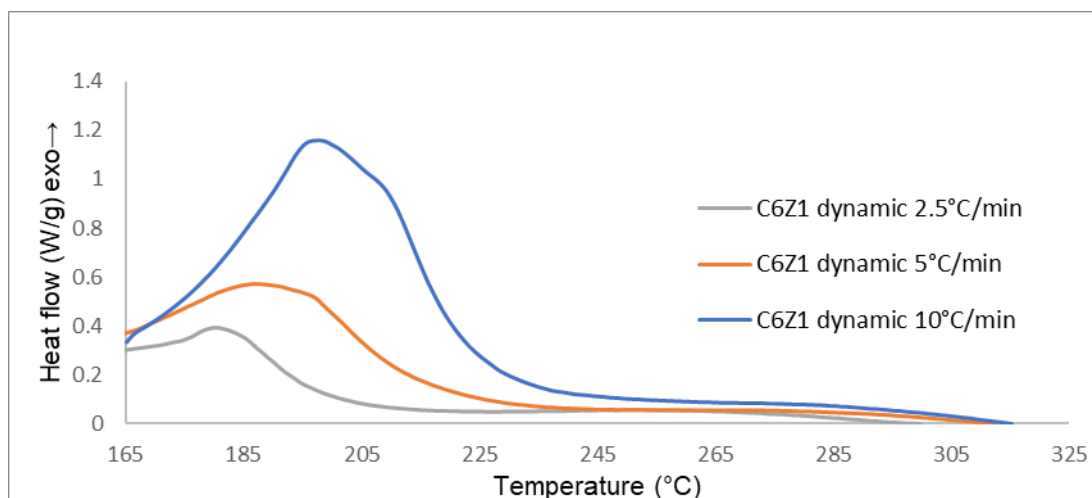


Figure 4.3: DSC heat flow as a function of temperature for heating rates for C6Z1

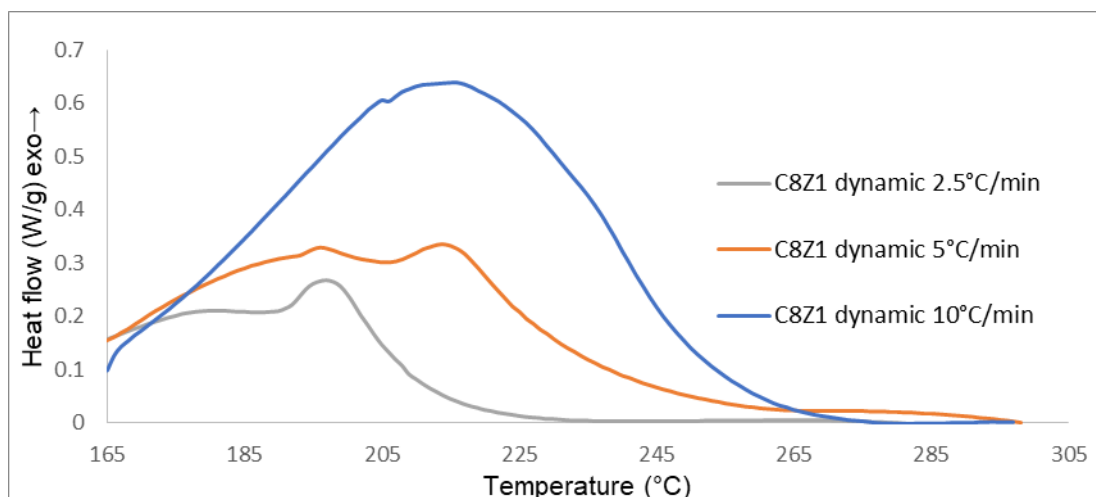


Figure 4.4: DSC heat flow as a function of temperature for heating rates for C8Z1

To compare the differences in curing behaviour between the different systems, the peak temperature (T_p), total enthalpy, and final temperature (T_f) for all rates and formulations are reported in Table 4.2. The results show a strong dependence of peak temperature (T_p), total enthalpy, and final temperature (T_f) on the heating rate for all rates and formulations. When subjected to a higher heating rate, the heat flow peaks tend to shift to a higher temperature, exhibit a higher magnitude, and appear broader. This behaviour is commonly observed in non-isothermal curing processes and can be attributed to the fact that a higher heating rate means the material stays at a particular temperature for a shorter period of time. Consequently, the peak for the heat flow is amplified for that specific temperature range.

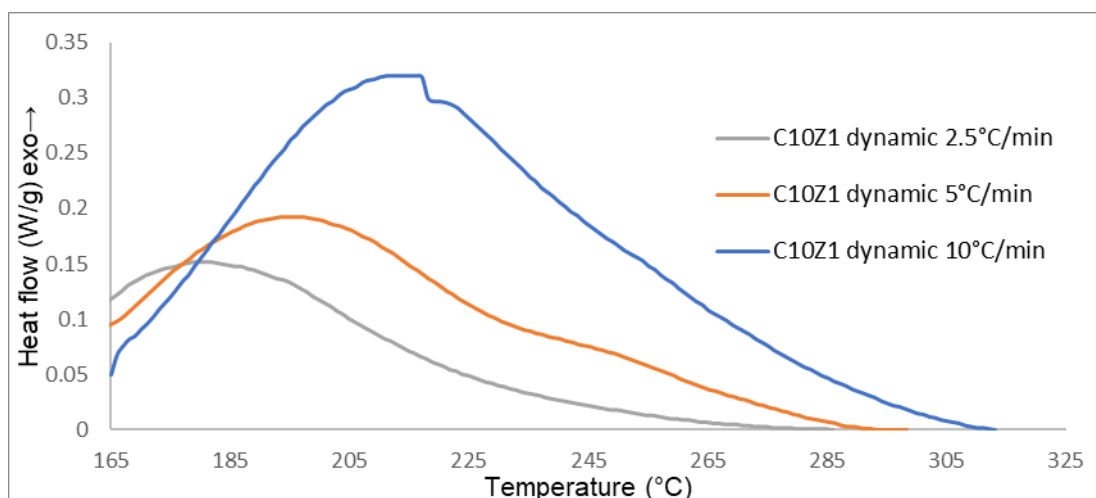


Figure 4.5: DSC heat flow as a function of temperature for heating rates for C10Z1

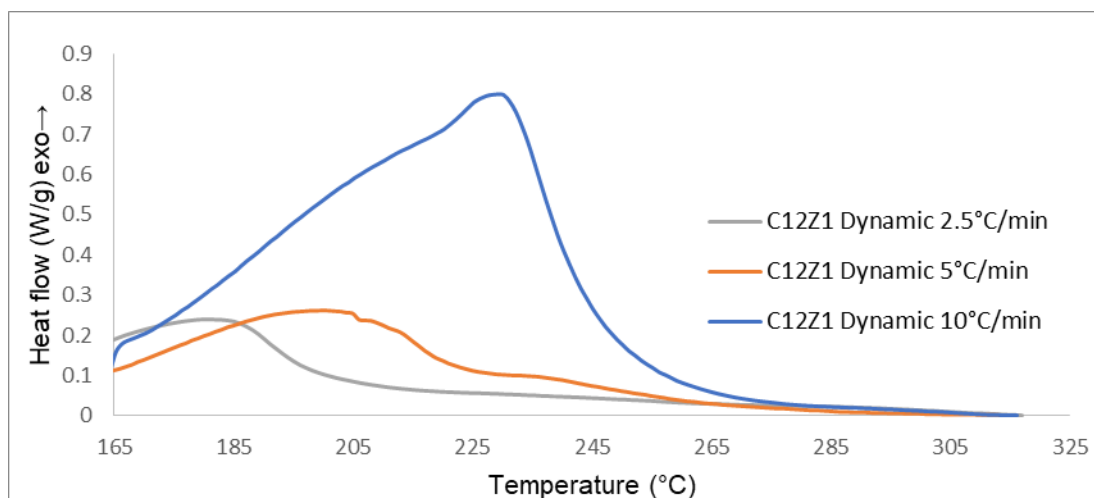


Figure 4.6: DSC heat flow as a function of temperature for heating rates for C12Z1

In addition to the main reaction peaks, two distinct types of secondary peaks are observed at higher temperatures. The first type is represented by minor peaks occurring at relatively high temperatures, such as the temperature range of 255-285°C for C6Z1 in Figure 4.3 and around 295°C during the 10°C/min run of C14Z1 in Figure 4.7. These peaks exhibit insignificant enthalpy release and may be associated with degradation or minor secondary reactions. The second type is characterised by noticeable shoulders adjacent to the main reaction peak. This phenomenon is evident in C8Z1 at heating rates of 2.5°C/min and 5°C/min, as well as the 5°C/min runs of C10Z1 and C12Z1. This could be linked to the incomplete portion of the reaction resulting from the crosslinking process. During the curing process, when crosslinks are being established, the movement of the reactants can sometimes be hindered which is termed as steric hindrance. However, the increase in temperature affects vitrimeric materials in a way that facilitates their movement, giving them a second opportunity to react. There is also a negative relationship between the total enthalpy of the reaction and the heating rate. At lower heating rates, the materials underwent a prolonged curing time, resulting in an average increase of 13.1% in enthalpy as indicated by the results provided in Table 4.2.

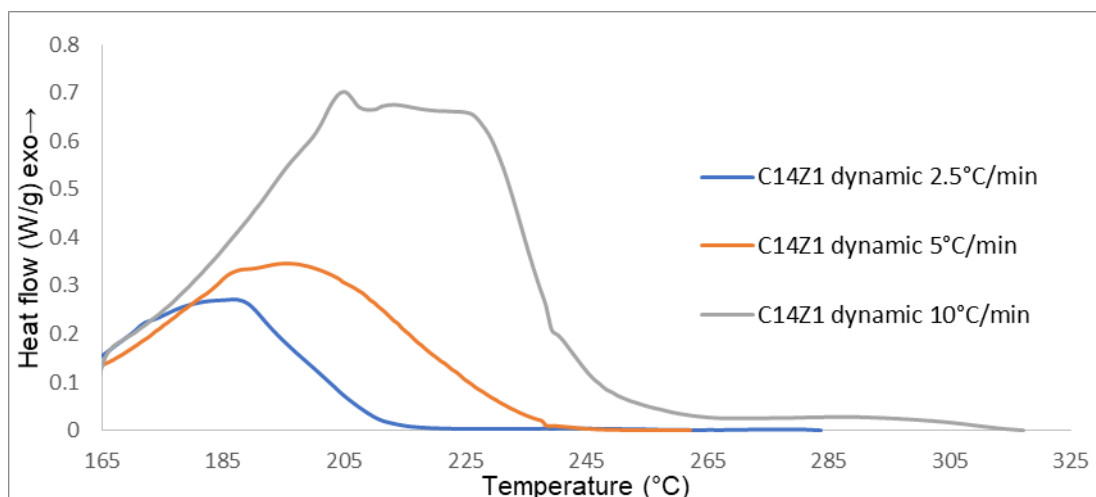


Figure 4.7: DSC heat flow as a function of temperature for heating rates for C14

Table 4.2: Curing data obtained from the dynamic DSC thermograms recorded at 2.5,5,10°C/min heating rate for all formulations

Material	Heating rate (°C/min)	T_P (°C)	T_f (°C)	ΔHT (J/g)	ΔHT (kJ/mol)
C6Z1	10	198	315	317	77.5
	5	187	312	344	84.1
	2.5	179	300	382	93.4
C8Z1	10	223	280	243	62.8
	5	208	298	245	63.4
	2.5	195	240	319	82.5
C10Z1	10	212	313	140	38.2
	5	197	298	155	42.3
	2.5	185	287	178	48.5
C12Z1	10	222	316	263	75.4
	5	204	315	189	54.2
	2.5	190	317	288	82.6
C14Z1	10	215	317	237	71.3
	5	198	238	194	58.4
	2.5	186	221	225	67.7

In the results reported in Table 4.2 there is significant variation in the values of total enthalpy among different formulations. Since each vitrimer composition has a different molar mass, the enthalpy values are also presented as molar values. The average enthalpy values as a function of dicarboxylic acid chain length are illustrated in Figure 4.8 and

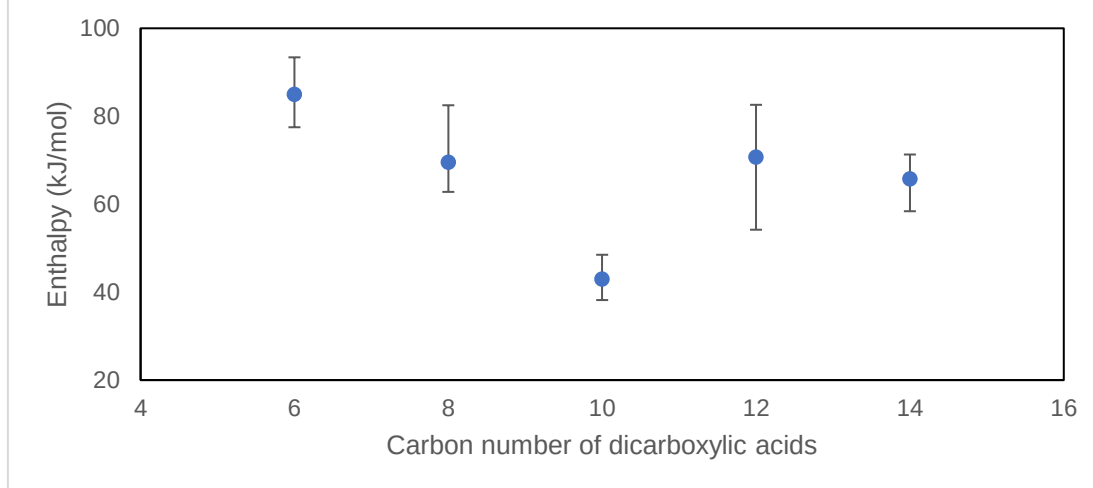


Figure 4.9. In Figure 4.8, the specific enthalpy appears to exhibit a slight decreasing trend as the dicarboxylic acid chain length increases, with the exception of C10, which shows a substantially lower value compared to the other materials. As shown in

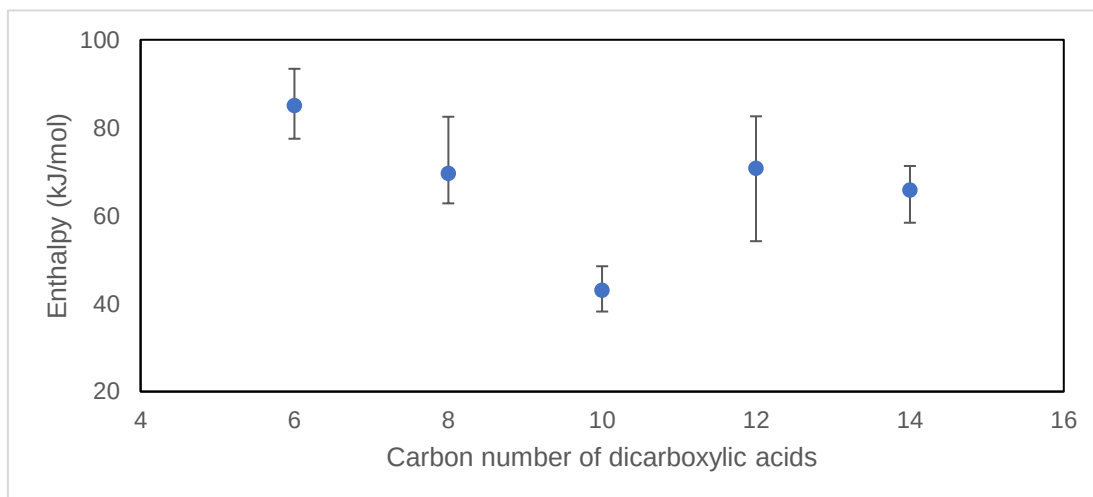


Figure 4.9, the majority of the molar reaction enthalpy falls within the range of 60-80 kJ/mol, with a weak decreasing trend and an 8.0% difference between the highest enthalpy range for C6 and the lowest for C14. It is relevant to consider the possibility of errors in sample preparation or during the tests for C10.

Figure 4.10 to Figure 4.14 show the reaction degree as a function of temperature. Across all materials, a consistent sigmoidal curve is evident throughout the reaction course. The initial stage of the reaction, approximately around 160°C, is characterised by a gradual increase in the cure degree. Subsequently, a more accelerated curing development ensues, leading to a pronounced steepening of the curve. Eventually, the curve levels off, indicating a deceleration in the reaction progress towards its completion upon consumption of the reactants. Within the same formulation, a rise in the heating rate triggers a shift in the sigmoidal curve representing the degree of cure towards higher temperatures. With a higher heating rate, the reaction initiates more gradually and concludes at a higher temperature. At the same given temperature, a faster heating rate results in a lower degree of curing for the sample. Achieving the same degree of cure requires a higher temperature when using a faster heating rate. This is due to the time that material spends at lower temperatures, which decreases with increasing heating rate.

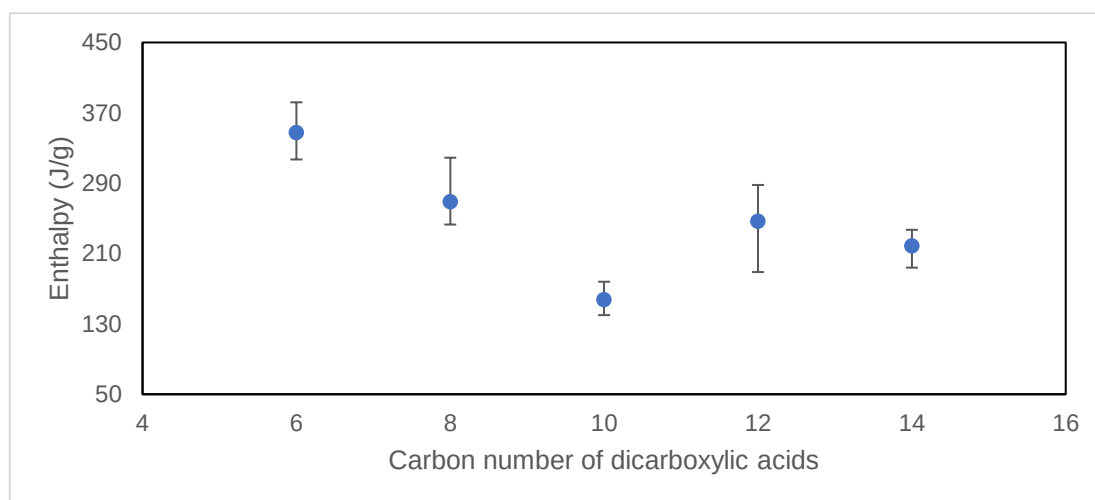


Figure 4.8: Average of the enthalpy for vitrimers. Error bars correspond to one standard deviation

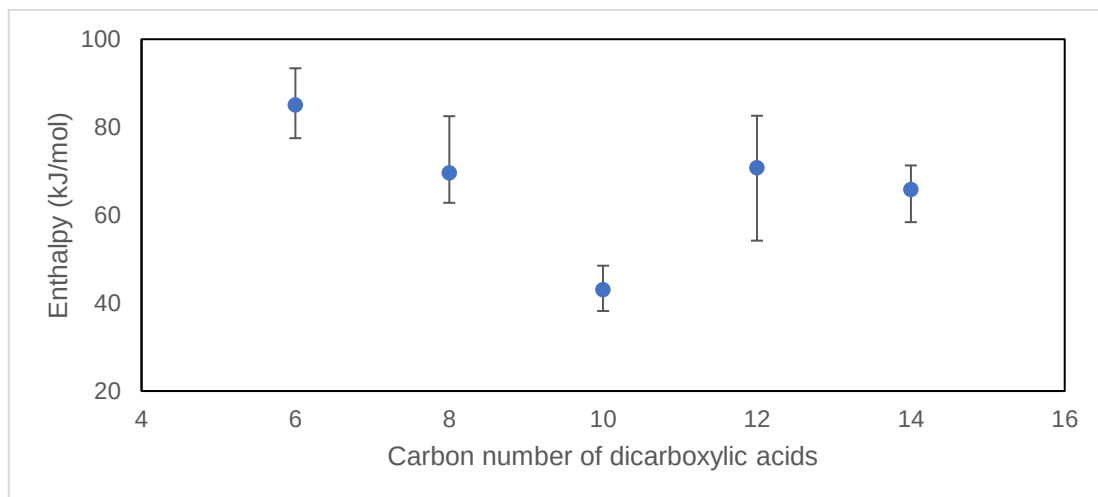


Figure 4.9: Average of the molar enthalpy for vitrimers. Error bars correspond to one standard deviation

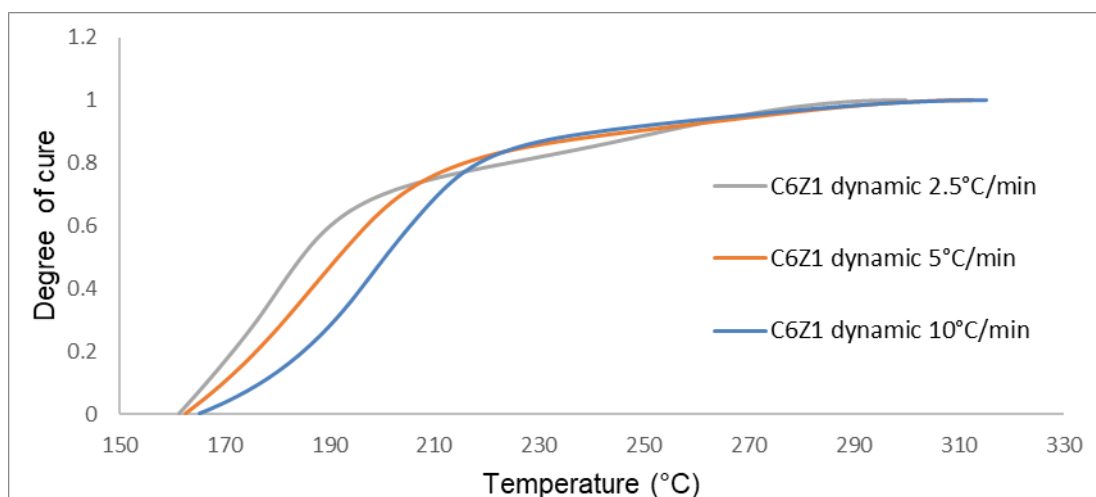


Figure 4.10: Curves of reaction degree and temperature at different heating rates for C6Z1 curing reactions

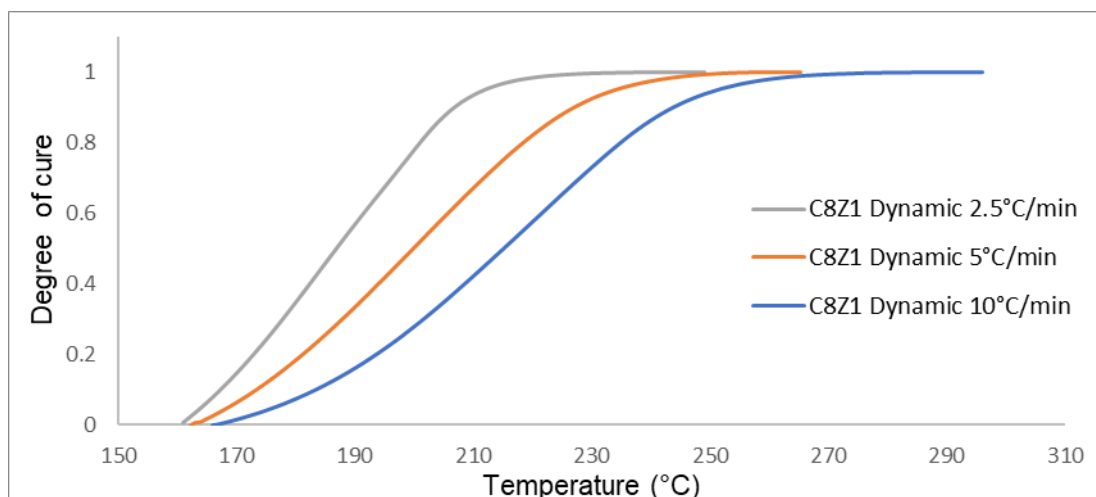


Figure 4.11: Curves of reaction degree and temperature at different heating rates for C8Z1 curing reactions

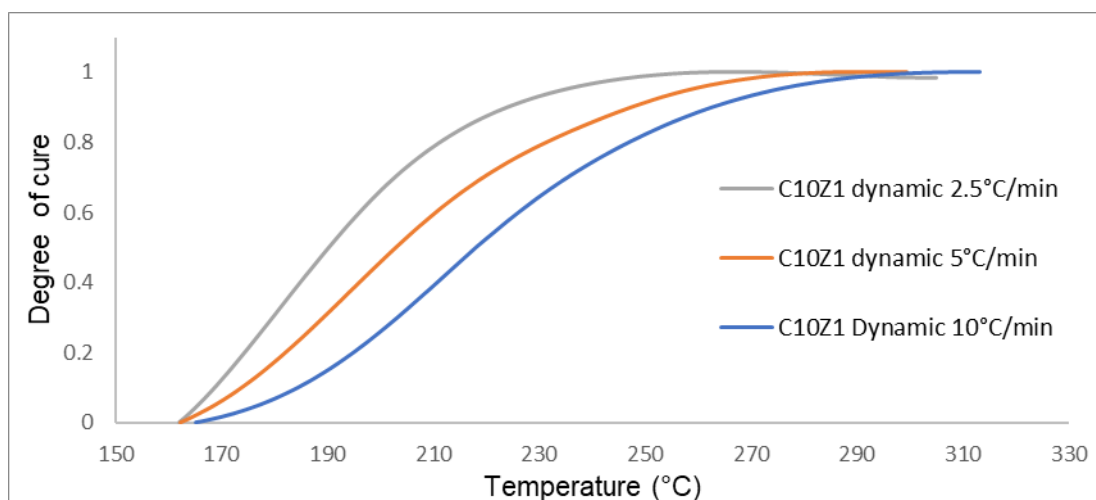


Figure 4.12: Curves of reaction degree and temperature at different heating rates for C10Z1 curing reactions

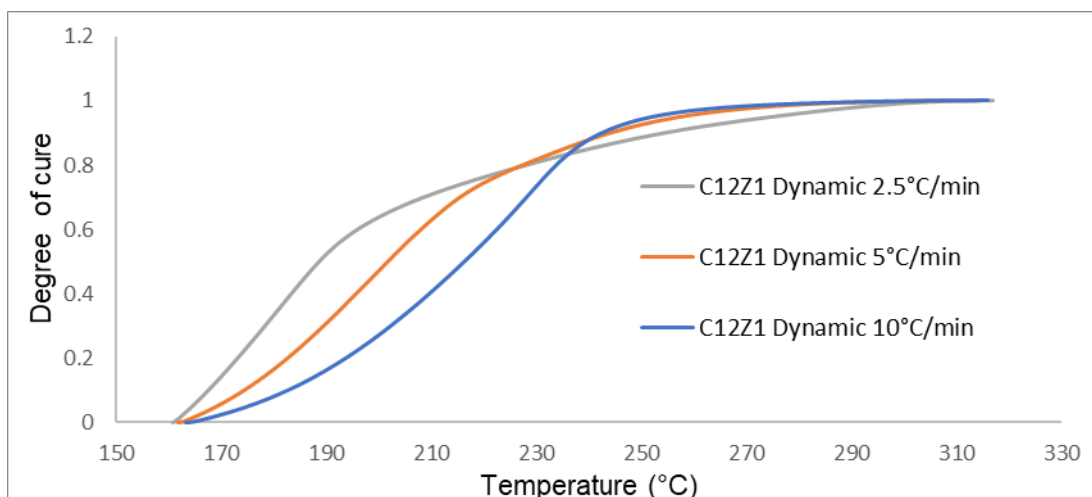


Figure 4.13: Curves of reaction degree and temperature at different heating rates for C12Z1 curing reactions

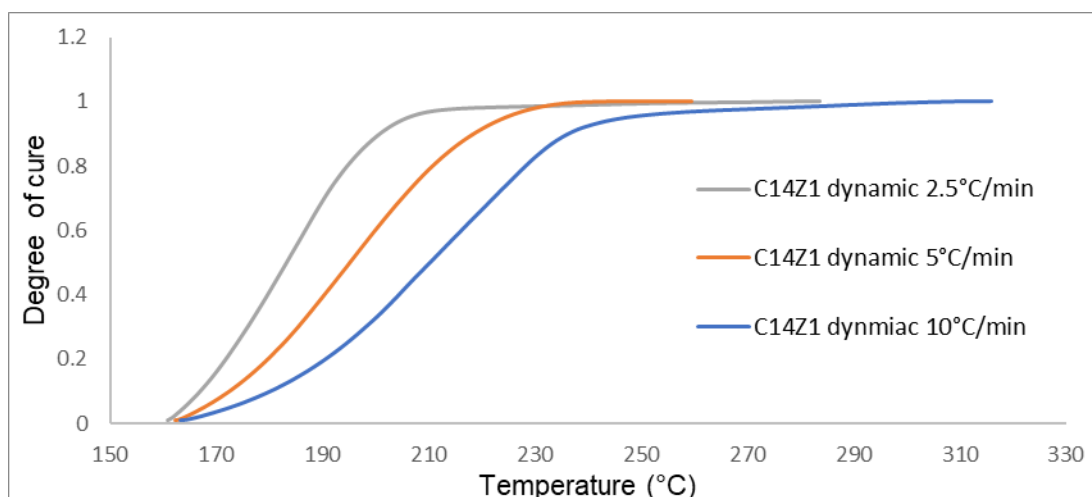


Figure 4.14: Curves of reaction degree and temperature at different heating rates for C14Z1 curing reactions

In contrast to the characteristic sigmoidal shape observed for the degree of cure *versus* temperature curves in C8Z1, C10Z1, and C14Z1, formulations C6Z1 and C12Z1, shown in Figure 4.10 and Figure 4.13 exhibit a distinct two-step increase in degree of cure during the heating process. Notably, the effect of heating rate on the curing kinetics of C6Z1 and C12Z1 demonstrates a significant deviation from the behaviour observed in the other three materials. As the heating rate increases, the degree of cure for these formulations exhibits a more rapid and pronounced rise at the initial stages of the reaction process. This phenomenon

can be attributed to nature of the reactions, whereby the impact of the first stage of the reaction becomes amplified at higher heating rates, while the contribution of the second stage becomes relatively less significant. Furthermore, this observation is substantiated by the reaction rate *versus* temperature curves shown in Figure 4.15-Figure 4.17. In the case of C6Z1 and C12Z1 shown in Figure 4.16 , prominent secondary reaction peaks are observed within the temperature range of 220-240°C for C6Z1 and 280-300°C for C12Z1, which is not evident in the other three compositions. Moreover, this trend becomes more pronounced at lower heating rates, providing further support to the findings derived from the reaction rate and degree of cure curves.

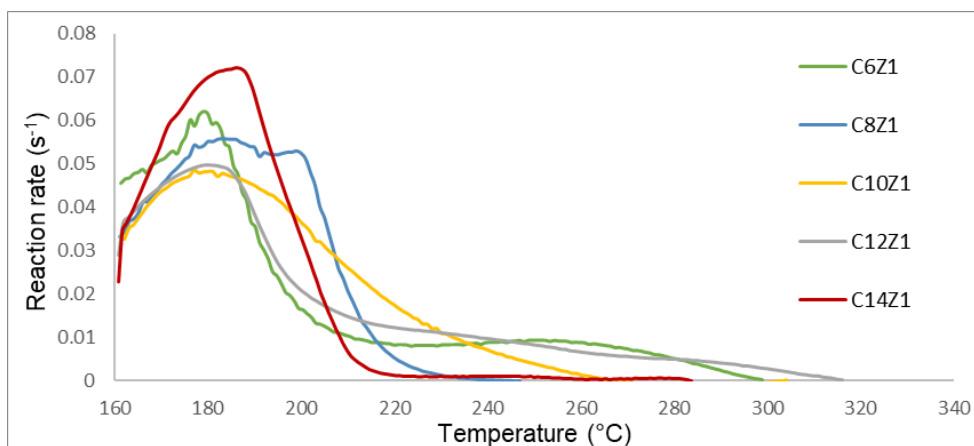


Figure 4.15: Curves of reaction rate and temperature for all formulations at heating rates of 2.5°C/min

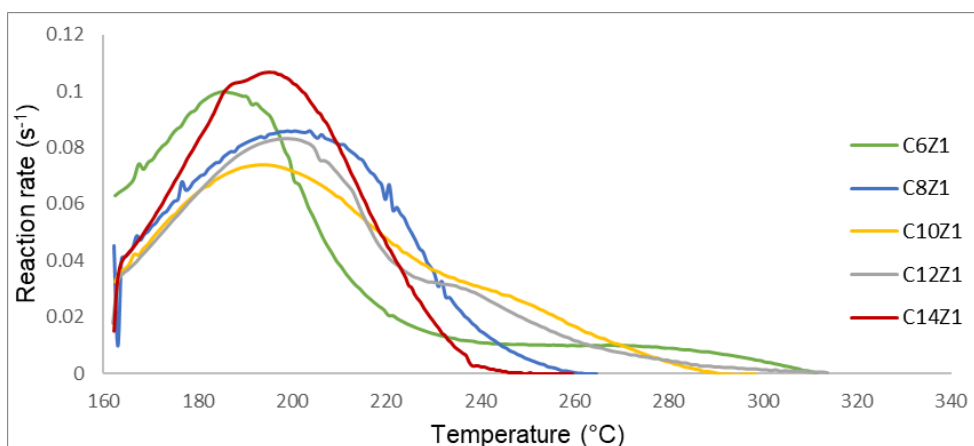


Figure 4.16: Curves of reaction rate and temperature for all formulations at heating rates of 5°C/min

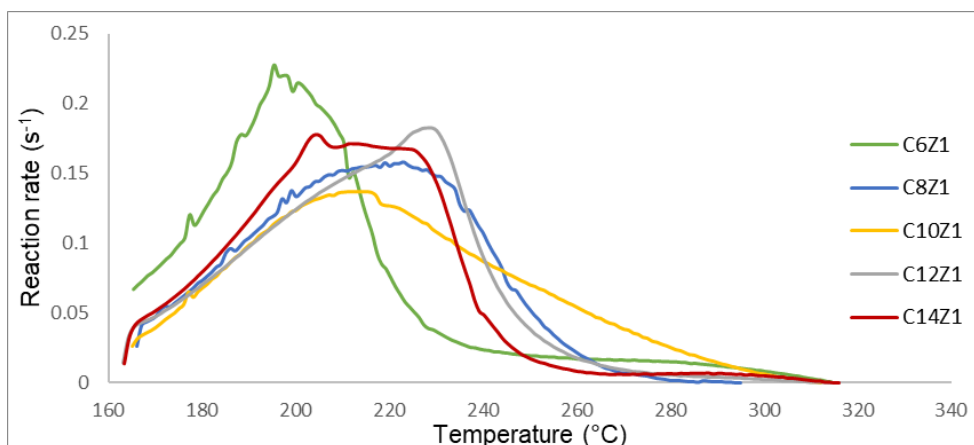


Figure 4.17: Curves of reaction rate and temperature for all formulations at heating rates of 10°C/min

The curing mechanism of these materials involves two primary reactions: (i) the addition esterification of epoxy and carboxylic acid groups (Figure 4.18); and (ii) the transesterification reaction, leading to the formation of a diester and a diol (Figure 4.19). The first reaction accounts for the abundant energy release while the second reaction creates a crosslinked structure and the adaptability for vitrimers. The process of transesterification happens at a much slower rate compared to the addition esterification reaction. The first reaction for the materials happens within 60 minutes at temperatures greater than 160°C. As in Figure 4.15, all the first peaks for all the materials are completed before 220°C except the C10 vitrimer for which the reaction ends up at around 260°C. In contrast, the second process can take dozens of hours to reach the final stage⁴⁷.

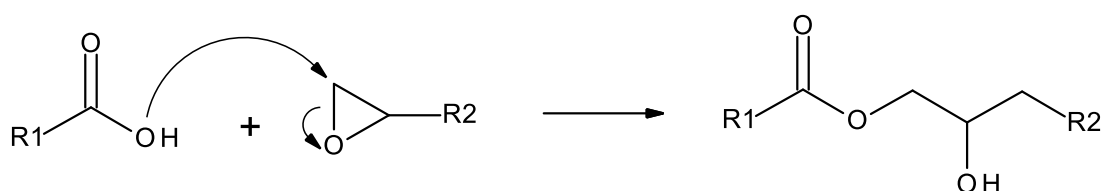


Figure 4.18: Addition reaction of a carboxylic acid to an epoxy group.

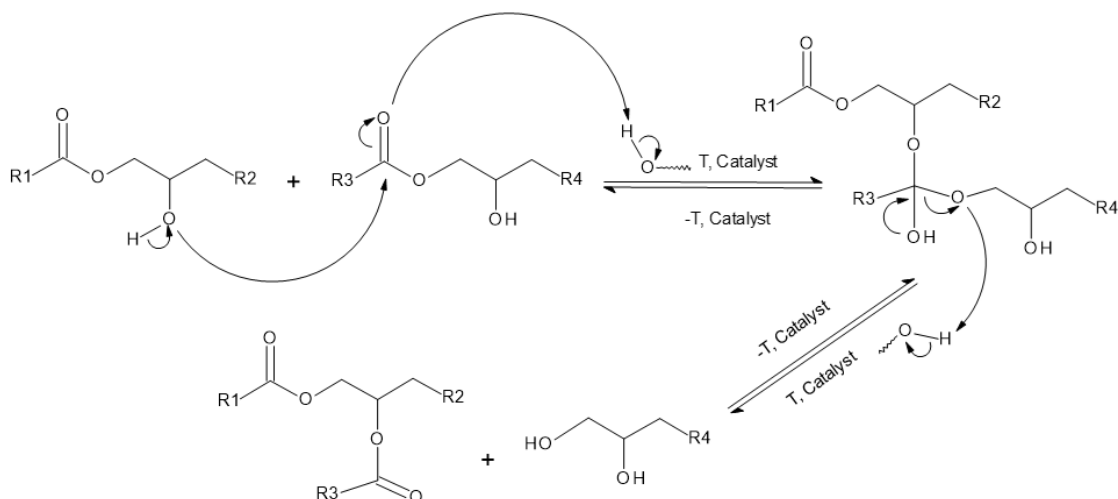


Figure 4.19: Transesterification converting monoesters into a glycol and a diester

In addition, when excess reactive groups are present after esterification usually in non-stoichiometric systems, two secondary reactions may occur as illustrated in Figure 4.20: (i) the etherification of hydroxyl and epoxy groups²⁰⁵; and (ii) the condensation polyesterification involving hydroxyl and carboxyl groups. However, the rates of these secondary reactions are significantly slower compared to the addition esterification reaction, particularly when transesterification takes precedence, and the availability of epoxy or carboxyl groups becomes limited. At the same time, these two reactions take place at higher temperatures compared to addition esterification of epoxy and carboxylic acid due to the higher activation energy.

Materials C6Z1 and C12Z1 exhibit a more evident occurrence of a second reaction during the curing process. This reaction appears to proceed at a slower rate and takes place at higher temperatures, which is most likely the result of transesterification. There is also a minor possibility of it being condensation polyesterification or etherification of hydroxyl and epoxy due to potential non-stoichiometric balance between the initial epoxy and carboxylic acid functionalities. Considering that transesterification is inherently slow and occurs over an extended period, the observed disparity in enthalpy values documented in Table 4.2 can be attributed to the supplementary energy released through transesterification during the prolonged reaction time for tests conducted at

different heating rates—namely, 2.5°C/min (60 minutes, spanning 160-310°C), 5°C/min (30 minutes), and 10°C/min (15 minutes).

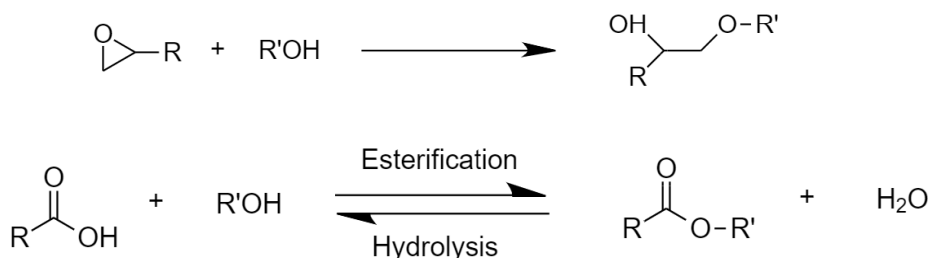


Figure 4.20: Schemes of etherification reaction and condensation polyesterification reaction

4.2.2 Isothermal DSC results

Figure 4.21 to Figure 4.25 present the isothermal DSC results for the five systems studied. For all materials, the reaction is fast at the beginning and the rate of reaction which is strongly dependent on temperature. After the initial fast reaction phase, the enthalpy curves start to level, and the differences appear at a much small scale. As the reaction is accelerated by increased temperature, curing at higher temperatures results in earlier completion. The cure of C6Z1, C8Z1, C10Z1 and C14Z1 at 180°C is completed, within 40 minutes. For C12Z1, the enthalpy change becomes nearly zero around 70 minutes into the reaction.

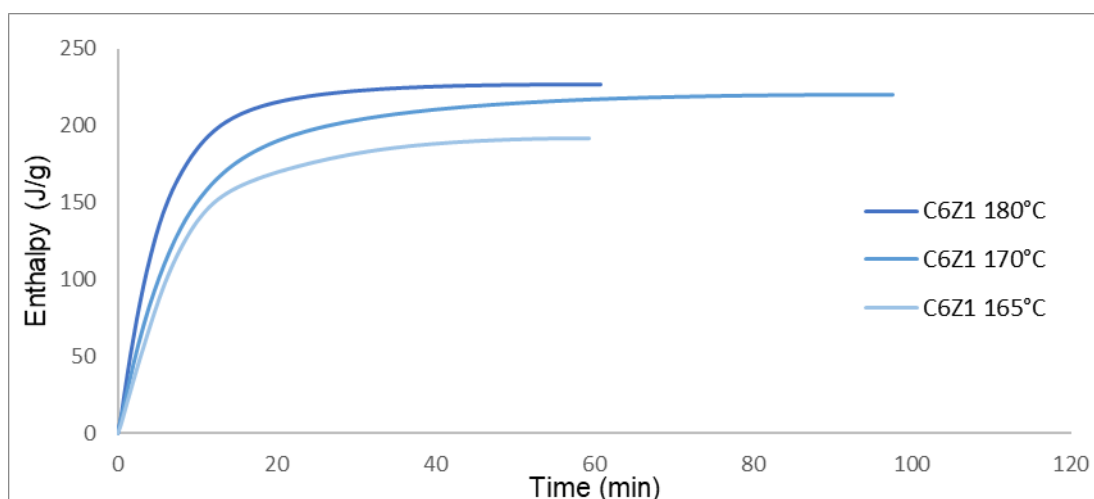


Figure 4.21: Isothermal enthalpy evolution of C6Z1

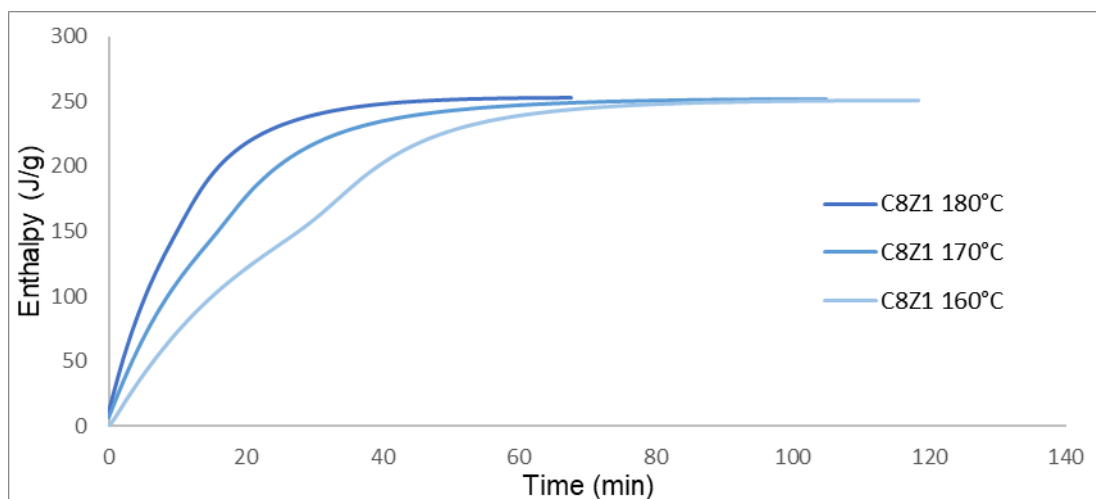


Figure 4.22: Isothermal enthalpy evolution of C8Z1

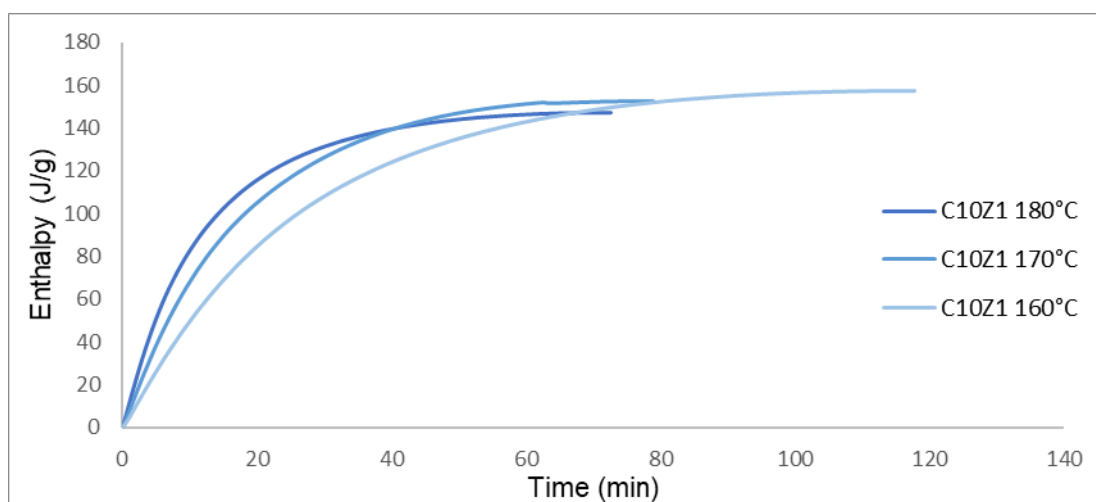


Figure 4.23: Isothermal enthalpy evolution of C10Z1

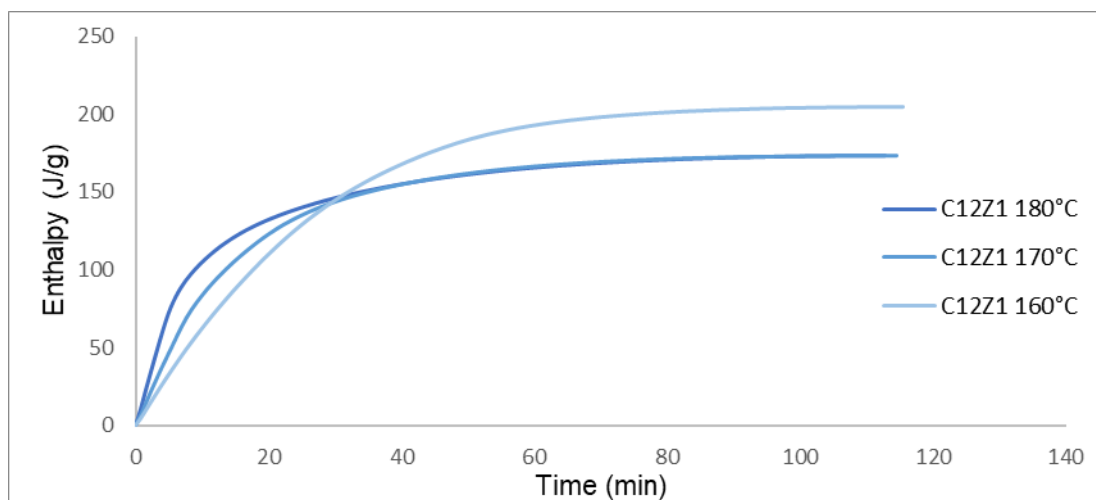


Figure 4.24: Isothermal enthalpy evolution of C12Z1

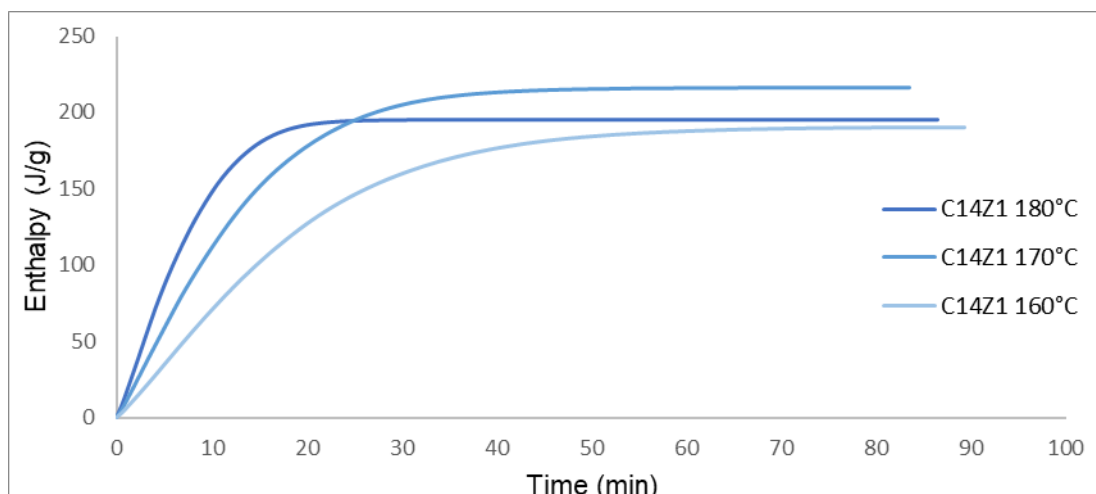


Figure 4.25: Isothermal enthalpy evolution of C14Z1

Total enthalpy of the isothermal tests does not reach the same value as for the dynamic tests. The enthalpy of isothermal tests are compared to the average of the dynamic tests in Table 4.3, where the apparent final degree of cure reached under isothermal conditions is also reported. In the case of C8Z1, C10Z1 and C14Z1, the total enthalpy of the isothermal tests account for more than 85%, while the degree of cure for C6Z1 and C12Z1 only reaches 55-65% and 70-85% of that of the dynamic tests. As observed in 2.5°C/min dynamic tests (Figure 4.10 and Figure 4.13), the secondary reaction start at a temperature around 230-240°C which is significantly higher than the temperature of the isothermal experiments. Therefore, the partial cure under isothermal conditions can be attributed to the limited occurrence of the secondary reactions.

Table 4.3: Isothermal enthalpy for all vitrimeric materials

Material	Temperature (°C)	Enthalpy (J/g)	Average total enthalpy (J/g)	Degree of cure
C6Z1	180	227	347.7	65%
	170	219.9		63%
	165	191.6		55%
C8Z1	180	252.4	269.2	94%
	170	251.4		93%
	160	250.9		93%
C10Z1	180	148.6	157.9	94%
	170	152.7		97%
	160	157.7		100%

C12Z1	180	173.3	246.6	70%
	170	173.7		70%
	160	204.3		83%
C14Z1	180	195	219.2	89%
	170	216.1		99%
	160	190.3		87%

4.2.3 Superposition of isothermal and dynamic cure kinetics data

Figure 4.26 to Figure 4.30 show of reaction rate as function of degree of cure for isothermal tests. Across most formulations, a distinct pattern emerges where the reaction rate exhibits an initial increase, culminating in a maximum value, succeeded by a subsequent deceleration. This initial increase transpires over a relatively brief interval and is somewhat less conspicuous for C8Z1 cured at 170 and 180°C, as depicted in Figure 4.27. This diminished clarity could stem from the rapidity of the initial increase. This behaviour strongly suggests an autocatalytic mechanism^{206,207} for the reaction, rather than nth order. In the context of the autocatalytic mechanism, the hydroxyl group generated during the initial phase of the reaction functions as a catalyst, inducing an acceleration of the reaction^{208,206} before the reaction rate commences a decline attributed to diminishing reactant concentration.

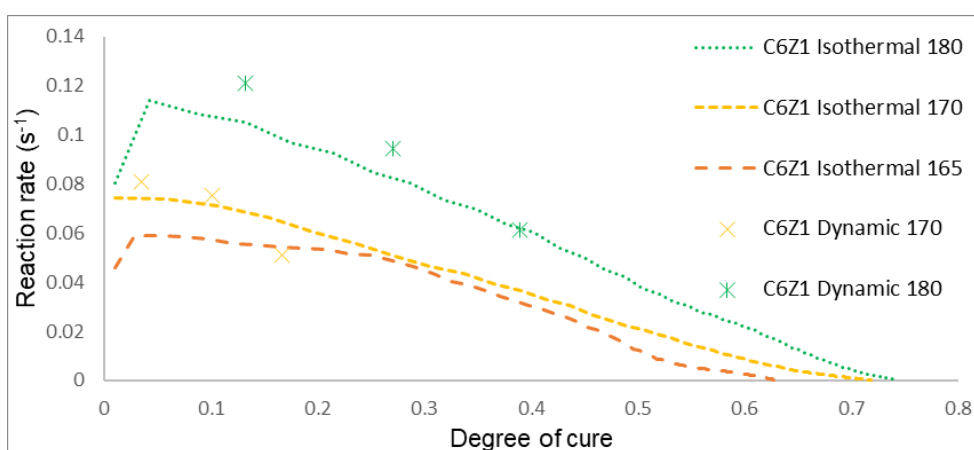


Figure 4.26: Superposition of dynamic and isothermal reaction rate versus degree of cure data of vitrimer C6Z1

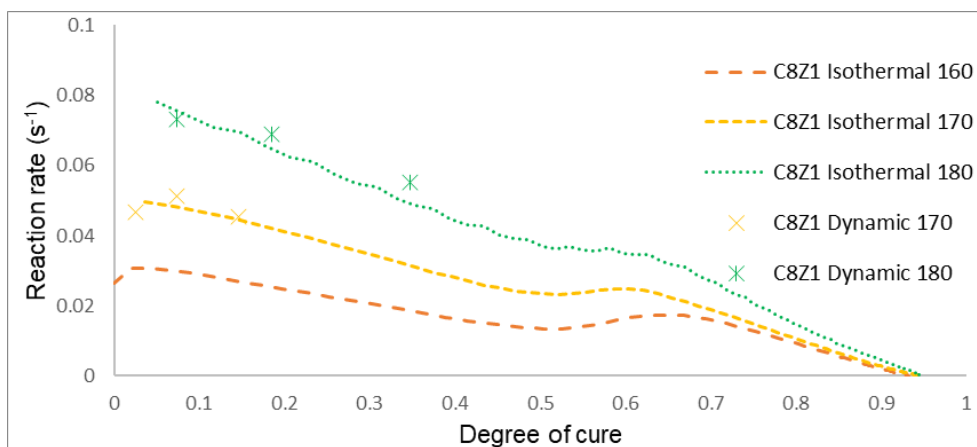


Figure 4.27: Superposition of dynamic and isothermal reaction rate *versus* degree of cure data of vitrimer C8Z1

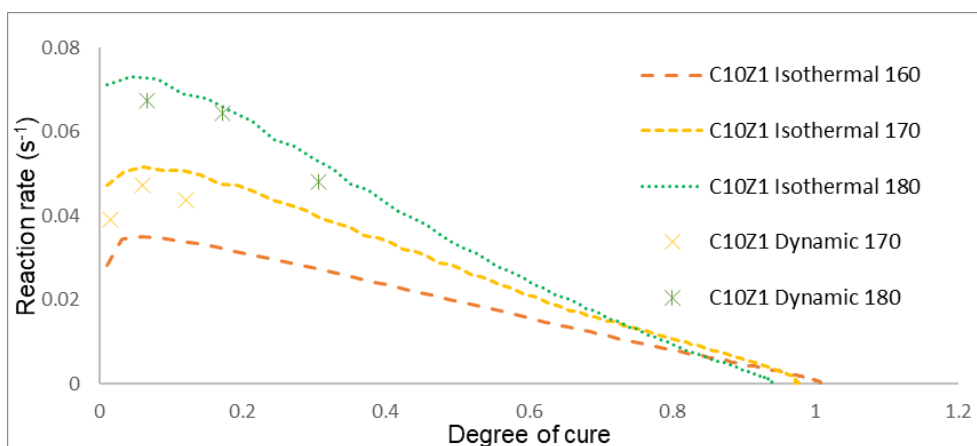


Figure 4.28: Superposition of dynamic and isothermal reaction rate *versus* degree of cure data of vitrimer C10Z1

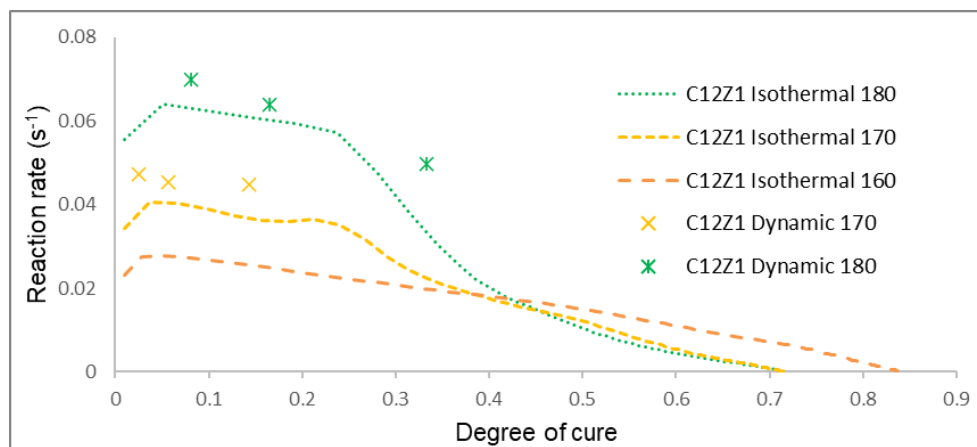


Figure 4.29: Superposition of dynamic and isothermal reaction rate *versus* degree of cure data of vitrimer C12Z1

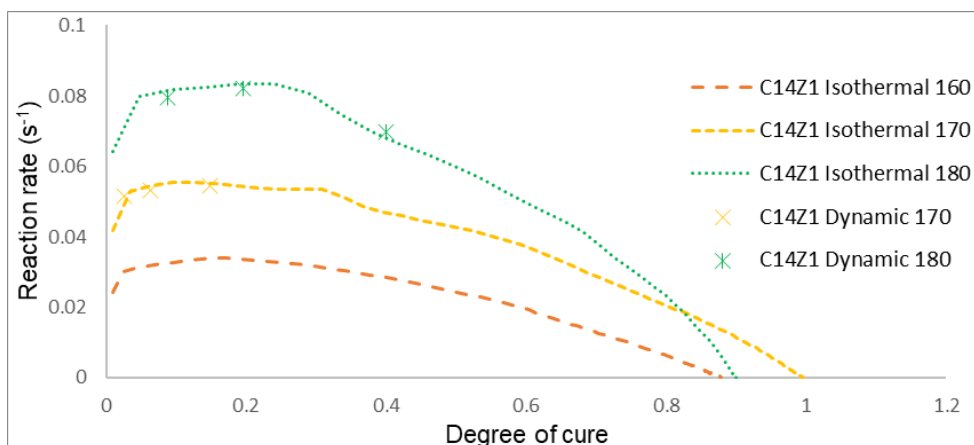


Figure 4.30: Superposition of dynamic and isothermal reaction rate *versus* degree of cure data of vitrimer C14Z1

To test the assumption of reaction rate being a unique function of degree of cure and temperature, dynamic data at identical temperature and degree of cure were superimposed with the isothermal reaction rates. Figure 4.26 to Figure 4.30 illustrate this comparison. The values and difference between the isothermal and dynamic data are listed in Table 4.4. Overall, there is a small difference between the data points obtained from the dynamic and isothermal tests, resulting in an overall relative error of 9.2% in terms of reaction accuracy. This confirms that the reaction mechanism remains consistent with a representation of the reaction rate as a unique function of temperature and degree of cure despite the variation in thermal history.

Table 4.4: Superposition data for vitrimers

Material	Temperature(°C)	Heating Rate (°C/min)	Relative Error	Average relative error	
C6Z1	170	10	9.5%	12.1%	11.2%
		5	5.7%		
		2.5	21.2%		
	180	10	15.4%	10.3%	
		5	14.6%		
		2.5	0.9%		
C8Z1	170	10	5.4%	4.4%	5.9%
		5	5.9%		
		2.5	2.0%		
	180	10	3.0%	7.4%	
		5	6.8%		

		2.5	12.4%		
C10Z1	170	10	18.6%	13.5%	9.9%
		5	8.2%		
		2.5	13.6%		
	180	10	7.3%	6.4%	
		5	2.6%		
		2.5	9.3%		
C12Z1	170	10	19.9%	16.3%	16.3%
		5	11.1%		
		2.5	18.0%		
	180	10	9.6%	16.2%	
		5	6.0%		
		2.5	33.0%		
C14Z1	170	10	5.4%	2.9%	2.6%
		5	2.3%		
		2.5	1.1%		
	180	10	2.4%	2.2%	
		5	1.6%		
		2.5	2.8%		

The data points obtained from interpolated dynamic DSC experiments have an unbiased distribution in relation to their correlation with the isothermal runs. This observation indicates the absence of a discernible connection between the effect of the heating rate on the reaction rate in terms of degree of cure at the interpreted temperatures. For example, in the case of C10Z1, the isothermal reaction curves appear slightly higher in reaction rate at the same degree of cure. Conversely, for C6Z1 and C12Z1, the isothermal runs exhibit lower behaviour compared to the results extracted from dynamic testing. Among all the formulations, C14Z1 demonstrates the most consistent results between the dynamic and isothermal data, with an average relative error of 2.6%. conversely, C12Z1 exhibits the largest disparity, showing an average difference of 16.3% between the dynamic and isothermal measurements.

4.3 Cure kinetics modelling of epoxy-dicarboxylic acid vitrimer systems

The modelling of cure kinetics is reported in this section. The initial approach utilising the straightforward Kissinger model to estimate the apparent activation energy for each of the vitrimer formulations is presented first. This is then contrasted with the outcomes from three isoconversional models to assess

accuracy. Subsequently, the derived activation energy values are integrated into an autocatalytic kinetic model that incorporates considerations for diffusion limitations.

4.3.1 Application of Kissinger model

The objective of conducting a kinetic analysis on the thermal stimulation process is to determine a mathematical correlation between the rate of reaction and the degree of cure and temperature, represented as follows:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (4-1)$$

The dependence of the reaction rate on temperature is $k(T)$ while $f(\alpha)$ represents the dependence on the extend of conversion. $K(T)$ typically follows an Arrhenius behaviour:

$$k(T) = A e^{-\frac{E_a}{RT}} \quad (4-2)$$

where E_a is the activation energy for the reaction, A represents the pre-exponential factor and R is the universal gas constant (8.314J/mol/K). Combining the two equations, the general expression of the curing behaviour can be expressed as:

$$\frac{d\alpha}{dt} = A e^{-\frac{E_a}{RT}} f(\alpha) \quad (4-3)$$

Determining the E_a , A and $f(\alpha)$ triplet is necessary to model the kinetics of the system. The activation energy can be obtained using various methods, each with different levels of accuracy depending on the compatibility between the method and the specific chemical transformation and reaction process. Among these methods, the Kissinger method²⁰⁹ is widely employed due to its simplicity.

The Kissinger method allows the estimation of the apparent activation energy based on peak temperature (T_p) measurements at the maximum curing rate. Derived from Eq.(4-3) under the condition of the maximum reaction rate at which point $\frac{d^2\alpha}{dt^2}$ is zero:

$$\frac{d^2\alpha}{dt^2} = \left[\frac{E_a\beta}{RT_p} + Af'(\alpha_p)e^{-\frac{E_a}{R\cdot T_p}} \right] \left(\frac{d\alpha}{dt} \right)_p = 0 \quad (4-4)$$

where $f'(\alpha) =$ and the subscript p denotes the values related to peak rate as T_p corresponds to the temperature at which the maximum reaction rate occurs, and β is the instantaneous heating rate:

$$\beta = \frac{dT}{dt} \quad (4-5)$$

After rearrangement:

$$\frac{E_a\beta}{RT_p} = -Af'(\alpha_p)e^{-\frac{E_a}{R\cdot T_p}} \quad (4-6)$$

By rearranging and taking the natural logarithm on both sides, Eq.(4-6) is transformed into the Kissinger equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A R}{E_a} f'(\alpha_p)\right) - \frac{E_a}{R T_p} \quad (4-7)$$

By plotting $\ln(\beta/T_p^2)$ against, the apparent activation energy can be determined, as the slope of the fitting is equal to $-E_a/R$. The Kissinger method is valid for one-step processes only where $f'(\alpha_p)$ is independent to β . Otherwise, the first term on the right side of Eq.(4-7) is constant resulting in a systematic deviation from the straight line of $\ln(\beta/T_p^2)$ vs. $1/T_p$.

The detailed linear fittings of Kissinger model and the corresponding slopes representing E_a for all five vitrimers are illustrated in Figure 4.31. The corresponding data are summarised in Table 4.5. The Kissinger model has certain limitations. It considers only the data related to the maximum reaction rate and is fully applicable to single-step reactions. The curing process of DGEBA and dicarboxylic acids is complex and involves multiple steps. Despite these limitations, the Kissinger model provides an initial estimation of the reaction kinetics parameters. One advantage of the Kissinger method is its applicability to different heating rates, as it can be used independently of the specific curing

process. This implies that the degree of cure α_p at the peak reaction rate should remain consistent regardless of the heating rate (β). Table 4.5 demonstrates that the difference in α_p values for the three heating rates is less than 6.8% across all formulations. This indicates a relatively good compatibility between the curing process and the Kissinger model, which is further supported by high R^2 values (>0.99) for all the fittings.

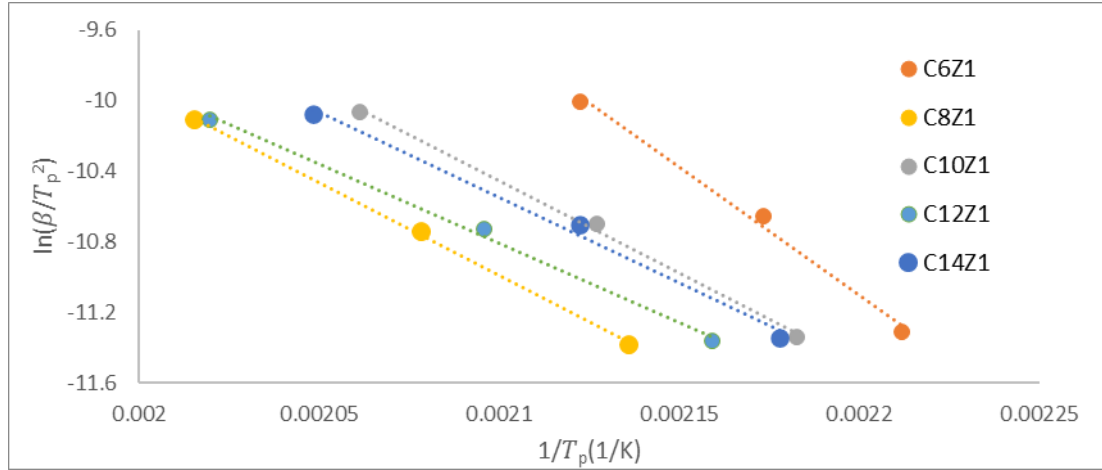


Figure 4.31: Fitting curve for the apparent activation energy for vitrimers

Figure 4.32 illustrates the relationship between carbon number and E_a . It can be observed that there is a decrease in E_a as the carbon number increases. This phenomenon can be attributed to the increased flexibility of the monomer backbone resulting from the addition of methylene units in the form of linear dicarboxylic acid chains. The enhanced flexibility facilitates the rotation of the monomer, leading to a decrease in the energy required for the reaction to occur²¹⁰. The difference in intermolecular forces can be disregarded in this case, as the only structural variation among the chains is the number of methylene units, which does not cause any significant shift in the interactions between the chains.

Table 4.5: Curing kinetic parameters, pre-exponential factor and the goodness of the fitting obtained from dynamic DSC runs of all five vitrimer formulations at different heating rate

Formulation	Heating rate (°C/min)	T_p (°C)	$\ln\left(\frac{\beta}{T_p^2}\right)$	$\frac{1}{T_p}$ (1/K)	E_a (kJ/mol)	α_p	R^2
-------------	--------------------------	------------	---------------------------------------	-----------------------	----------------	------------	-------

C6Z1	10	198	-10.01	0.00212	120.7	47.0%	0.9928
	5	187	-10.65	0.00217		44.4%	
	2.5	179	-11.31	0.00221		45.6%	
C8Z1	10	223	-10.11	0.00202	87.5	62.6%	0.9992
	5	208	-10.74	0.00208		64.2%	
	2.5	195	-11.38	0.00214		67.4%	
C10Z1	10	212	-10.07	0.00206	86.8	42.2%	0.9972
	5	197	-10.70	0.00213		41.9%	
	2.5	185	-11.34	0.00218		40.8%	
C12Z1	10	222	-10.11	0.00202	74.4	59.5%	0.9964
	5	204	-10.73	0.00210		54.0%	
	2.5	190	-11.36	0.00218		52.7%	
C14Z1	10	215	-10.08	0.00205	80.6	57.8%	0.9918
	5	198	-10.70	0.00212		55.9%	
	2.5	186	-11.34	0.00218		57.5%	

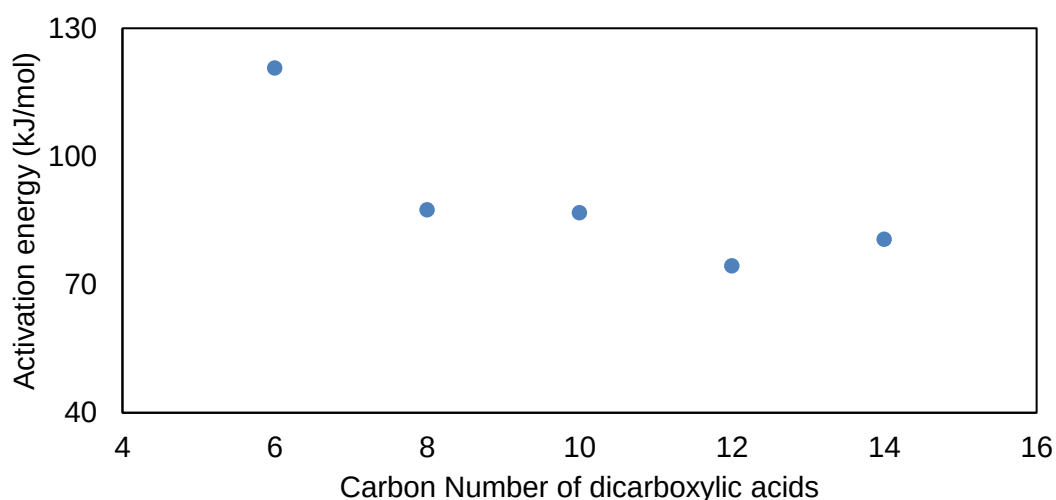


Figure 4.32: Relationship between apparent activation energy obtained using the Kissinger model and dicarboxylic acid chain length

4.3.2 Application of isoconversional analysis

Despite demonstrating significant agreement in determining the degree of cure under different heating rates, the Kissinger model is specifically designed for a single-step reaction process, relying on a single set of data obtained at the maximum reaction rate to determine the activation energy (E_a) value. To address this limitation, isoconversional methods have been used. These methods involve analysing the entire curing process based on the degree of cure, operating on the principle that the reaction rate is solely influenced by temperature for a

constant extent of conversion. Consequently, the activation energy dependence can be evaluated without making any assumptions about the reaction mechanism, using:

$$\left[\frac{d \ln (d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = \left[\frac{d \ln k(T)}{dT^{-1}} \right]_{\alpha} + \left[\frac{d \ln f(\alpha)}{dT^{-1}} \right]_{\alpha} \quad (4-8)$$

The rate constant is influenced by the reaction model $f(\alpha)$. In this particular case, when the extent of conversion remains constant, the reaction model $f(\alpha)$ is also constant. This condition leads to the expression $\left[\frac{d \ln f(\alpha)}{dT^{-1}} \right]_{\alpha} = 0$ ²¹¹. As a result, the following relationship holds true:

$$\left[\frac{d \ln (d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_a}{R} \quad (4-9)$$

By relying solely on the temperature dependence of the isoconversional rate, it becomes possible to evaluate the isoconversional values of the activation energy without making any assumptions or specifying a particular reaction model, except for the Arrhenius behaviour of the system. The accuracy of these methods depends on the numerical approximation obtained from solving the temperature-dependent integral, known as the Arrhenius temperature integral $p(y)$. Various approximations for the temperature integral have been proposed and described as follows:

$$p(y) \cong \frac{e^{-Ay+B}}{y^K} \quad (4-10)$$

where $y = E_a/RT$ while A, B and K are constants with values determined to minimise the deviation between the approximation function and the exact integral. Then $p(y)$ is used to derive isoconversional models for activation energy determination in the general form of:

$$\ln \frac{\beta}{T_{\alpha}^K} = -A \frac{E_a}{RT_{\alpha}} + C \quad (4-11)$$

Table 4.6: Values of the parameters for three integral isoconversional methods

Model	K	A
Flynn-Wall-Ozawa (FWO)	0	1.052
Kissinger-Akahira-Sunose (KAS)	2	1.000
Starink	1.92	1.0008

The temperature at an equivalent fixed state of transformation is denoted as T_α . In this study, three isoconversional integral methods were utilised: the Flynn-Wall-Ozawa (FWO) method²¹², the Kissinger-Akahira-Sunose (KAS) method¹⁷⁶, and the Starink method²¹³. These three methods used different values of A and K aiming to achieve high accurate approximation. The values of the constants are listed in Table 4.6.

In the FWO method, with $K = 0$, the activation energy is determined from the slope of plots of $\ln(\beta)$ versus $1/T_\alpha$. The KAS method and Starink method, on the other hand, determine E_a by the slope of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$ and $\ln(\beta/T_\alpha^{1.92})$ versus $1/T_\alpha$, respectively. All three methods assume a consistent reaction model throughout the entire process and provide valuable information despite the approximation of the actual crosslinking process. Among these methods, the Starink method demonstrates lower deviations and higher accuracy, particularly when $y < 10$.

$$\ln(\beta) = C - 1.052 \frac{E_a}{R T_\alpha} \quad (4-12)$$

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = C - 1.00 \frac{E_a}{R T_\alpha} \quad (4-13)$$

$$\ln\left(\frac{\beta}{T_\alpha^{1.92}}\right) = C - 1.08 \frac{E_a}{R T_\alpha} \quad (4-14)$$

The reaction mechanism can lead to variations in activation energy across a wide range of α . In this regard, the method of Vyazovkin *et al.*²¹¹ was followed, where a range of α values from 0.05 to 0.95 was examined with increments of 0.05.

The $\ln(\beta/T_\alpha^{1.92})$ value for three different temperature ramp rates against inverse temperature for five materials are plotted as Figure 4.33 to Figure 4.37. The

dotted lines correspond to the best linear fitting for each of the degree of conversion based on the value of the three heating rates. In Figure 4.33, there is a noticeable deviation observed between the data points and the linear fit at the extremes of the spectrum, as seen when the degree of cure exceeds 0.8. This suggests that under these conditions, the model fails to accurately predict the curing behaviour, likely due to hindered mobility resulting from diffusion limitations towards the latter stages of the reaction. This discrepancy implies that caution should be exercised when utilising the results to evaluate the activation energy under such conditions.

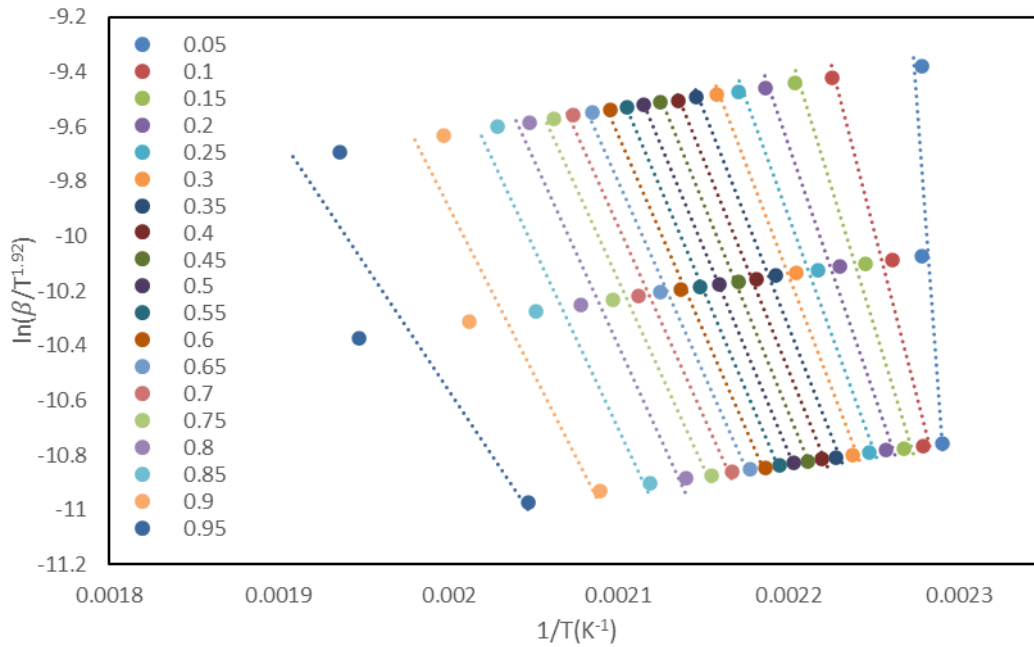


Figure 4.33: Plot corresponding to Starink method for vitrimer C6Z1 in the degree cure range of 0.05-0.95

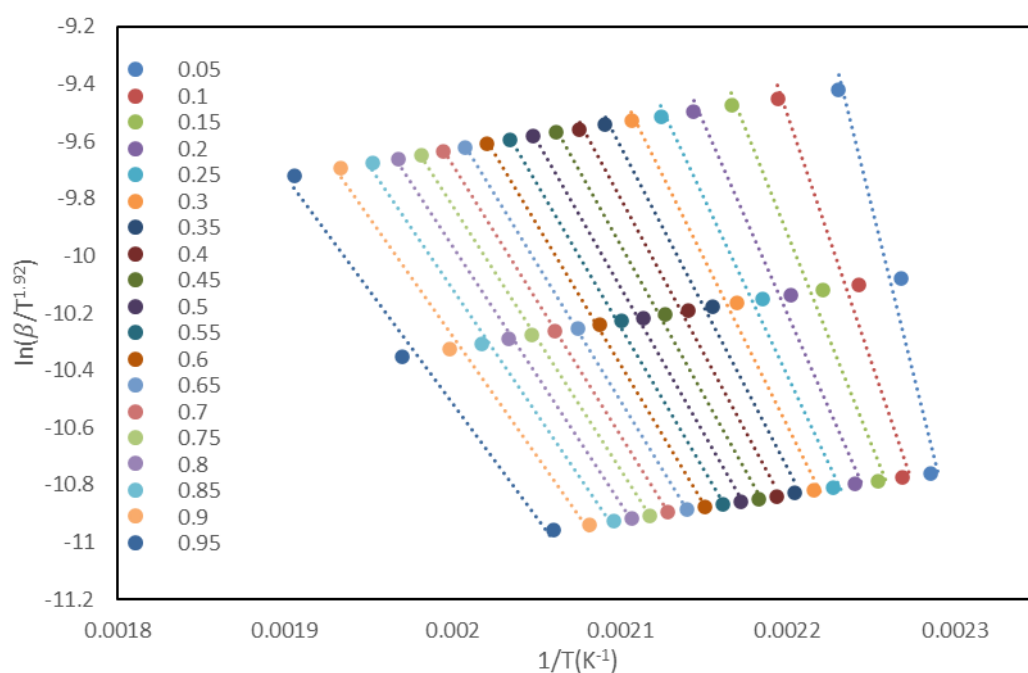


Figure 4.34: Plot corresponding to Starink method for vitrimer C8Z1 in the degree cure range of 0.05-0.95

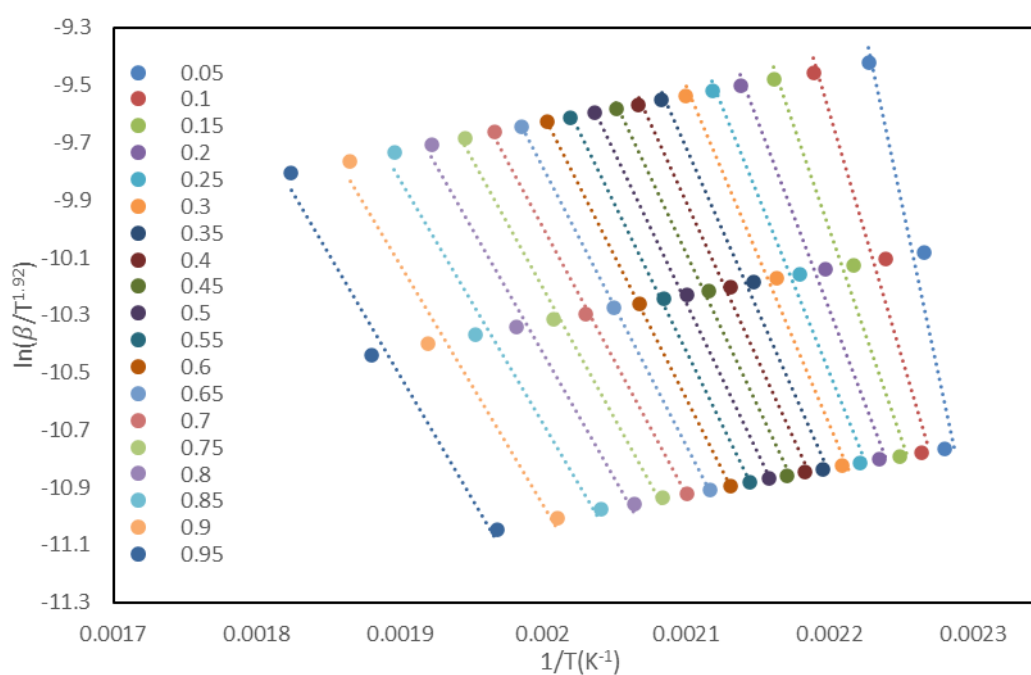


Figure 4.35: Plot corresponding to Starink method for vitrimer C10Z1 in the degree cure range of 0.05-0.95

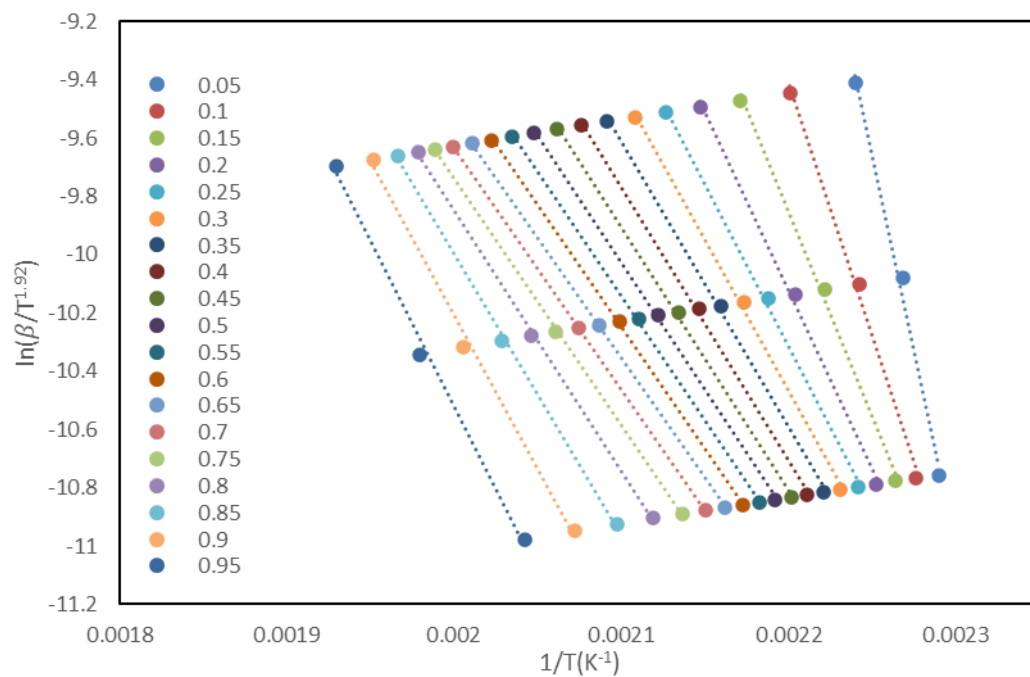


Figure 4.36: Plot corresponding to Starink method for vitrimer C12Z1 in the degree cure range of 0.05-0.95

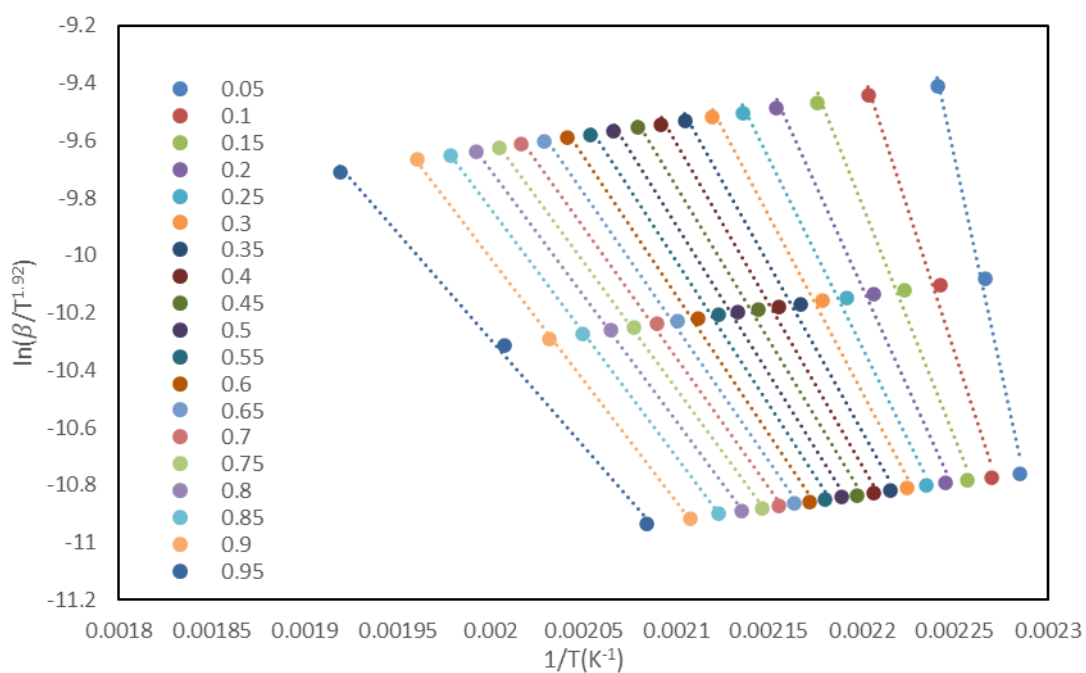


Figure 4.37: Plot corresponding to Starink method for vitrimer C14Z1 in the degree cure range of 0.05-0.95

The data obtained, which are summarised in Table 4.8, demonstrate remarkable agreement in terms of the activation energy across the three models. The greatest difference, observed between the Kissinger method and Starink method, is 8.23% for the E_a of C14Z1 when the reaction reaches 0.95 of total cure. Meanwhile, the disparities between the FWO method and Kissinger method are consistently below 1% across all cases. The substantial variation of activation energy with degree of cure indicates the presence of kinetic complexity in the process. The reaction can be divided into three stages based on the change in activation energy:

- Early reaction stage: At the onset of the reaction, when the autocatalytic effect is prominent, there is a significant drop in activation energy. This drop is particularly pronounced when degree of cure increases from 0.05 to 0.1, with C6Z1 exhibiting a decrease of approximately 71%. However, such data may be unreliable due to the rapid temperature increase before the dynamic runs. Even after excluding these unreliable data, a substantial drop of about 30%-40% in activation energy is still observed for the early stage of the reaction ($\alpha < 0.3$). This rapid decay in activation energy suggests a significant change in the reaction mechanism, transitioning from a non-catalysed reaction to an autocatalytic reaction due to the increase in hydroxyl groups^{207,180}.
- Stabilised reaction stage: Throughout most of the reaction, the activation energy remains relatively stable for all formulations. However, towards the end of the reaction, a decrease of 10%-20% in E_a occurs when α reaches 0.8 compared with the value at 30% of the cure. This is also the stage where the reaction rate is only determined by the concentrations of the reactants raised to various powers.
- Diffusion-controlled stage: Other researchers have also observed a continuous reduction in activation energy during the final stage of curing, particularly when the system reaches high conversion ($\alpha > 0.8$)^{142,214}. This suggests a transition in the reaction from being chemically controlled to diffusion control. The mobility of the reactants is hindered as the polymer chains grow and the system approaches vitrification, requiring small

molecules to undergo a series of diffusion jumps before participating in a chemical reaction²¹⁵.

A varied behaviour is observed in the change of activation energy with respect to the reaction progress, specifically for C12Z1. Starting from a degree of cure of 0.65, the activation energy undergoes an increase of approximately 42%. From a data perspective, this phenomenon indicates that the reaction mechanism undergoes a more significant shift in the case of C12Z1 compared to the other systems. Referring to Figure 4.6, it can be observed that the reaction peak for a heating rate of 10°C/min exhibits a slower initiation and a delayed, more concentrated, single peak at a later stage of the reaction. This suggests the possibility of the second reaction mechanism becoming more prominent, resulting in a blending of the energy release from both mechanisms. However, when the heating rate is reduced to 2.5°C/min, the energy release appears to be concentrated in the early stages of the reaction process. Furthermore, under a heating rate of 5°C/min, there is a clear separation of the two peaks. The variation in energy release across different temperatures for each heating rate leads to a more pronounced change in activation energy for each stage of the reaction when calculated using this heating rate-dependent model.

Table 4.7: Activation energy obtained from three isoconversional methods with degree of cure from 0.05-0.95

Model/Activation energy (kJ/mol)	Degree of cure (1)	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
Kissinger	0.05	672	193	192	219	243
	0.1	198	143	141	144	163
	0.15	166	123	121	117	135
	0.2	150	112	111	103	120
	0.25	141	105	105	95	110
	0.3	136	100	100	89	104
	0.35	132	96	97	84	99
	0.4	129	93	94	81	95
	0.45	127	90	92	78	92
	0.5	125	88	90	76	89
	0.55	122	86	88	74	86
	0.6	120	84	86	73	84

Model/Activation energy (kJ/mol)	Degree of cure (1)	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
	0.65	118	83	84	72	81
	0.7	116	82	81	73	79
	0.75	115	80	79	74	77
	0.8	115	78	77	78	77
	0.85	113	76	75	84	76
	0.9	104	73	74	91	75
	0.95	82	70	75	97	66
FWO	Degree of cure	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
	0.05	699	195	195	223	248
	0.1	201	143	140	144	165
	0.15	167	122	120	116	134
	0.2	151	110	109	101	118
	0.25	141	103	102	92	108
	0.3	135	98	98	86	101
	0.35	131	93	94	81	96
	0.4	128	90	91	77	93
	0.45	126	87	89	74	90
	0.5	123	85	87	72	86
	0.55	121	83	84	70	83
	0.6	118	81	82	69	80
	0.65	116	79	80	68	77
	0.7	114	78	77	68	75
	0.75	114	76	75	70	73
	0.8	113	74	72	74	73
	0.85	110	72	70	80	72
	0.9	101	69	69	87	70
	0.95	77	66	70	94	61
Starink	Degree of cure	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
	0.05	694	194	193	222	246
	0.1	199	142	140	143	164
	0.15	166	121	119	115	134
	0.2	150	110	109	101	118
	0.25	140	102	102	92	108
	0.3	134	97	97	85	101
	0.35	130	93	93	81	96
	0.4	128	90	91	77	92
	0.45	125	87	88	74	89
	0.5	123	84	86	72	86
	0.55	120	82	84	70	83
	0.6	118	81	82	69	80
	0.65	115	79	80	68	77

Model/Activation energy (kJ/mol)	Degree of cure (1)	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
	0.7	114	78	77	68	75
	0.75	113	76	75	70	73
	0.8	112	74	72	74	72
	0.85	110	71	70	80	72
	0.9	101	69	69	87	70
	0.95	77	65	70	93	61

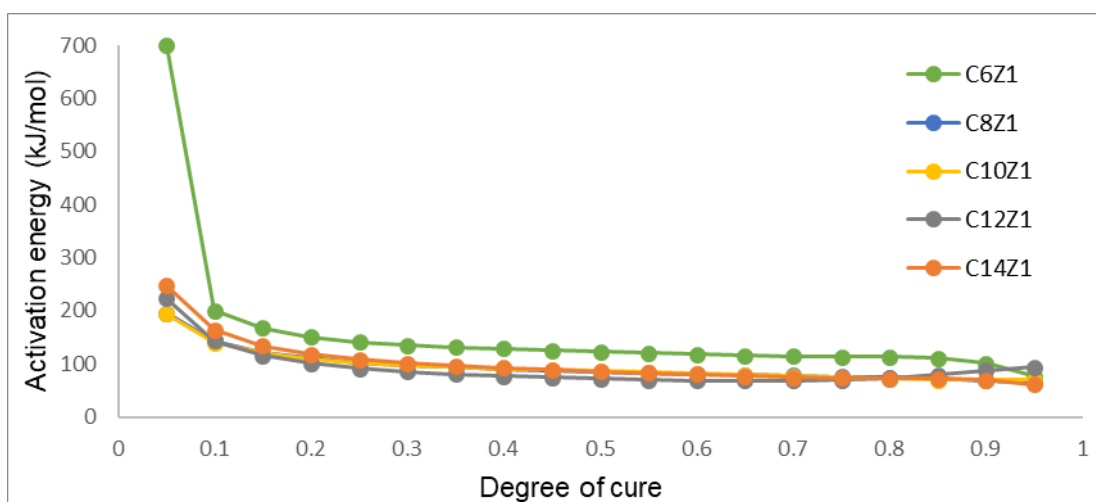


Figure 4.38: Relationship between degree of cure and apparent activation energy obtained using Kissinger's model

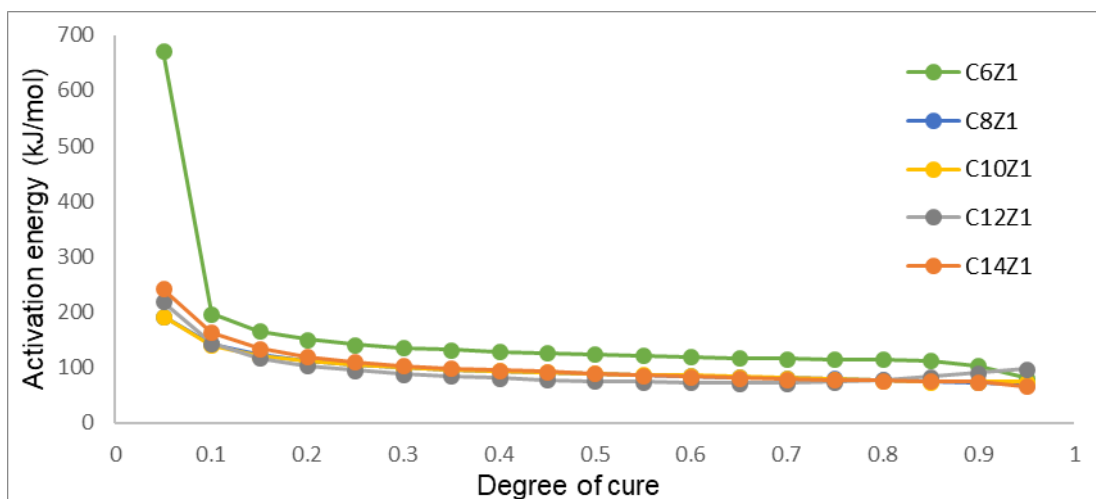


Figure 4.39: Relationship between degree of cure and apparent activation energy obtained using Flynn-Wall-Ozawa's model

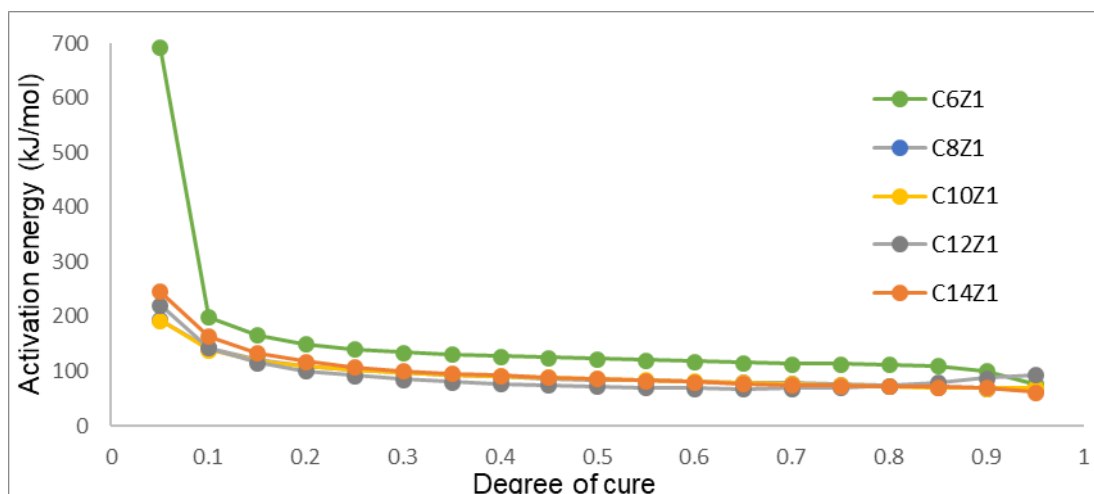


Figure 4.40: Relationship between degree of cure and apparent activation energy obtained using Starink's model

The reported apparent activation energies (E_a) for each material, calculated using three isoconversional methods throughout the entire curing process, are detailed in Table 4.7. These values cover a conversion range from 0.05 to 0.95, with an increment of 0.05. The highest reaction rates for all materials are consistently achieved within the 41.6%-64.7% range, which aligns with the region of stabilised reaction. Notably, while a connection between activation energy and cure degree was established, the resultant values – which are integral to the upcoming model development- exhibit a remarkable level of coherence with those derived from the three isoconversional techniques. This congruence might arise from the modest decrease in activation energy throughout the stabilised reaction stage. It is worth mentioning that the simplistic Kissinger model fails to account for this change in activation energy depending on the cure degree, offering instead an average value for the entire duration. This limitation tends to lead to an underestimation for early-stage reactions and an overestimation for the latter stages. Across all formulations, variations span from 5.2% to 9.7%, with the most significant divergence observed in C8Z1 at 9.7%. Nonetheless, even this maximum deviation remains within an acceptable margin of error - less than 10%. For formulations such as C8Z1 and C12Z1, Kissinger's model predicts slightly elevated activation energies compared to the isothermal methods. Conversely, formulations C6Z1, C10Z1, and C14Z1, exhibit diminished activation energies. These observations underscore the trustworthiness and resilience of the

Kissinger's method, instilling a high degree of confidence in the derived activation energy values. This confidence served as the basis for fitting kinetics models, based on the apparent activation values from Kissinger's method.

Table 4.8: Comparison of the apparent activation energy at the peak of the reaction obtained from Kissinger's model and three different isoconversional methods

Material	α for the peak of reaction	E_a of Kissinger's model (kJ/mol)	Iso E_a (kJ/mol)	Max Difference
C6Z1	45.7%	120.7	127	5.2%
			126	
			125	
C8Z1	64.7%	87.5	83	9.7%
			79	
			79	
C10Z1	41.6%	86.6	94	8.5%
			91	
			91	
C12Z1	60.6%	74.4	73	7.3%
			69	
			69	
C14Z1	57.1%	80.6	86	6.7%
			83	
			83	

To determine the most suitable model for the reaction according to the mathematical approach stated in 3.2.3. The calculated values of α_M and α_p^∞ using both Kissinger's model and isoconversional model are listed in Table 4.9.

Although Significant changes in activation energy are observed throughout the entire reaction process shown in isoconversional methods, E_a remains relatively stable during the stage where the maximum reaction rate is achieved. Which leads to the finding that when comparing the value of α_M and α_p^∞ in most cases, the difference falls within the range of 1-4%, except for three instances where the α_p^∞ difference exceeds 5%. Specifically, for C6Z1, C8Z1, and C10Z1 at heating rates of 5°C/min and 2.5°C/min, the differences amount to 8.38%, 6.35%, and

9.61%, respectively. According to the Malek method, when $\alpha_p^\infty \neq 0.632$ and $0 < \alpha_M < \alpha_p^\infty$, the empirical Sestak-Berggren model Eq.(3-7) proves to be the most suitable kinetics model for analysing thermal data.

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (4-15)$$

where α is the degree of cure, m and n are the reaction orders.

Table 4.9: Calculated vales of α_M and α_p^∞ for all vitrimers for three heating rates from isoconversional for kinetic model determination.

Material	$\beta(^{\circ}\text{C}/\text{min})$	Iso α_M	Iso α_p^∞	α_M	α_p^∞	α_M Difference	α_p^∞ Difference
C6Z1	2.5	0.47	0.46	0.45	0.45	3.30%	1.16%
	5	0.41	0.41	0.4	0.45	2.98%	8.38%
	10	0.41	0.41	0.4	0.4	1.83%	1.83%
C8Z1	2.5	0.41	0.48	0.4	0.45	3.28%	6.35%
	5	0.49	0.57	0.5	0.55	1.88%	3.83%
	10	0.63	0.63	0.6	0.6	4.17%	4.17%
C10Z1	2.5	0.26	0.33	0.25	0.3	2.40%	9.61%
	5	0.37	0.39	0.35	0.4	4.16%	1.37%
	10	0.44	0.47	0.45	0.45	2.61%	3.30%
C12Z1	2.5	0.43	0.46	0.45	0.45	4.17%	1.44%
	5	0.52	0.54	0.5	0.55	4.37%	1.50%
	10	0.73	0.75	0.75	0.75	2.75%	0.26%
C14Z1	2.5	0.59	0.59	0.6	0.6	1.24%	1.24%
	5	0.50	0.53	0.5	0.5	0.27%	4.92%
	10	0.40	0.40	0.4	0.4	1.05%	1.05%

4.3.3 Cure kinetics model fitting and prediction

A diffusion control modified autocatalytic kinetic model is employed for this study, following:

$$\frac{d\alpha}{dt} = \frac{A \cdot \exp(-\frac{E_a}{RT}) \cdot \alpha^m(1 - \alpha)^n}{1 + e^{[c(\alpha - (\alpha_{c0} + \alpha_{cT}T))]} \quad (4-16)$$

The model's parameters obtained by fitting for each of the materials are listed in

Table 4.10.

Table 4.10: Curing kinetic parameters for the autocatalytic model of vitrimers

Model parameters	C6Z1	C8Z1	C10Z1	C12Z1	C14Z1
$A \text{ (s}^{-1}\text{)}$	2.10×10^{13}	1.53×10^9	8.52×10^8	4.42×10^7	3.26×10^8
$E_a \text{ (kJ/mol)}$	120.7	87.5	86.8	74.0	80.6
n	2.08	1.14	1.84	1.85	1.45
m	0.139	0.026	0.002	0.177	0.227
c	61.16	0.98	4.50	4.99	13.33
α_{C0}	4.75	-0.85	2.96	2.15	-0.14
$\alpha_{CT} \text{ (K}^{-1}\text{)}$	0.0120	0.0002	0.0086	0.0065	0.0019
Total error	4.51	3.83	4.95	9.48	5.49

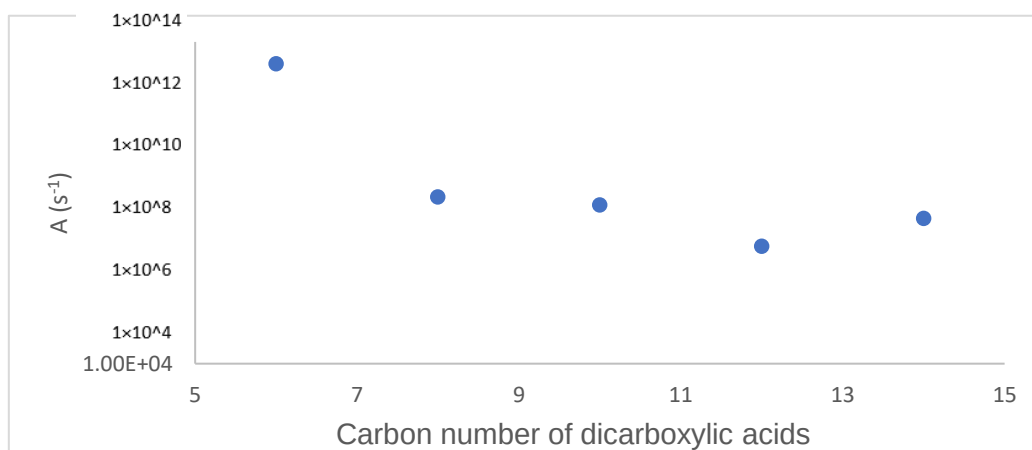


Figure 4.41: The relationship between the pre-exponential factor and dicarboxylic acid length

The value of the obtained pre-exponential factor follows a similar trend to that of activation energy reported in Figure 4.32 showing a general reduction as the dicarboxylic acid chain length increases with the exception of C12Z1, whose value is abnormally low compared to the expected trend. Since the value of pre-exponential factor presents the frequency of collision for the reaction to take place, this result is in agreement with the fact that increasing the chain length results in a reduction in functional group density and thus with lower probability of reaction.

The autocatalytic reaction order (m) ranges from 0.02 to 0.227 0.02 whilst the value of n is 1.14-2.08. The value of m represents the influence of the autocatalytic process of the reaction and plays a role in the initial stages of the reaction. In the case of C8Z1 and C10Z1, the models predict a much weaker influence of the autocatalytic effect caused by the generated hydroxyl.

Table 4.11: The comparison between the degree of cure for the isothermal tests compared to their dynamic test and the degree of cure when diffusion limitation was effective for all vitrimeric materials

Material	T (K)	$(\alpha_{c0} + \alpha_{CT}T)$	α	Difference	Average difference
C6Z1	438.15	0.63	0.62	1.0%	5.0%
	443.15	0.72	0.72	0.0%	
	453.15	0.88	0.74	14.0%	
C8Z1	433.15	0.92	1.00	8.0%	4.0%
	443.15	0.92	0.94	2.0%	
	453.15	0.93	0.95	2.0%	
C10Z1	433.15	0.75	1.00	25.0%	11.0%
	438.15	0.79	0.77	2.0%	
	443.15	0.83	0.98	15.0%	
	453.15	0.92	0.94	2.0%	
C12Z1	433.15	0.67	0.84	17.0%	9.3%
	443.15	0.73	0.71	2.0%	
	453.15	0.80	0.71	9.0%	
C14Z1	433.15	0.95	0.88	7.0%	6.3%
	443.15	0.97	1.00	3.0%	
	453.15	0.99	0.90	9.0%	

Figure 4.42-Figure 4.51 present the evolution of reaction rate in dynamic and

The values of α_{c0} and α_{cT} are of importance in terms of when the diffusion starts to play a role in the reaction. The systems are not expected to experience such behaviour at the early stage of the cure when the mobility is high. The value of $(\alpha_{c0} + \alpha_{cT}T)$ at the isothermal experiments temperatures should be close to the final degree of cure at the correspondent temperature. Table 4.11 lists the values of this terms for isothermal experiments and compare them to the final degree of cure obtained in the DSC experiment. Overall, there is a 4% to 11% difference between the value of the degree of the cure and $(\alpha_{c0} + \alpha_{cT}T)$ at the cured isothermal temperature, showing an appropriate choice of the parameters.

isothermal experiments for all formulations, alongside the cure kinetics model prediction. The model fitting for C6Z1 exhibits very good agreement across all dynamic tests, with the most favourable alignment observed for the 2.5°C/min experiment. In the case of the 5°C/min experiment, the model demonstrates a tendency to overestimate the reaction rate starting from 210°C and onwards. On the other hand, for the 10°C/min test, the model showcased an underestimation of the reaction rate following the peak, commencing from 190°C. Among the isothermal test data collected for C6Z1, the model best performance is observed for the experiment conducted at 170°C. However, the model performance is inferior for the lowest and highest temperature tests. The model yields lower estimates for the lower temperature and substantially higher estimations for the highest temperature experiment conducted at 180°C. This discrepancy becomes particularly pronounced during in initial stages of the reaction, leading to the lowest R-squared value of 0.794 for this material. Moreover, the experimental data shows a less pronounced autocatalytic effect compared to the model predictions. The initial surge in reaction rate is not as prominent as expected.

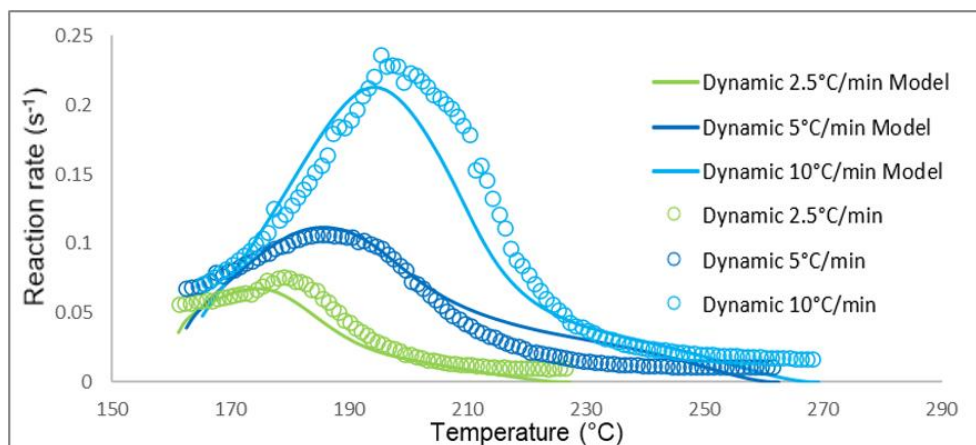


Figure 4.42: Comparison of autocatalytic cure kinetics model and experimental data for C6Z1 under dynamic conditions

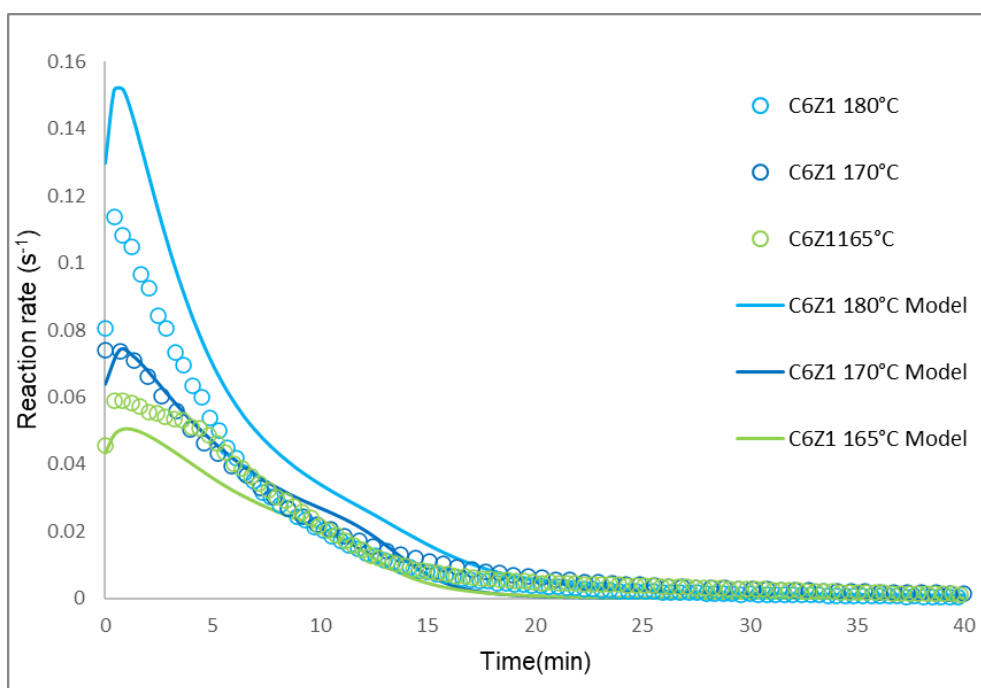


Figure 4.43: Comparison of autocatalytic cure kinetics model and experimental data for C6Z1 under isothermal conditions

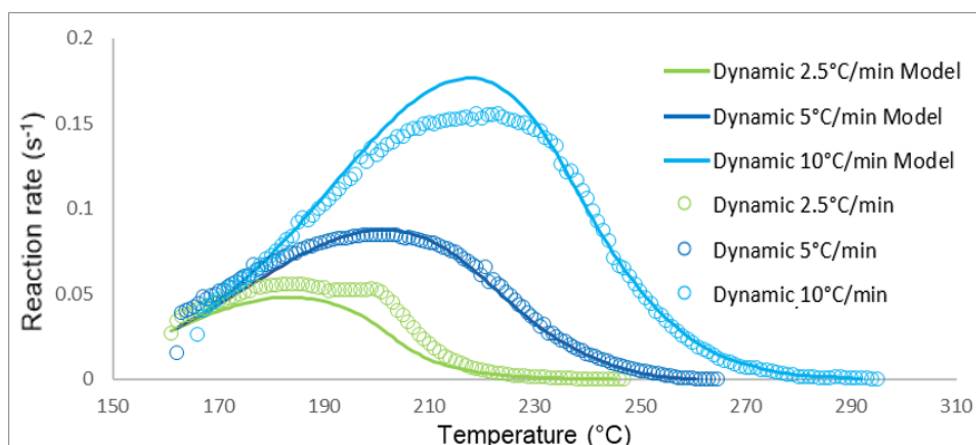


Figure 4.44: Comparison of autocatalytic cure kinetics model and experimental data for C8Z1 under dynamic conditions

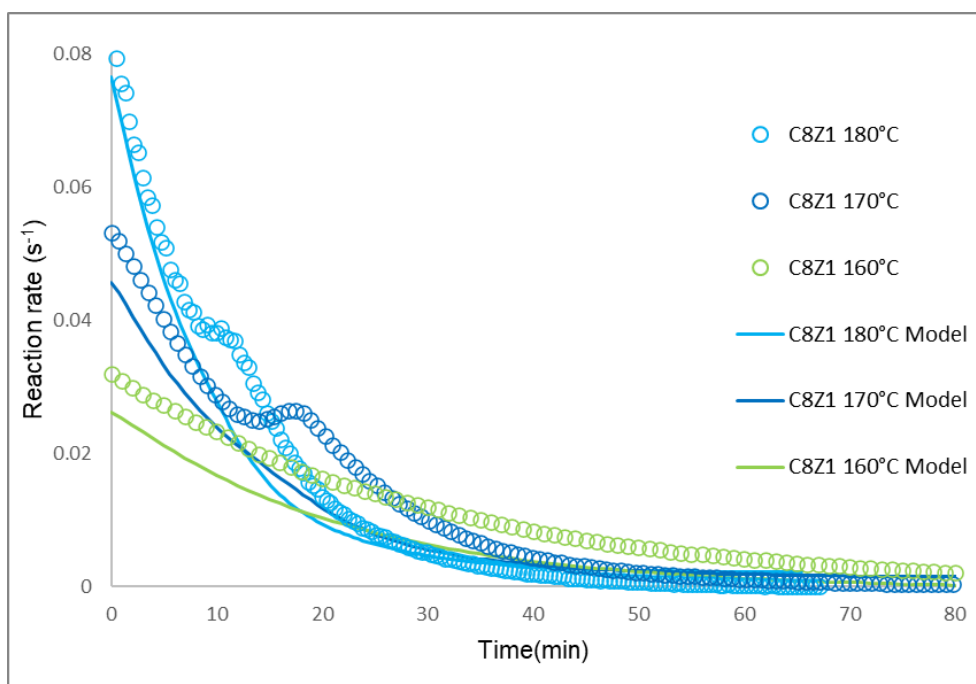


Figure 4.45: Comparison of autocatalytic cure kinetics model and experimental data for C8Z1 under isothermal conditions

For formulation C8Z1, the model exhibits a consistently strong alignment with the experimental data. The model exhibits an R-square value of 0.982 for the dynamic test at 5°C/min. The performance of the model begins to shift when the curing duration extends, particularly in scenarios involving slow dynamic rates (such as 2.5°C/min) and isothermal runs at 180°C and 170°C. In these instances, a noticeable shoulder emerges in the reaction curves, indicative of a secondary

reactions. The model formulation does not account for the influence of secondary reactions. Consequently, this discrepancy becomes evident as a lack of reaction rate in the reaction curves. This supplementary reaction becomes considerably less significant with higher heating rates, causing the experimental values to fall below the predictions around the peak. This effect is also observed in the isothermal cure carried out at 160°C.

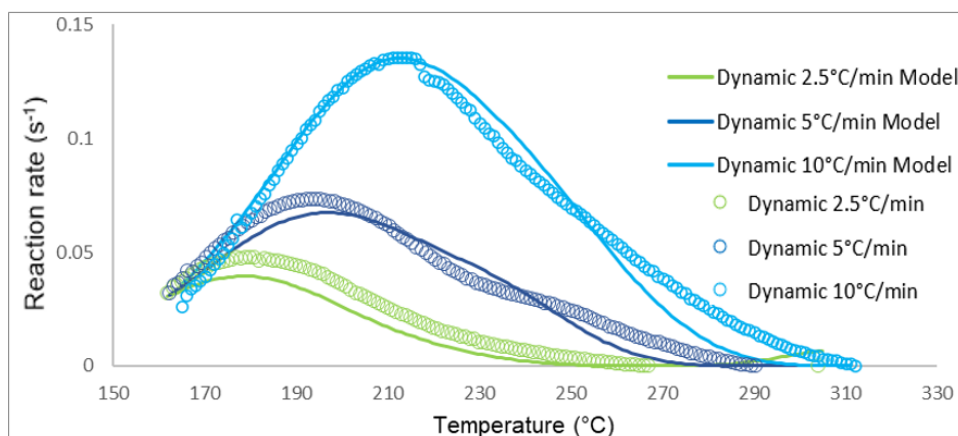


Figure 4.46: Comparison of autocatalytic cure kinetics model and experimental data for C10Z1 under dynamic conditions

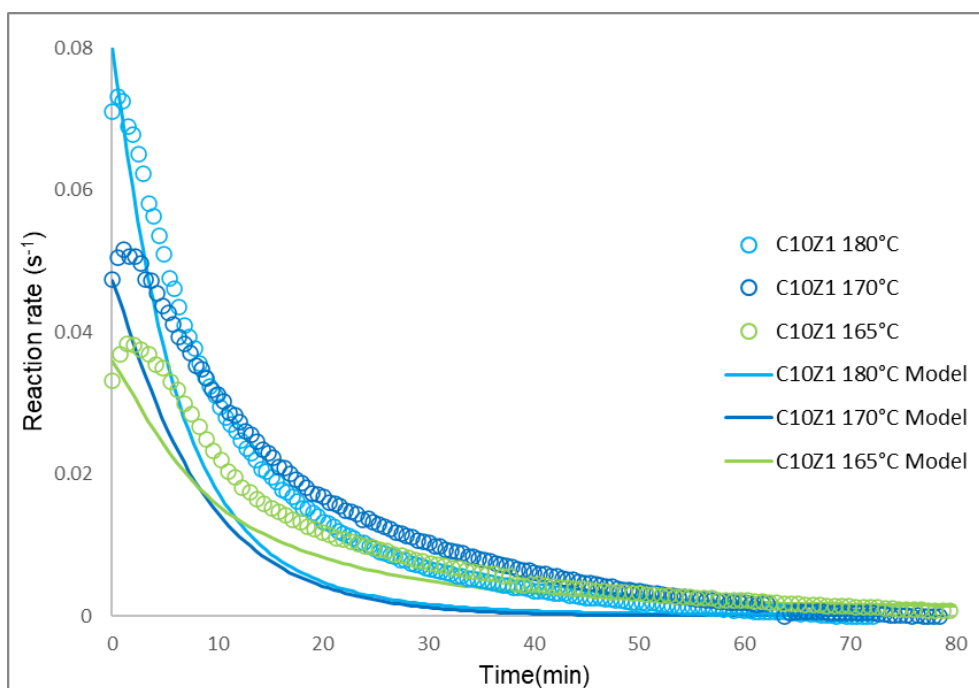


Figure 4.47: Comparison of autocatalytic cure kinetics model and experimental data for C10Z1 under isothermal conditions

The kinetics model applied to C10Z1 demonstrates a generally good agreement with the experimental data. The dynamic fitting exhibits an average R-square value of 0.937, which is greater than the R-square value for isothermal data at 0.843. This discrepancy can be attributed to the model tendency to underestimate the significance of the autocatalytic effect. This underestimation subsequently leads to deviations between the isothermal data and the model results.

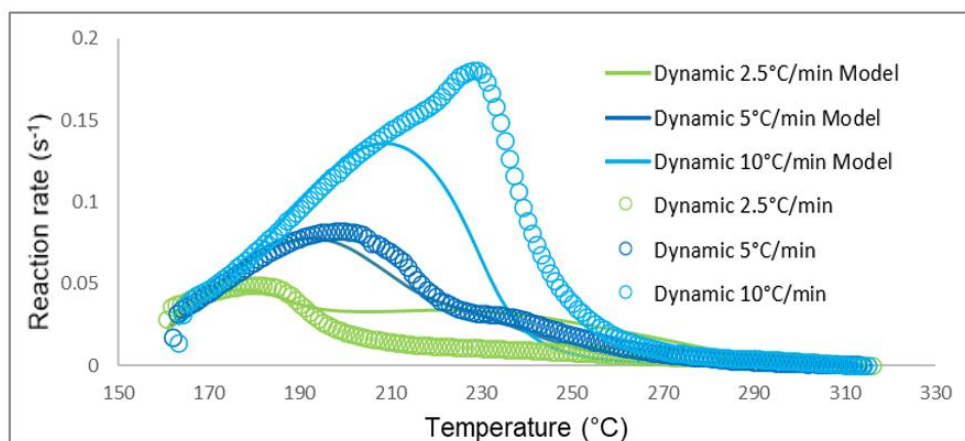


Figure 4.48: Comparison of autocatalytic cure kinetics model and experimental data for C12Z1 under dynamic conditions

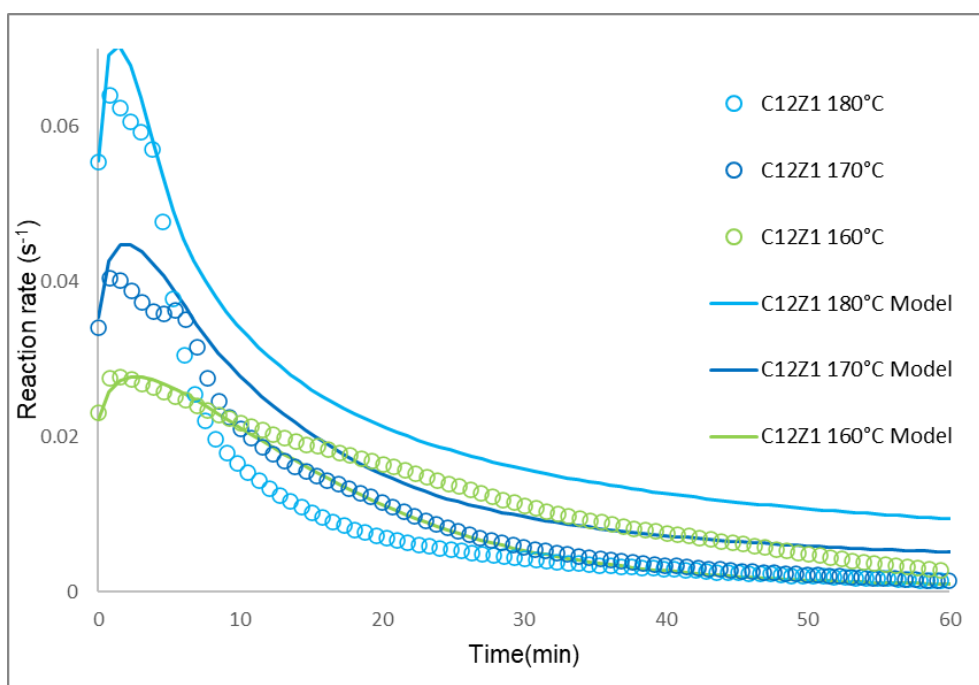


Figure 4.49: Comparison of autocatalytic cure kinetics model and experimental data for C12Z1 under isothermal conditions

The model for C12Z1 displays the weakest alignment with experimental data. This model exhibits the lowest R-square values at 0.46 for dynamic fitting and 0.70 for isothermal fitting. This discrepancy can largely be attributed to the inherent dissimilarities in the reaction mechanisms between the dynamic and isothermal curing processes. A pivotal factor contributing to this disparity is the divergence in enthalpy generation due to a secondary reaction that unfolds within the higher temperature range during dynamic curing. This significant reaction is absent in the isothermal curing process. Notably, the reaction vs. temperature curves display peaks at 230°C and 240°C for the 10°C/min and 5°C/min runs, respectively. However, the influence of the secondary reaction diminishes in the dynamic experiment at 2.5°C/min. Given that the model only accommodates the primary reaction, it fails to capture a substantial portion of the reaction that transpires during the dynamic 10°C/min test beyond 210°C. Also, by generalising the reactions into one, the model projections are marked by an elevated reaction rate for the higher temperature range of the dynamic experiment at 2.5°C/min. Furthermore, the final degree of cure for the isothermal cures only reaches 80% of the total cure compared to the dynamic conditions. The discrepancy in degree of cure towards the end of the isothermal cure causes an overestimation by the model.

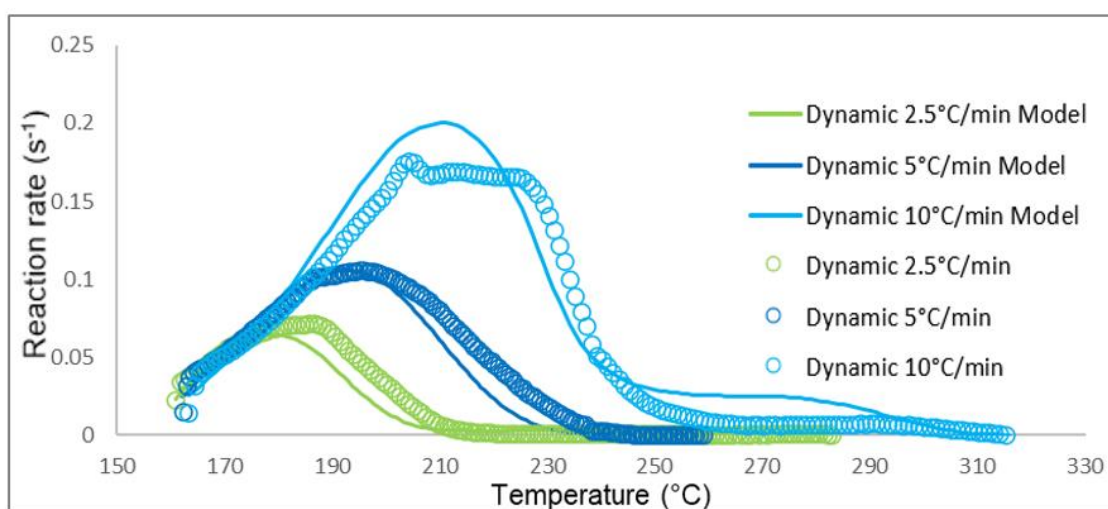


Figure 4.50: Comparison of autocatalytic cure kinetics model and experimental data for C14Z1 under dynamic conditions

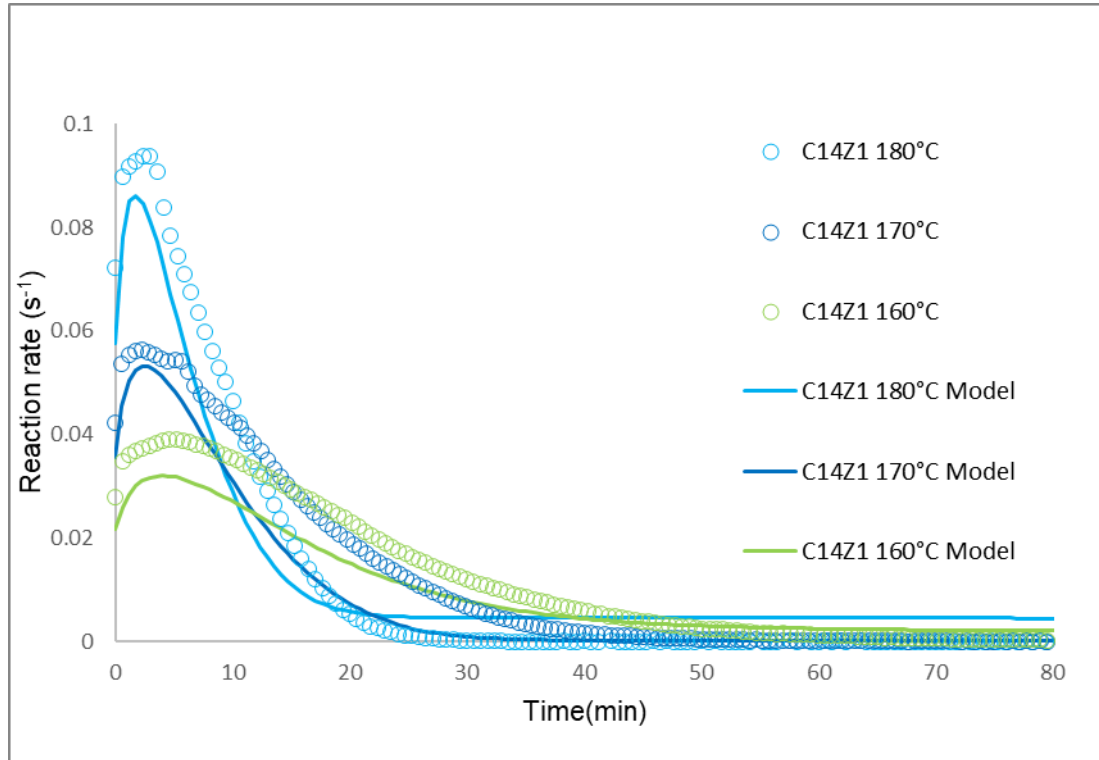


Figure 4.51: Comparison of autocatalytic cure kinetics model and experimental data for C14Z1 under isothermal conditions

The model employed for C14Z1 exhibits good agreement with both dynamic and isothermal experimental data, evident through R-square values surpassing 0.9 for both scenarios. However, there is a consistent pattern of underestimation in the reaction rate by the model post the reaction peak, except for the dynamic experiment at 10°C/min. This unique case shows a distinct behaviour, wherein the experimental data indicate a slower initial rate and a lower peak during the initial phase. This anomaly is subsequently compensated by a reaction shoulder post the plateau, roughly at 230°C. Notably, this behaviour is exclusive to the dynamic experiment at 10°C/min. This could possibly be due to the fact that at this heating rate, the reaction peaks become more challenging to distinguish. Furthermore, in comparison to all the models, the C14Z1 model accentuates the impact of autocatalysis. This is exemplified by its high m value of 0.227, which

is the highest among the models. This autocatalytic effect becomes particularly evident in the isothermal curves, characterised by their steep peaks.

Table 4.12: MSR, RMSR and R^2 values of the autocatalytic model for all the vitrimer formulations

Formulation	DSC Method	Heating rate (°C/min) / Temperature (°C)	MSE(s ⁻²)	RMSE(s ⁻¹)	R-square
C6Z1	Dynamic	2.5	0.0088	0.089	0.945
		5	0.0079	0.099	0.959
		10	0.0151	0.214	0.951
	Isothermal	165	0.0029	0.049	0.940
		170	0.0018	0.031	0.972
		180	0.0056	0.136	0.794
C8Z1	Dynamic	2.5	0.0063	0.079	0.855
		5	0.0031	0.045	0.982
		10	0.0057	0.101	0.975
	Isothermal	160	0.0028	0.047	0.708
		170	0.0024	0.043	0.922
		180	0.0027	0.048	0.962
C10Z1	Dynamic	2.5	0.0053	0.073	0.889
		5	0.0047	0.063	0.954
		10	0.0062	0.093	0.967
	Isothermal	165	0.0022	0.040	0.886
		170	0.0070	0.110	0.780
		180	0.0049	0.081	0.862
C12Z1	Dynamic	2.5	0.057	0.155	0.081
		5	0.009	0.063	0.942
		10	0.044	0.454	0.362
	Isothermal	160	0.002	0.037	0.861
		170	0.002	0.049	0.837
		180	0.006	0.121	0.403
C14Z1	Dynamic	2.5	0.0048	0.099	0.904
		5	0.0072	0.130	0.917
		10	0.0137	0.207	0.927
	Isothermal	160	0.0022	0.031	0.951
		170	0.0038	0.072	0.885
		180	0.0047	0.062	0.947
Average			0.0084	0.0973	0.8439

The accuracy of the estimation of the models are quantified as the mean square error, root mean square error and R-square values listed in Table 4.12. Based on

the results presented in Table 4.12, the MSE values for all formulations indicate small errors, demonstrating a high level of goodness of fit. The overall closeness between the observed and fitted values is quantified at 84.4%, with the majority of the fittings exceeding 90%. However, there are exceptions, notably the fitting for C12Z1. While its dynamic run at heating rates of 5°C/min, along with the isothermal test conducted at 160°C and 170°C, exhibit high R^2 values of 94.2%, 86.1%, and 83.7% respectively, the remaining experimental data do not align well with the established model. The R^2 values for the dynamic test with a heating rate of 2.5°C/min and 10°C/min, and the isothermal tests conducted at 180°C, are notably lower at 8.1%, 36.2%, and 40.3% respectively. One possible explanation for this discrepancy could be associated with the occurrence of significant secondary reactions at temperatures higher than those utilised in the isothermal tests, as well as the variation in the reaction mechanism observed in dynamic tests under different heating rates. The fitting of the data best describes the behaviour observed in the dynamic test at a heating rate of 5°C/min. However, in the case of the dynamic tests at a heating rate of 10°C/min, the corresponding fit appears to be shifted to a lower temperature range, indicating a failure to adequately account for the contribution of the secondary reaction. Conversely, for the dynamic test at a heating rate of 2.5°C/min, the fit seems to overestimate the influence of the secondary reaction. Considering the characteristic behaviours of vitrimeric materials, one plausible explanation for this phenomenon is that the rapid initiation of the reaction results in a swift increase in crosslink density, thereby impeding the movement of reactive molecules with higher temperature ramp rates. Consequently, a higher proportion of the secondary reaction is likely to occur, leading to the observed discrepancies in the fitting results.

In summary, the DSC analysis showed that the curing reaction is dominated by one main reaction peak with evident secondary reaction peaks. The reproducibility of DSC results was examined and found to be high, with only minor enthalpy differences in of 2-4% observed between sets of dynamic experiments. In dynamic experiments, the total enthalpy appears to increase with decreasing rate with the 2.5°C/min experiments result in about 13% higher enthalpy than

10°C/min tests. This indicates that additional reactions may be happening at a much slower rate.

The curing mechanism of epoxy and dicarboxylic acid involves addition esterification of epoxy and carboxylic acid groups, and transesterification, leading to diester and diol formation. Transesterification occurs more slowly than addition esterification, contributing to crosslinked structure and vitrimer adaptability. The first reaction usually completes within the first hour once the reaction starts, while the second reaction takes longer, in the order of hours to tens of hours. In off-stoichiometric conditions insufficient carboxylic acid content could lead to the formation of ethers through anionic homopolymerisation of the remaining epoxy^{50,47} and extra amount of carboxylic acid would lead to condensation polyesterification¹⁵⁸. These reactions are slower and much less likely to occur in stoichiometric balanced system at higher temperatures due to higher activation energy. Therefore, in a stoichiometric system it is most likely that the slow reaction causing the variation of the total enthalpy among the tests with different heating rates is the slow transesterification reaction.

There is significant variation in total specific enthalpy among different formulations which reaches up to 40%. Part of this is attributed to the difference in molecular weight of the dicarboxylic acids. Once this is taken into account by comparing molar enthalpies variation is about 20%. This variation is likely to be linked to the effect of secondary reactions.

The enthalpy measured in isothermal DSC experiments tends to be lower than the total enthalpy of dynamic tests. The differences vary with formulations and are on average in the 55-85% range. This effect can be attributed to secondary reactions that initiate at higher temperatures in dynamic tests, around 230-240°C, which is significantly over the temperatures of isothermal tests. In terms of cure analysis this effect was taken into account by computing the degree of cure based on total enthalpies determined under dynamic conditions. This results in partial curing under isothermal conditions, which can be as low as 55%. To validate this analysis and the consistency of the cure kinetics framework data from dynamic tests were overlaid with isothermal reaction rates corresponding to the same point

in the degree of cure-temperature space. The results showed minor discrepancies between dynamic and isothermal tests, with an average relative error of about 9%, indicating a consistent reaction rate regardless of thermal history. Some formulations showed closer alignment between dynamic and isothermal data with difference of about 3%, while in the worst case the difference reached 16%.

The reaction mechanism was found to be autocatalytic based on the isothermal experiments observations of a maximum rate not occurring right at the start of cure. The autocatalytic character which is attributed to hydroxyl produced in the early stages acting as a catalyst^{180,208,206}, was found to weak for some formulations.

Kissinger' method was employed to estimate the activation energy of the reaction of epoxy and carboxylic acid using the peak reaction temperature and the heating rate. Kissinger's method only applies to single step reactions, but it still provides a good estimation of the reaction in the systems considered in this work. When comparing the degree of cure at the peak reaction rate there is less than 7% variation indicating a consistent reaction mechanism for the same formulation. According to this analysis, a decline in activation energy is observed as the carbon chain length of the dicarboxylic acid increases. This effect is attributed to the added flexibility from increased methylene units in linear dicarboxylic acid chains. This added flexibility facilitates monomer rotation, lowering the energy needed for the reaction²¹⁰.

Three isoconversional methods were employed to examine the kinetics of the formulations, removing some of the simplifying aspects of Kissinger's method. There is a good consistency between three methods with less than about 8% difference in the estimated activation energy. The dependence of apparent activation energy on degree of cure shows three stages: an early reaction stage; (ii) the stabilised reaction stage; and (iii) the diffusion-controlled stage. In the early reaction stage, which extends up to about 30% degree of cure, the reaction shifts from non-catalysed to autocatalytic reaction due to increased hydroxyl groups which is associated with a major reduction of apparent activation energy by 30%-

70% depending on the formulation. In the stabilised stage, which extends from 30% to about 80% depending on the formulation, the apparent activation energy remains almost constant with variations of up to 10%. In the latest stage, occurring for degrees of cure over 80%, there is a consistent reduction in activation energy, indicating a shift from chemical to diffusion control²¹⁶. A comparison of activation energy value obtained with the three isoconversional method and Kissinger's method, as well as of the peak reaction degrees of cure highlight the reliability of Kissinger's method as a starting point for fitting cure kinetics models.

An autocatalytic reaction model incorporating a diffusion limitations term was utilised to fit experimental data, using the activation energies obtained by Kissinger's method, obtaining a satisfactory approximation of experimental cure kinetics results. Some of the cure kinetics model parameters have a strong dependence on the dicarboxylic acid structure. The pre-exponential factor value decreases as the dicarboxylic acid chain length increases, mirroring the trend of activation energy. The autocatalytic exponent value, mirrors closely the intensity of autocatalytic effects, with systems that showed maximum reaction very early in the cure having a low exponent, that makes autocatalytic effects almost negligible. Some discrepancies exist highlighting the cure kinetics model limitation in accounting for secondary reactions and for their impact on the overall reaction process.

5 Influence of catalyst and dicarboxylic acid structure on transition of vitrimers

At the heart of vitrimer behaviour lies the crucial role of catalysts and the fundamental structure of dicarboxylic acid components. This chapter undertakes a thorough investigation into the sophisticated relationship between these elements, scrutinizing their joint impact on the transition dynamics of vitrimers. By delving into a meticulous analysis, the chapter aspires to unveil the core mechanisms and provide valuable insights that could further the development of vitrimer applications.

5.1 Influence of catalyst and dicarboxylic acid structure on the glass transition temperature on vitrimeric materials

The study of the glass transition temperature (T_g) holds paramount significance for vitrimers, a class of dynamic polymers with reversible chemical bonds. T_g identifies the point at which a shift from a rigid, glassy state to a flexible, rubbery state occurs as temperature rises. This pivotal parameter profoundly influences vitrimer properties and applications, impacting mechanical traits, processing conditions, material stability, shape memory, and compatibility with other materials. In essence, understanding T_g is essential for tailoring vitrimers to specific uses and harnessing their versatile potential.

Table 5.1: Measured glass transition temperature (°C) for vitrimer

Material/catalyst	C6	C8	C10	C12	C14
1%	37.78±2.71	22.55±0.57	17.38±0.37	4.45±1.15	5.58±0.50
2.5%	34.17±3.11	25.52±2.46	18.92±3.79	9.30±0.32	9.88±0.41
5%	35.73±1.47	30.18±1.67	17.18±0.49	5.35±1.13	4.10±0.62
Overall	35.89±2.76	26.08±3.71	17.83±2.26	6.00±2.26	6.52±2.64

The DSC thermograms used to measure the T_g for all formulations are reported in Figure 5.1-Figure 5.5. Table 5.1 presents the T_g for all the vitrimer formulations of the study. The range of the T_g for the synthesised vitrimer formulations is quite broad according to the DSC results, spanning from a maximum of 37.8°C for formulation C6Z1 to a minimum of 4.1°C for C14Z5. This broad range indicates significant variation in the thermal properties of the vitrimers synthesised. The

results are summarised in Figure 5.6. A key observation is that materials made of the same dicarboxylic acid display only a slight variation in T_g between different formulations with varying catalyst concentrations. The spread of the three groups for each composition is around 3°C with a highest value of 3.7°C for C8 and the lowest of 2.3 for C10 and C12. Formulations C10, C12, C14 have a T_g peak at 2.5 mol% catalyst while for C6 and C8 the peaks are observed at 1 mol% and 5 mol% respectively. Upon considering the T_g values, the range, and the spread of the values, the experimental data give a clear indication that the T_g of the formulations remains unaltered by the amount of catalyst added, which aligns with results in the literature⁷⁹. Upon comparing the difference across the lines, it is evident that there is a considerable variation in T_g values between the formulations synthesised using different dicarboxylic acids, except for C12 and C14. That is a drop of 9.8°C, 8.2°C and 11.8°C of the value from the highest T_g of 35.9°C for C6 to 26.1°C for C8, 17.8°C for C10 and about 6.0-6.5°C for C12 and C14. This trend shows a strong correlation between the number of methane repetitions in the dicarboxylic acid chain and the reduction in the glass transition temperature of the synthesised formulations. However, the T_g of C12 and C14 is very similar, 6°C and 6.5°C respectively.

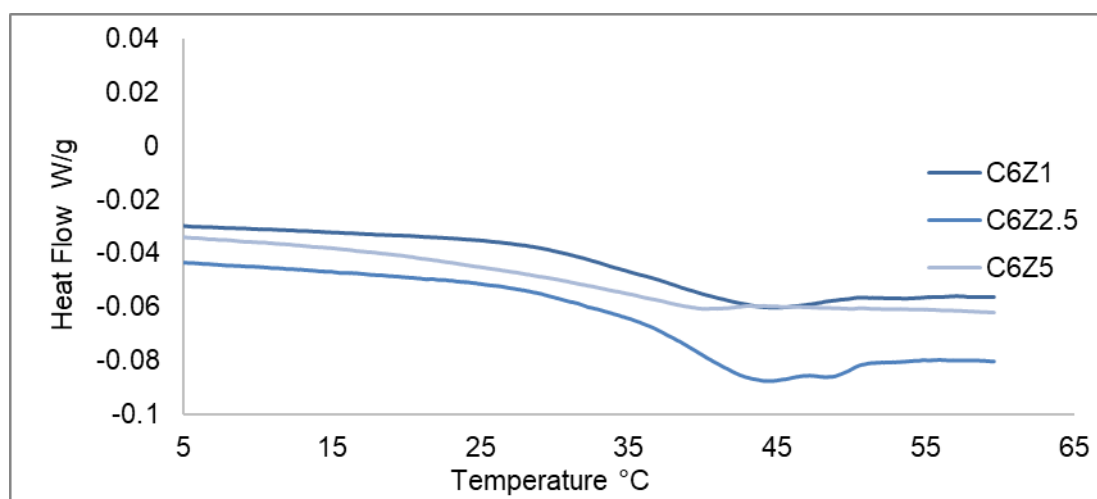


Figure 5.1: DSC scans for glass transition measurements for C6

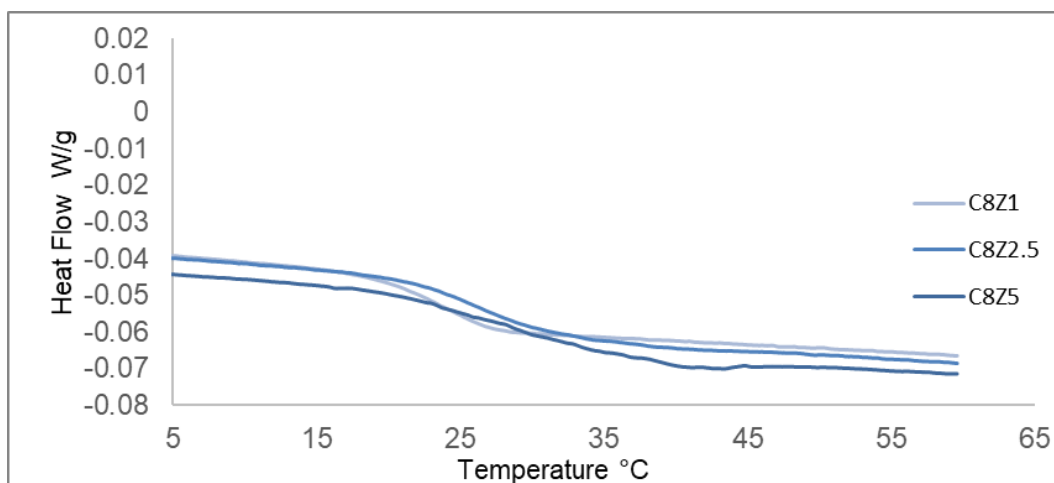


Figure 5.2: DSC scans for glass transition measurements for C8

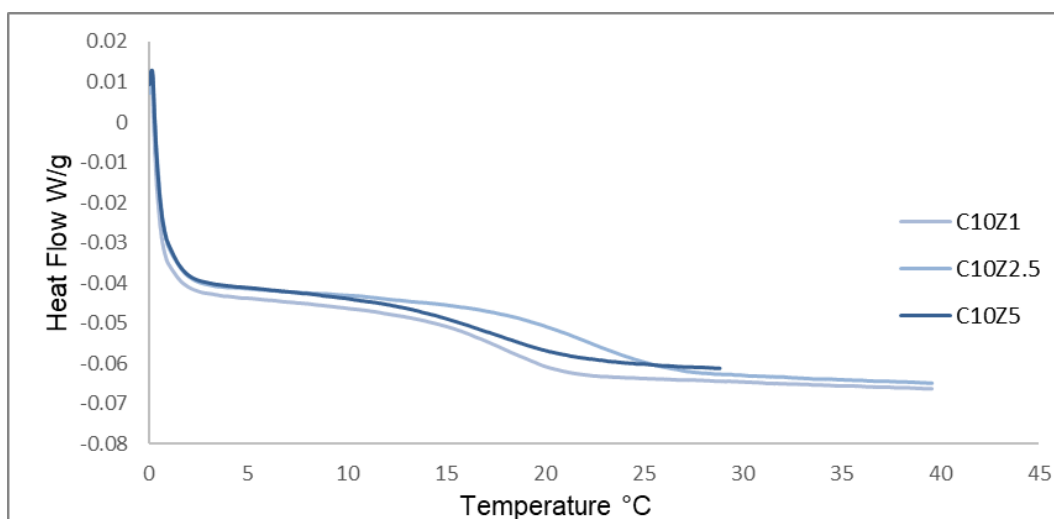


Figure 5.3: DSC scans for glass transition measurements for C10

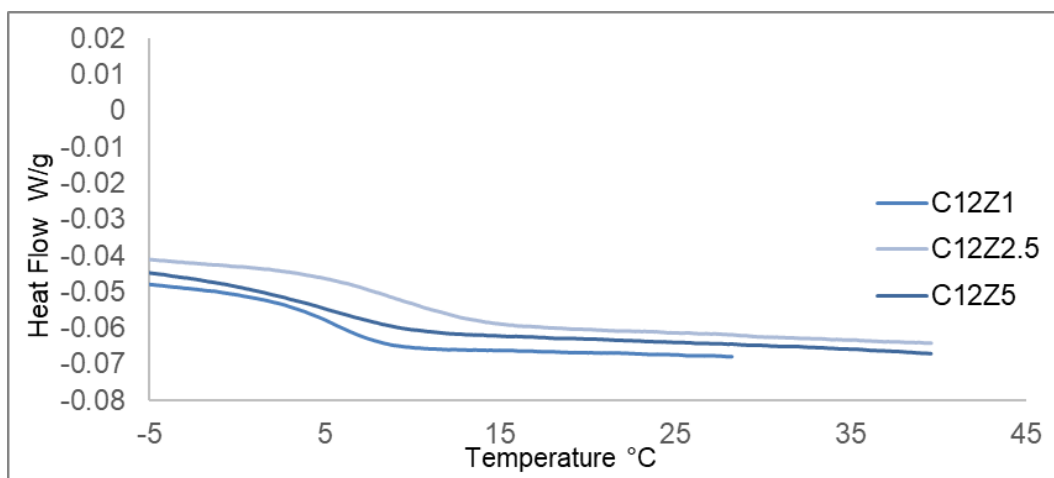


Figure 5.4: DSC scans for glass transition measurements for C12

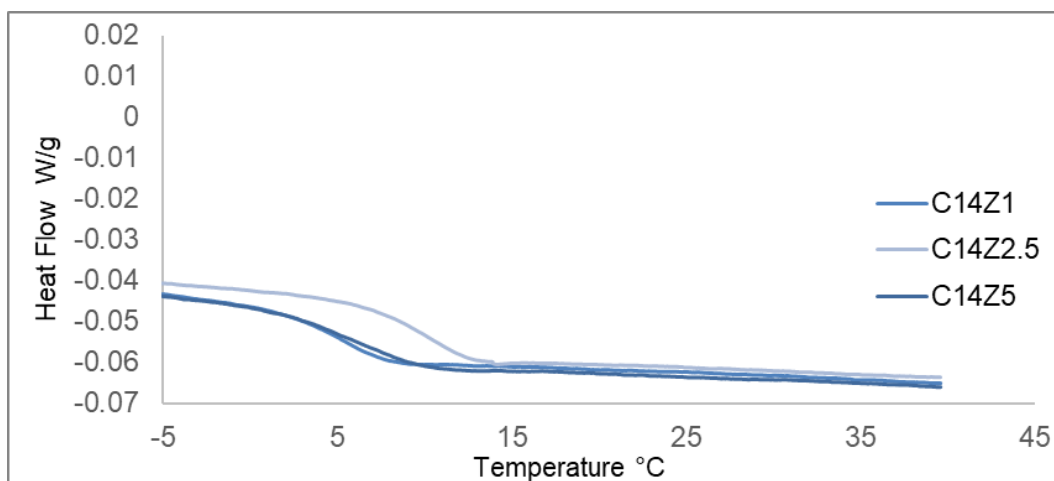


Figure 5.5: DSC scans for glass transition measurements for C14

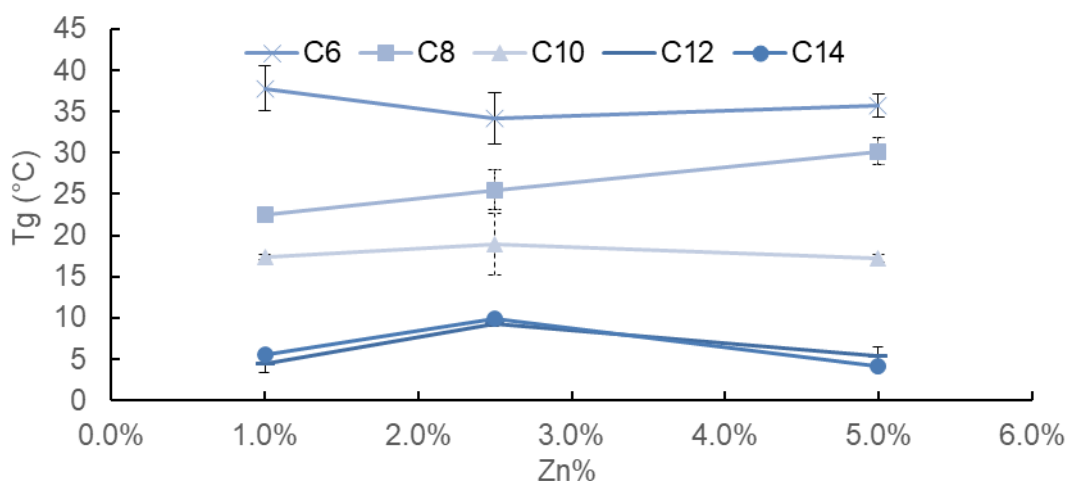


Figure 5.6: The relationship between catalyst content and glass transition temperature

The catalyst has a dual role in the systems: stimulating the ring opening of the epoxy during the polymerisation of the uncured reactants and facilitating transesterification for both network-forming and the adaptability of the crosslinked chains. During the curing process the additional catalyst expedite the cure process²¹⁷, and subsequently influences the time for the system to reach full curing. However, the formulations for this study were synthesised at a temperature where only the additional esterification and transesterification occurred. Complete crosslinking is achieved by the end of the reaction progress for all the formulations, meaning that the final degree of crosslinking is the same

for the formulations of the same dicarboxylic acid and epoxy composition regardless of their catalyst level. The FTIR results presented in Figure 5.7 confirm this. The increase of hydroxyl groups after curing is manifested as a rise of the OH peak at 3450 cm^{-1} [1]; the increase of ester groups after curing is shown in the C=O ester peak at 1730 cm^{-1} ; and the disappearance of epoxy groups after curing is shown as the drop of COC at 910 cm^{-1} .

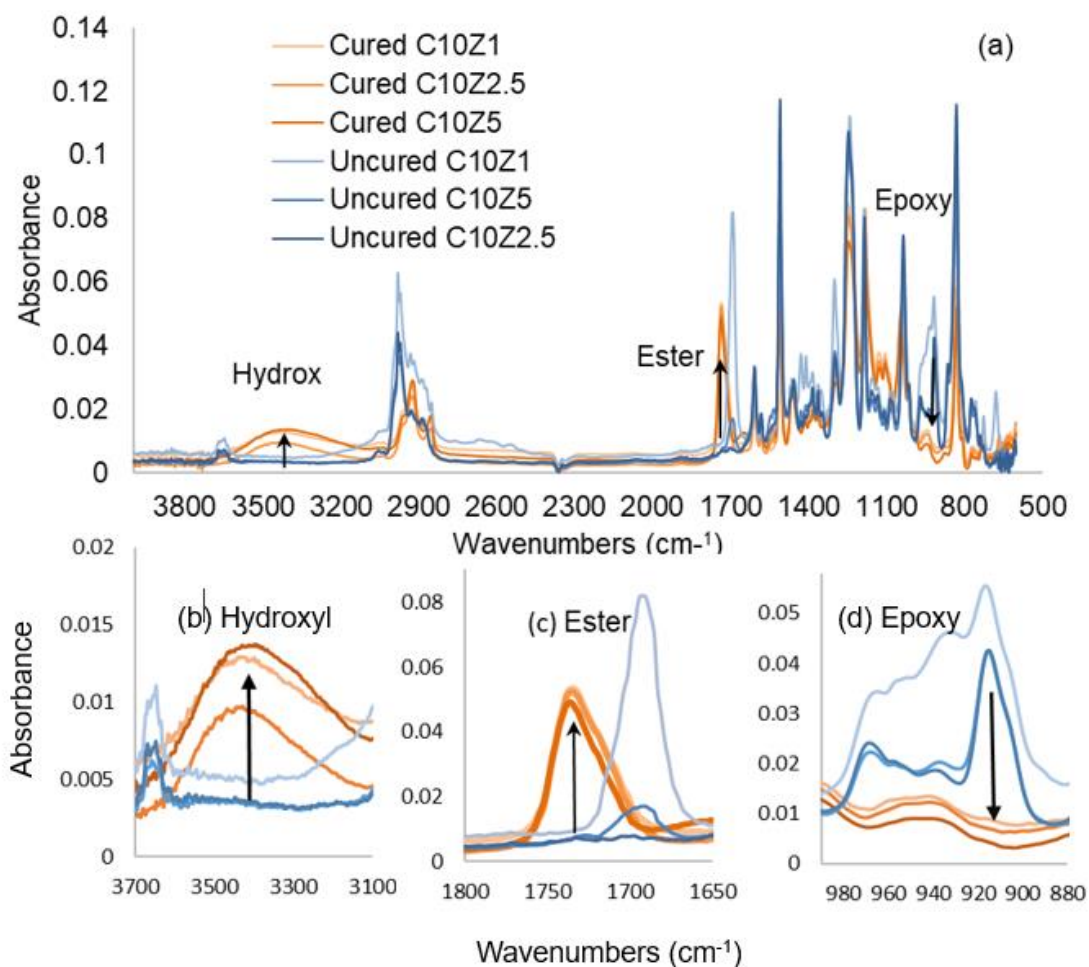


Figure 5.7: FTIR spectra of the cured and uncured vitrimer material for formulation C10 and the enlarged details of change in peak intensity in three zones with interest: (a), hydroxyl group in $3700\text{--}3100\text{ cm}^{-1}$; (b), ester group in $1800\text{--}1650\text{ cm}^{-1}$; and (c), epoxy group in $990\text{--}880\text{ cm}^{-1}$

Homopolymerisation of the epoxy does not take place during the manufacturing process for any of the formulation regardless of catalyst concentration because

the reaction temperature is not high enough for this reaction to take place across all the formulation groups²¹⁸. Otherwise, the homopolymerisation would lead to an increase in T_g . On the other hand, one of the roles of the catalyst is to accelerate the bond exchange reaction; the availability of the bond exchange at the temperature of the experiment also plays a role. In results shown later in this chapter it is shown that the vitrification temperatures of the formulations far surpass the range of measured T_v . At temperatures much lower than T_v , where the rearrangement of the macromolecules is predominantly constrained, the bond exchange process occurs at an extremely slow rate.

Figure 5.8 illustrates the glass transition temperature of as a function of chain lengths. The catalyst concentration does not influence the T_g of formulations, and that is the reason that the three lines intersect and entangle with each other. Figure 5.9 is similar, but in this case the average and standard deviation of T_g of each dicarboxylic acid group over all measurements at different catalyst concentrations are reported. There is a clear decreasing trend of the glass transition temperature as a function of dicarboxylic acid length. This phenomenon can be attributed to two factors. First, despite the differences in the structure of the reactant carboxylic acids, the likelihood of crosslink formation remains constant. However, the size of the molecules continually increases, resulting in a reduction in the statistical count of crosslink density. Lower crosslinking density results in a lower T_g ²¹⁷. The overall structure of the carboxylic acids is the same, meaning that no variation in branches, rigid building blocks, or cyclic structures can influence the comparisons. Thus, the flexibility of the chain within the polymer rises as reactant moiety elongates, inducing a drop in T_g . Such phenomenon has been described in a study based on epoxy resin and diamines of with different length of oxypropylene units gave clear results that increasing in crosslinking length reduces T_g ²¹⁹. The enhanced flexibility causes a lower energy requirement to overcome intermolecular forces and facilitates the transition of the material from a rigid, glassy state to a more flexible, rubbery state. This structural variation also influences the flow behaviour of the material, *i.e.*, bulky molecular structures and high crosslink density can compromise the polymer malleability and

reparability. Regarding the difference in T_g between C12 and C14, the findings indicate that the mean T_g is the same. One possible explanation for this observation is that when there is a sufficient amount of methylene repetition in the polymer, the impact of increased flexibility and reduced crosslinking density on T_g is less pronounced compared to its epoxy nature.

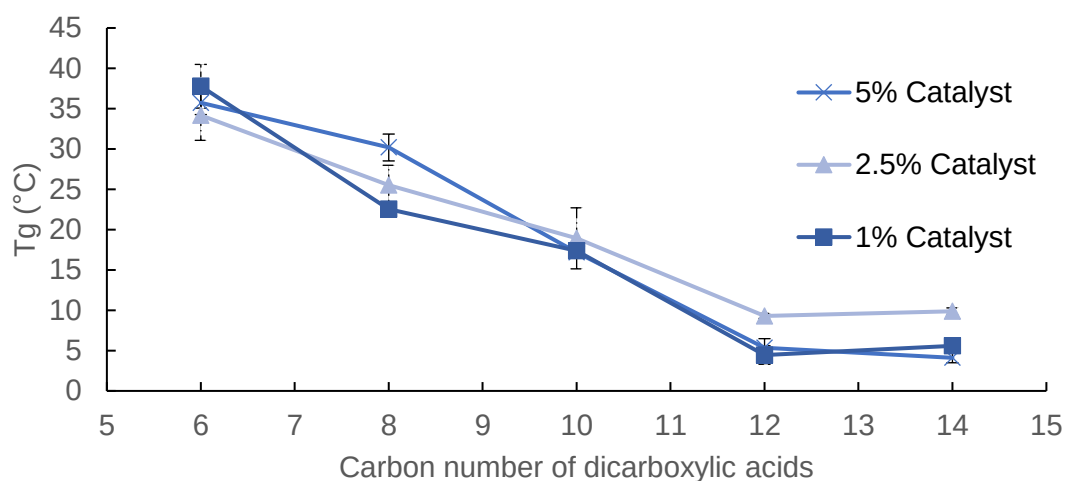


Figure 5.8: The relationship between dicarboxylic acid carbon number and glass transition temperature

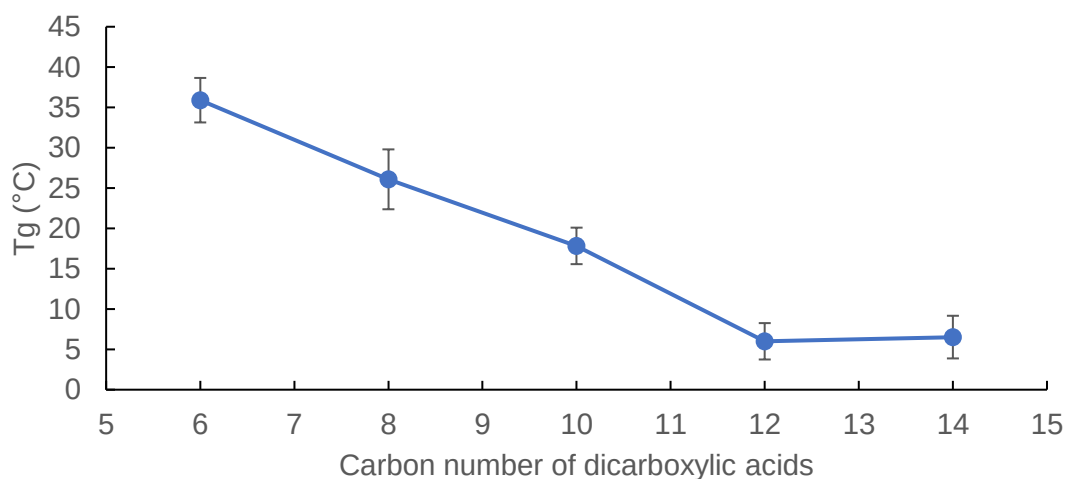


Figure 5.9: The overall trend of dicarboxylic acid carbon number and glass transition temperature

5.2 Influence of catalyst and dicarboxylic acid structure on topological transition

5.2.1 Stress relaxation results

During transesterification bond exchange, as the reactants and products have the same chemical properties and the concentration of the ester and hydroxyl groups before ($[A - B - B']$ and $[A']$) and after ($[A' - B']$ and $[A - B]$) the reaction is balanced, there is no thermodynamic preference for either side. In that case, the speed for the forward (k_f) and reverse (k_r) reactions is the same. Temperature affect the reaction kinetics in the form of Arrhenius equation as follows:

$$K_{eq} = \frac{[A - B - B'] [A']}{[A - B] [A' - B']} = 1, k_f = k_r = A_r e^{\frac{-E_{ar}}{RT}} \quad (5-1)$$

where A_r is the pre-exponential factor E_{ar} is the activation energy for relaxation, R is the universal gas constant and T the absolute temperature. This characteristic of transesterification bond exchange is responsible for the temperature-dependent viscosity of associative CANs type of vitrimers. To demonstrate this behaviour, the stress relaxation behaviour of vitrimer formulation C6Z5 across temperatures ranging from 200°C to 230°C was picked out and is depicted in Figure 5.10 as an example. The results indicate a positive correlation between temperature and the rate of stress relaxation.

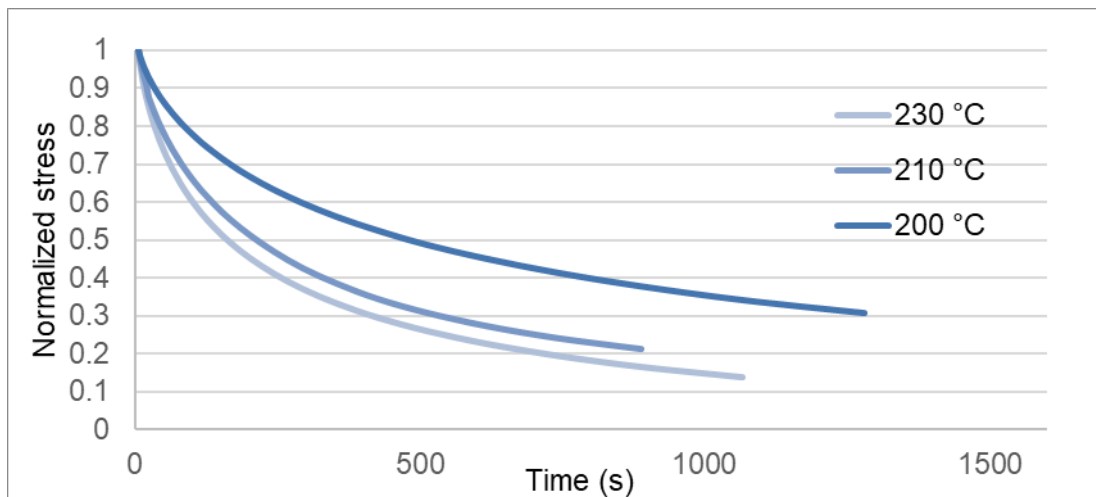


Figure 5.10: The stress relaxation behaviour of the crosslinked vitrimer C6Z5 at different temperatures from DMA analysis

Since the system is a pure transesterification vitrimer, the stress relaxation behaviour $\sigma(t)$ of the material is represented as an exponential function depending on time as follows²²⁰:

$$\frac{\sigma}{\sigma_0} = e^{-\frac{t}{\tau}} \quad (5-2)$$

where σ_0 is the initial applied stress and τ is the characteristic relaxation time. The dependence of relaxation time on temperature follows an Arrhenius law:

$$\tau = \frac{1}{K_0} e^{\frac{E_{ar}}{RT}} \quad (5-3)$$

The pre-exponential factor K_0 is the frequency of collisions and E_{ar} is comparable to the activation energy for the chemical reaction. Taking natural logarithm on both sides of the equation, there is a linear relationship between the natural logarithm of the relaxation time τ , with an intercept equal to $\ln \frac{1}{K_0}$ and slope equal to $\frac{E_a}{R}$.

$$\ln \tau = \ln \frac{1}{K_0} + \frac{E_{ar}}{R} \frac{1}{T} \quad (5-4)$$

The activation energy E_a in the context of viscous flow describes how sensitive the viscosity of associative CANs (Covalent Adaptable Networks) is to changes in temperature. Higher values of E_{ar} mean that the viscosity decreases rapidly as the temperature increases, whilst vitrimers with lower E_a show less pronounced viscosity changes. This characteristic can be advantageous when incorporating vitrimeric materials into practical applications. Systems with high E_{ar} values are expected to exhibit improved dimensional stability at service temperatures due to the high energy barrier of the bonds, while also allowing for fast processing at the required reprocessing temperature. The y-intercept of the Arrhenius fit is $\ln(1/K_0)$, which can be interpreted as the relaxation time without thermal constraints²²¹. The coefficients obtained by fitting Eq. (5-4) to experimental data for all formulations are reported in Table 5.2.

Table 5.2: Intercepts and slopes for the Arrhenius fitting for the vitrimer formulations

Material	$\ln(1/K_0)$	E_{ar}/R
C6Z1	-11.513	97615
C6Z2.5	-11.513	89973
C6Z5	-8.5172	71594
C8Z1	-23.131	15635
C8Z2.5	-17.728	12515
C8Z5	-18.421	11777
C101	-15.425	11551
C10Z2.5	-17.322	12153
C10Z5	-18.644	11834
C12Z1	-13.921	10742
C12Z2.5	-23.719	13713
C12Z5	-18.932	11201
C14Z1	-13.816	10240
C14Z2.5	-16.629	10650
C14Z5	-16.341	10417

5.2.2 Influence of catalyst

Figure 5.11-Figure 5.15 illustrate the stress relaxation behaviour of vitrimer formulations made of the same dicarboxylic acid and epoxy composition with different catalyst levels (1 mol%, 2.5 mol%, 5 mol%) under the same temperature. Formulations with higher catalyst content exhibit faster stress relaxation. This phenomenon has also been observed in other studies^{79,222,223,224}. The presence of the catalyst provides a pathway for the reaction to happen with a much lower energy barrier by activating both the ester and alcohol groups simultaneously²²⁵. The mechanism of lowering the energy barrier remains consistent for a specific type of bond exchange associated with a particular catalyst. This is characterised by a constant activation energy, which remains unchanged despite variations in catalyst concentration^{79,4,221}. However, an increase in catalyst content provides more sites for bond exchange to occur therefore increases the overall rate of transesterification. As the activation energy (E_{ar}) and the amount of catalyst together determine the reaction rate. This relationship is described by Eq.(5-2), where the activation energy is constant for all catalyst concentrations, but the pre-exponential coefficient (A_r). increases with increasing catalyst content.

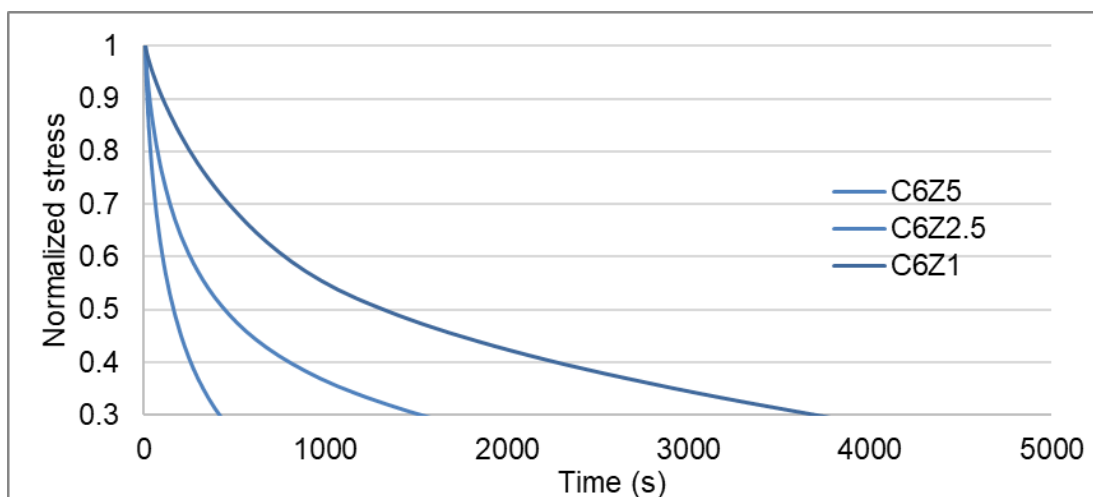


Figure 5.11: Vitrimer C6 stress relaxation at 230°C from DMA analysis

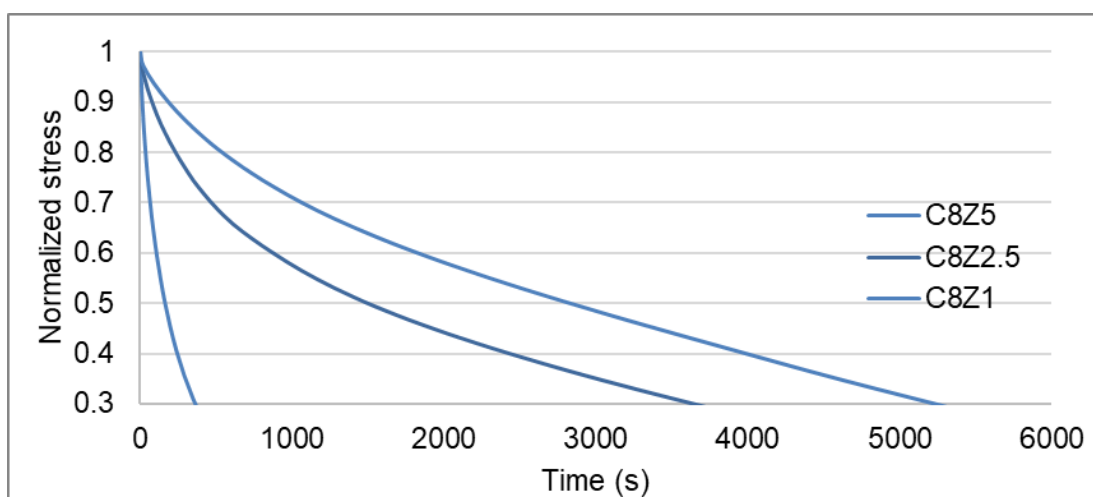


Figure 5.12: Vitrimer C8 stress relaxation at 230°C from DMA analysis

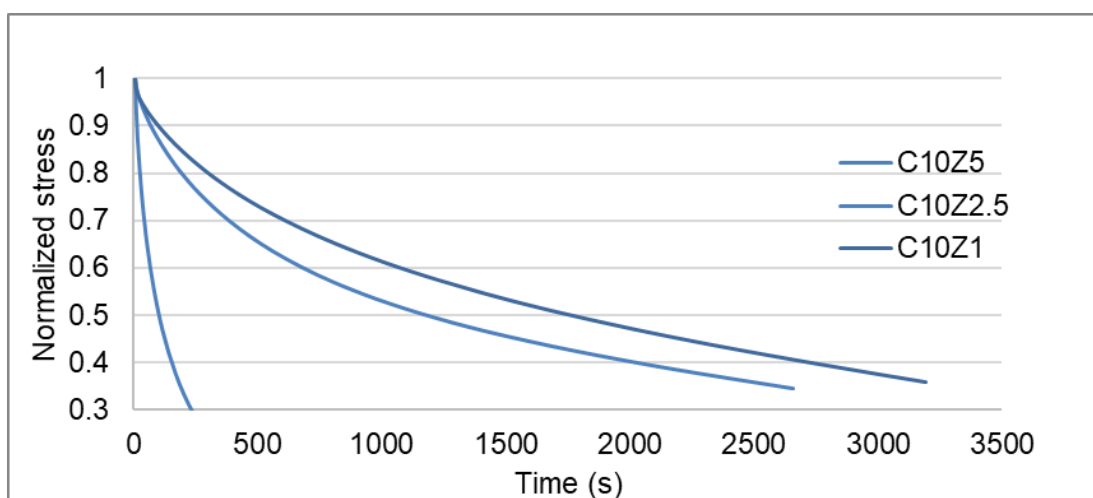


Figure 5.13: Vitrimer C10 stress relaxation at 230°C from DMA analysis

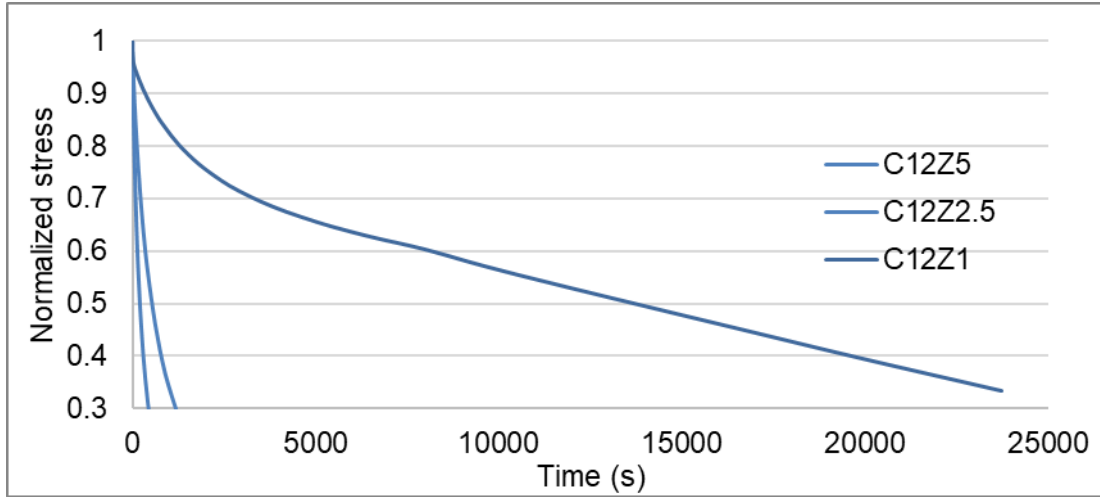


Figure 5.14: Vitrimer C12 stress relaxation at 180°C from DMA analysis

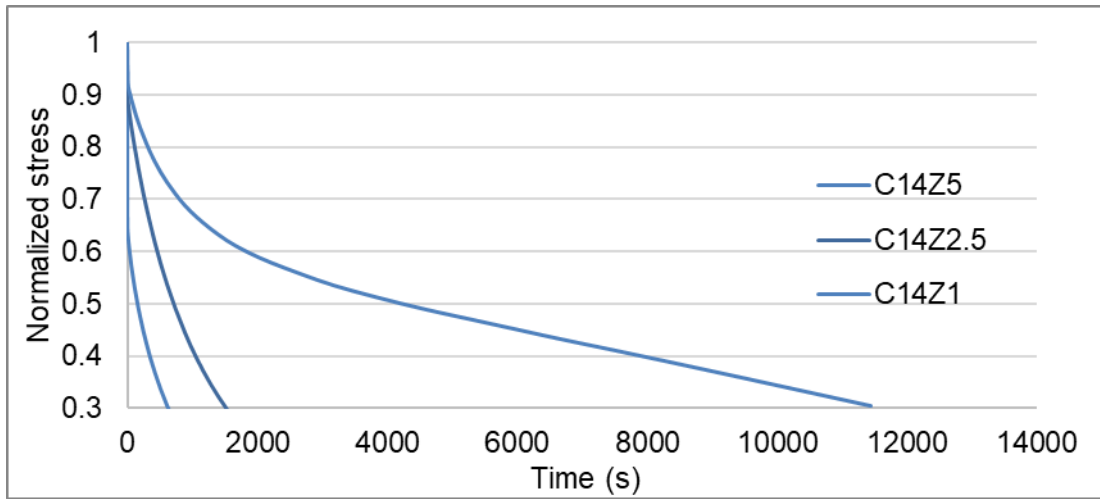


Figure 5.15: Vitrimer C14 stress relaxation at 180°C from DMA analysis

The topological transition temperature (T_v) is utilised as an indication of the solid-to-liquid transition temperature when the material reaches a viscosity of 10^{12} Pa·s.¹ This is calculated from the relaxation time recorded by stress relaxation experiments with the employed Maxwell relation:

$$\eta = G\tau^* \quad (5-5)$$

$G = 1$ MPa as a default value for rubbers; therefore T_v is the temperature at which the relaxation time τ^* reaches 10^6 s. This value greatly exceeds the time frame of laboratory observation. Therefore, the temperature at which τ^* reaches 10^6 s

is extrapolated using the Arrhenius fitting from Eq.(5-2), using the activation energy and pre-exponential factor value reported in Table 5.3.

The data and the fitting are illustrated in Figure 5.15-Figure 5.20. The issue of limited testing temperature ranges, which has historically led to potentially unreliable predictions, is a critical point of consideration. Traditionally, tests have been conducted within a narrow 20-30°C range, primarily due to the limited window that allows for effective observation—a constraint deeply rooted in the field's legacy. In recognition of this significant limitation, this thesis has adopted an innovative approach. The methodology involves adjusting the data points through the application of exponential decay fitting to the relaxation times obtained from the actual data. This strategy is aimed at yielding more reliable and accurate predictions, thus addressing a long-standing limitation in the field. The T_v values for all the formulations are listed in Table 5.3 and shown in Figure 5.21. The results show that catalyst content has significant effect on T_v . A decrease of 30 to 65°C in T_v is observed when the catalyst concentration increases from 1% to 5%. The obtained fittings for all formulations follow an exponential dependence.

Table 5.3: Topological transition temperatures for all formulations

Formulation	T_v (°C)	Activation Energy (kJ/mol)	Average E_{ar} (kJ/mol)	Fitted E_{ar} (kJ/mol)	Fitted T_v (°C)
C6Z1	112.25	81.16	71.83	73.44	104.25
C6Z2.5	82.08	74.8			83.92
C6Z5	47.43	59.52			66.12
C8Z1	150.02	112.82	104.93	107.63	136.34
C8Z2.5	123.61	104.05			126.31
C8Z5	92.19	97.91			104.09
C10Z1	121.89	96.04	98.49	98.17	123.63
C10Z2.5	117.15	101.04			113.68
C10Z5	91.43	98.39			91.42
C12Z1	114.15	85.39	93.85	99.85	121.20
C12Z2.5	92.35	107.1			84.54
C12Z5	68.89	89.08			74.13
C14Z1	97.45	101.76	85.62	86.95	99.27
C14Z2.5	76.67	82.01			76.29
C14Z5	72.27	73.08			72.36

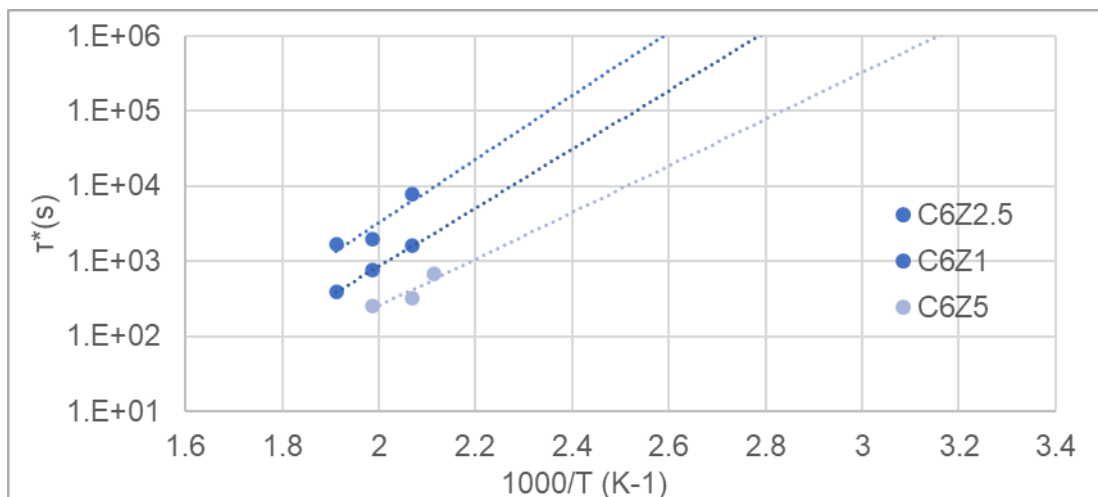


Figure 5.16: Dependence of the relaxation time on temperature of vitrimer C6

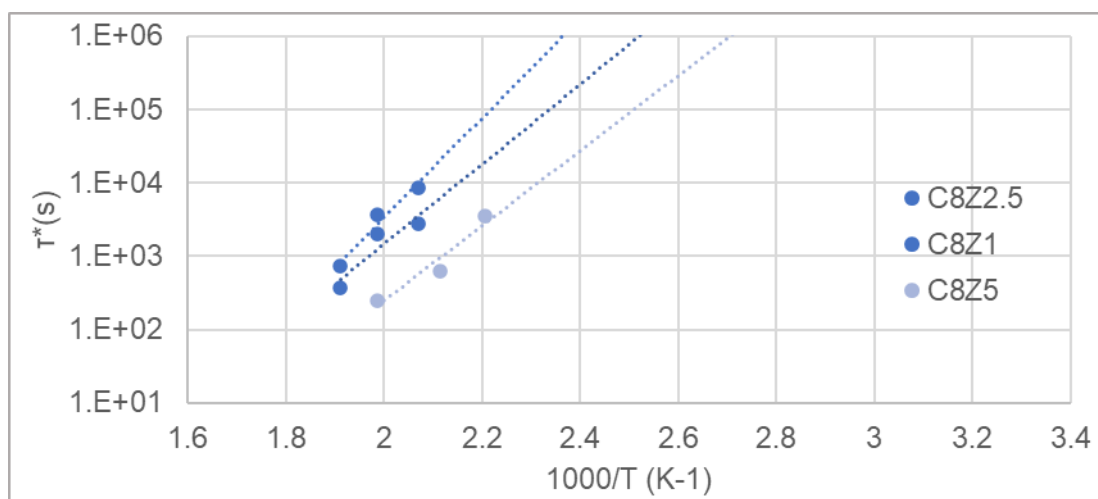


Figure 5.17: Dependence of the relaxation time on temperature of vitrimer C8

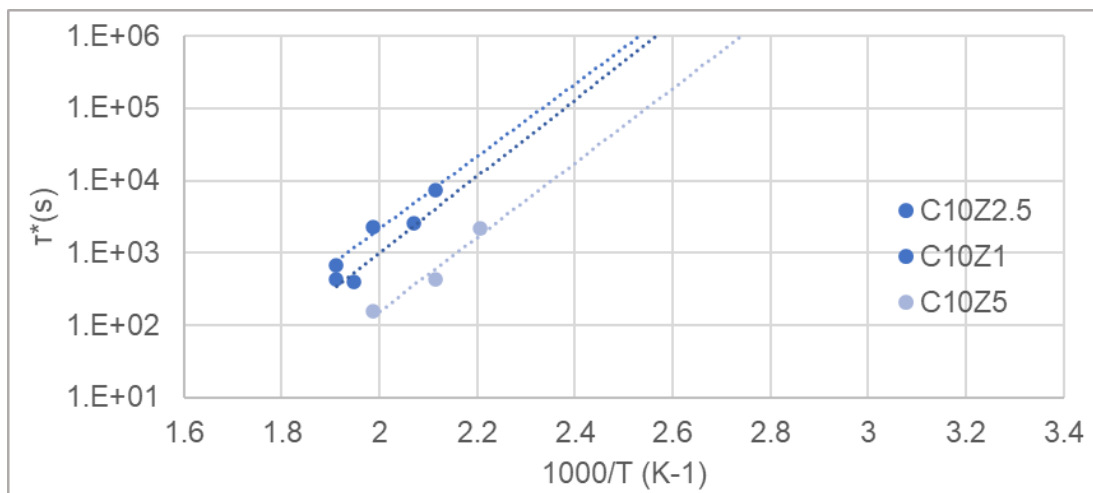


Figure 5.18: Dependence of the relaxation time on temperature of vitrimer C10

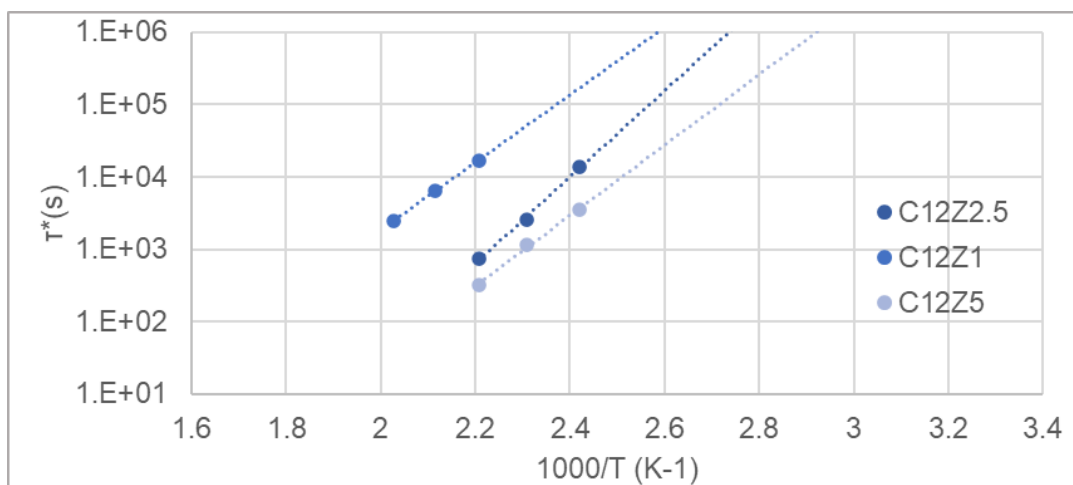


Figure 5.19: Dependence of the relaxation time on temperature of vitrimer C12

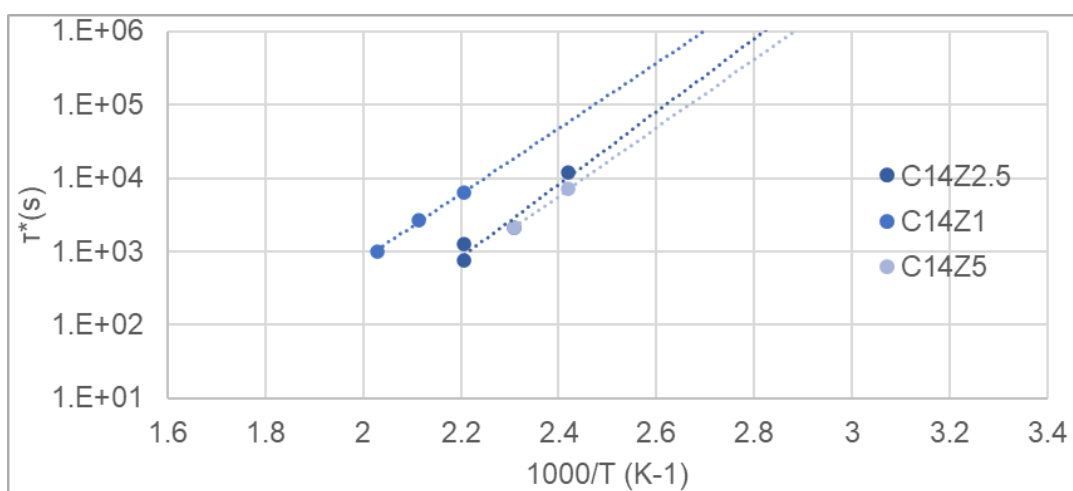


Figure 5.20: Dependence of the relaxation time on temperature of vitrimer C14

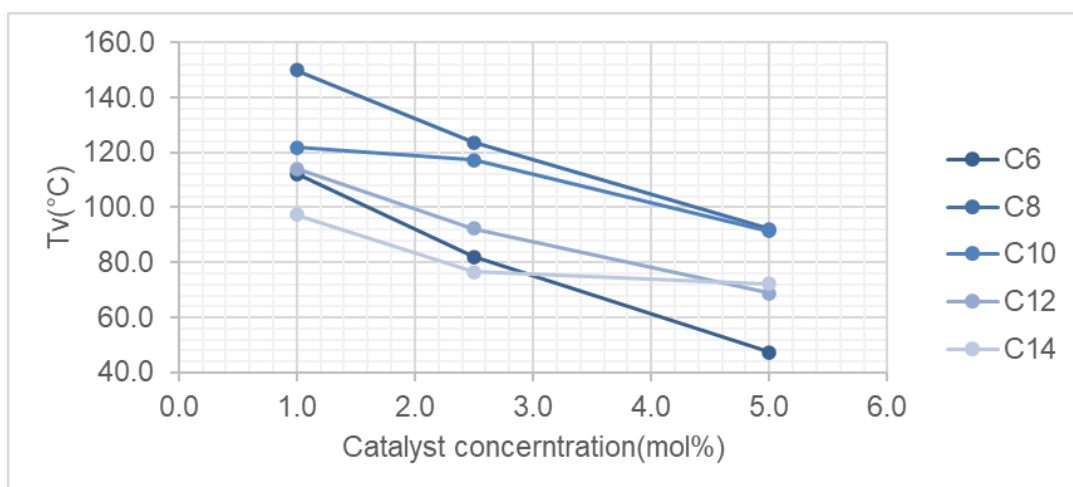


Figure 5.21: Topological transition temperature as function of catalyst content

5.2.3 The effect of monomer dicarboxylic acid structure on vitrimer relaxation

The macroscopic flow and stress relaxation behaviour is the result of the bond exchange reaction, the speed of which is a statistical effect. The speed it is determined by two factors: (i) the amount of the reacting groups; and (ii) their accessibility. Taking into consideration the molecule structure and the reaction pattern, there are five factors that influence the bond exchange rate: the amount of hydroxyl and ester groups, chain flexibility, catalyst concentration, crosslinking density, and the statistical distance between reaction groups²²⁶. To examine the influence of dicarboxylic acid chain length on the overall topology rearrangement and stress relaxation behaviour, it is necessary to take into account all five factors. However, the impact of catalyst concentration on bond exchange has been extensively investigated and does not contribute to the other factors on the dicarboxylic acid structure level.

Table 5.4: Influence of increasing methylene groups in dicarboxylic acid chains on bond exchange rate

Factor/property	Effect of increasing CH ₂ repetition in linear dicarboxylic acid chain	Effect on bond exchange
Crosslink density	↓	↑
Chain flexibility	↑	↑
Functional groups	↓	↓
Distance between functional groups	↑	↓

The individual influence of increasing methylene units in the linear dicarboxylic acid chain for crosslinking density, chain flexibility, the availability of functional groups, and the distance between the functional groups for transesterification are listed in Table 5.4. Longer chain length leads to fewer crosslinks in the same space and it is easier for hydroxyl ends and ester groups to move through the network and reach each other to complete transesterification. Also, longer chains

bring more flexibility to the backbone which grants more adaptability to the backbones to change their configuration. Conversely, lengthening the chain introduces two factors that inhibit bond exchange: a reduction in the relative density of functional groups and an increased distance that exchangeable ends must travel to take part in the reaction.

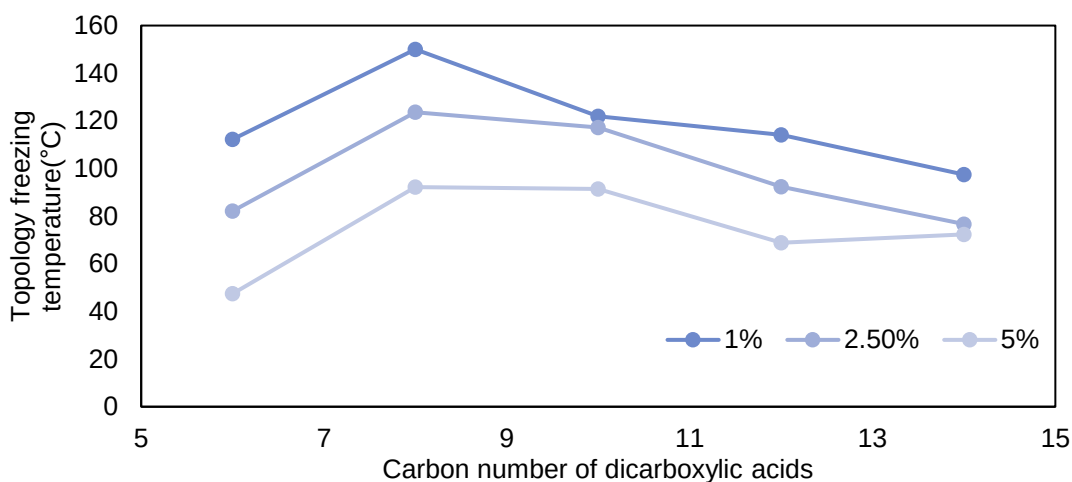


Figure 5.22 illustrates the dependence of T_v on chain length and catalyst concentration. T_v shows an increase-plateau-decrease pattern as chain length increases. After reaching the peak, the disparity in T_v between formulation groups decreases as the chain length approaches its upper limit. Formulation C6, with the shortest linear methylene chain in the chain, exhibits the fastest stress relaxation and bond exchange, along with the lowest corresponding T_v when 5 mol% catalyst is present. This vitrimer has the highest functional group density and the shortest travel distance, promoting localised and vigorous bond exchange. Consequently, the potential hindrances of diffusion, resulting from high crosslink density and stiff chains, are comparatively less significant. The fact that vitrimers synthesised using suberic acid and sebacic acid (formulations C8 and C10) have the highest T_v and the decreasing trend after that, gives a clear indication that when gradually increasing the length of the dicarboxylic acid chain, at first, the end-to-end distance plays a more significant role in the transesterification reaction. This is due to the greater relative difference created by the addition of chain length, considering the short repeating units. This effect is attenuated as the number of methylene groups increases further.

Simultaneously, the reduction in crosslink density and the presence of longer chains allow for more flexibility within the network. This effect overrides the influence of the increase in reaction end distance and decrease in functional group density. A similar influence of the longer alkyl chains on T_v is reported by Yang *et al.*²²⁷ where a 12°C drop in T_v was observed between epoxy vitrimers cured by dodecanedioic acid and octadecanedioic acid with the same catalyst content. As the chain length increases continuously, and the molecular weight of the backbone between exchangeable crosslinks reaches a certain level, there is a threshold beyond which the change in chain length no longer affects the entanglement or flow rate of the network but instead dilutes the density of reaction ends²²⁸. This leads to a decrease in the bond exchange rate, resulting in slower stress relaxation and a higher T_v .

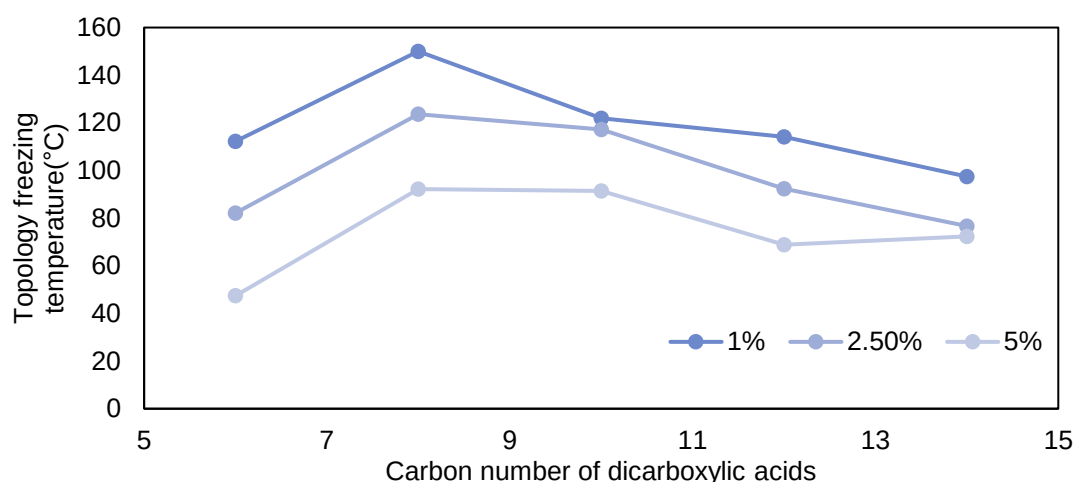


Figure 5.22: Topology freezing temperature of all formulations

5.2.4 Relationship between catalyst concentration, activation energy and the kinetics coefficient of bond exchange

Figure 5.23 report the activation energy for the relaxation of materials. The value of the activation energy is greatly affected by the difference in the dicarboxylic acid structure. The result in Figure 5.23 shows the lowest average E_{ar} of 71.8 kJ/mol for C6 before a peak in E_{ar} for C8 of 104.9 kJ/mol. Then the value steadily decreases to 85.6 KJ · mol⁻¹ as the length of the dicarboxylic acid goes up to C14.

Since the catalyst used is same for all materials for this work, the variations could only be the result of the different chemical construction based on the various studies that the amount of the catalyst does not affect the activation energy for the bond exchange and the relaxation. The change of also has a great agreement to the trend of the influence of their structure on T_v . Similar principles for the probability of the reaction to take place based on the crosslink density and the abundance of the functional groups, chain flexibility also applies to this case²²⁹. The activation energy is related to the nature of both the catalyst and the reaction the range of the value across a great span. For the transesterification reaction catalysed by $\text{Zn}(\text{acac})_2$, the reported E_{ar} varies from 24 kJ/mol to 163 kJ/mol^{229,230}.

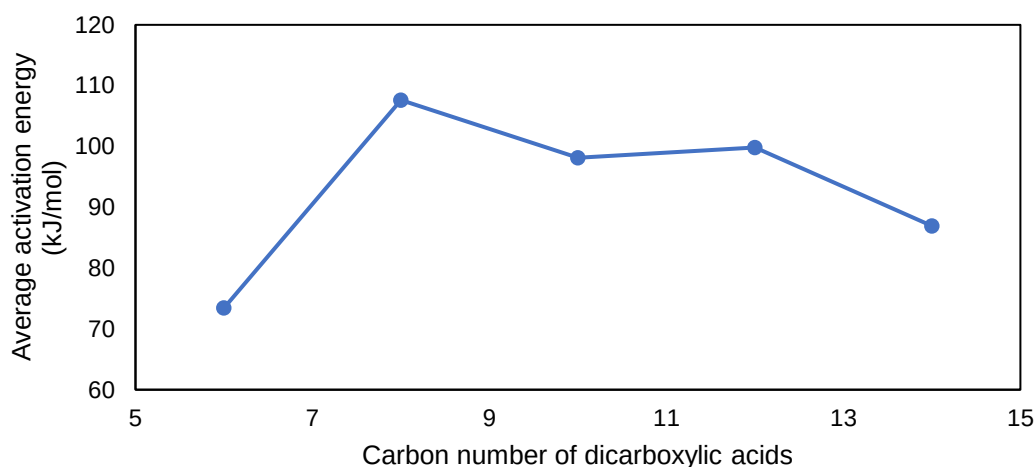


Figure 5.23: Activation energy as a function of chain length

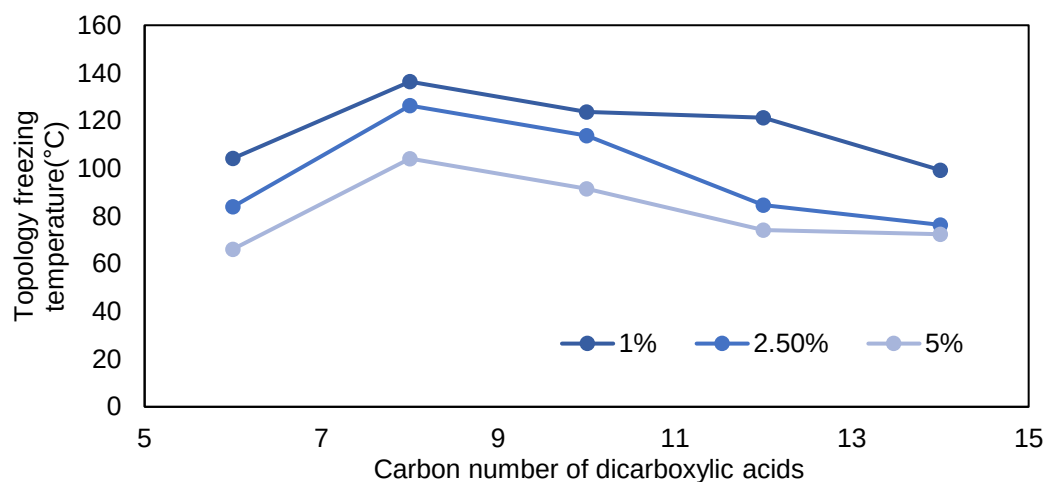


Figure 5.24: Topology freezing temperature as a function of chain length

As discussed in 5.1, the effect of the amount of catalyst on the system does not play a significant role in determining its glass transition temperature. The utilisation of the stress relaxation model provides a valuable estimation of the extent of catalyst-induced bond exchange that would bring into the system at a temperature, much lower than the topology transition temperature. Therefore, to better visualise the effects, the expected relaxation time for each formulation is obtained from the modified fittings based on Eq.(5-5) is listed in Table 5.5. Across the table, the relaxation time ranges from 1.30×10^7 s to 3.65×10^{11} s. The relaxation time does decrease with the increase in catalyst content. However, for the DSC tests, the overall testing time is on a scale of 10^3 s, and even the shortest relaxation time is on a scale of 4 orders of magnitudes greater than this. This the idea that bond exchange around a temperature that is much lower than its topology transition temperature is insignificant to alter the results of glass transition behaviour. When the measurement of the T_g is conducted over an extended time frame that is at an extremely slow temperature ramp rate, the result would possibly show some dependency between catalyst concentration and T_g .

Table 5.5: Estimated relaxation time for all vitrimer formulations at their T_g

	C6	C8	C10	C12	C14
1%	1.49×10^8 s	1.92×10^{11} s	5.33×10^{10} s	3.65×10^{11} s	1.26×10^{10} s
2.5%	5.49×10^7 s	5.62×10^{10} s	2.00×10^{10} s	7.66×10^9 s	1.12×10^9 s
5%	1.30×10^7 s	4.28×10^9 s	3.95×10^9 s	5.12×10^9 s	1.72×10^9 s

To conclude, the findings of this study indicate T_g is largely consistent for the same dicarboxylic acid-based formulation regardless of catalyst content, T_g is unaffected by catalyst, in agreement with previous research^{79,5}. This is due to the fact that the catalyst influences the bond exchange and bond exchange is very slow at the temperature at which glass transition occurs. This underscores the notion that bond exchange at a temperature substantially lower than its topology transition temperature has a negligible impact on altering the glass transition behaviour. There is a marked variation in T_g between formulations made using different dicarboxylic acids highlighting a strong correlation between methylene repetitions in the dicarboxylic acid chain and T_g . Increased number of repetitions

is linked to decreased T_g . As the dicarboxylic acid chain reached length over 12 methylene repetition, the value of T_g starts to stabilise. The overall trend observed is attributed to the fact that longer dicarboxylic acid chains result in a lower T_g due to decreased crosslink density^{135,136} and increased chain flexibility¹¹⁵. Additionally, the stabilisation of these longer chains may involve the adoption of cyclic conformations, further influencing their thermal properties. This is crucial for tailoring vitrimers to specific applications.

The change of functional groups before and after the cure was examined using FTIR. The result shows the completion of the addition esterification. A marked increase in hydroxyl and ester groups is observed, evidenced by the elevation of the broadened O-H stretching peak at 3450 cm^{-1} and the C=O stretching peak at 1730 cm^{-1} respectively. Concurrently, a notable disappearance of epoxy groups is recorded, as indicated by the decline of the oxirane ring breathing stretch at 910 cm^{-1} . These changes collectively signify the successful reaction between the epoxy and dicarboxylic acids. The catalyst plays a pivotal role in this transformation, actively stimulating the epoxy ring opening during polymerisation and further facilitating transesterification for both network formation and the adaptability of the crosslinked chains. Despite the active involvement of the catalyst, the study confirms that homopolymerisation of the epoxy does not transpire during the manufacturing process across all formulation groups. This is attributed to the controlled reaction temperature, which is maintained below the threshold required for homopolymerisation, effectively preventing any inadvertent rise in T_g . This approach ensures the achievement of complete crosslinking by the conclusion of the reaction progress for all formulations, establishing a consistent final degree of crosslinking for formulations with identical dicarboxylic acid and epoxy composition, irrespective of their catalyst level.

The transesterification bond exchange reaction involves reactants and products that maintain balanced concentrations, leading to no thermodynamic preference for either side of the reaction. This balance results in equal forward and reverse reaction speeds, with the rate following Arrhenius temperature dependence¹. The link between temperature and the rate of stress relaxation which is reflected by

the activation energy of the Arrhenius relationship is directly influenced by the chemical nature of the material. The results of stress relaxation show a strong acceleration of bond exchange with increasing catalyst concentration, which is in agreement with previous findings in the literature^{80,16}. Quantification of this influence through fitting of the Arrhenius dependence shows that the activation energy of the bond exchange reaction is not affected significantly by the concentration of the catalyst. This is because the pathway and mechanism of the bond exchange reaction depend on the chemical nature of the catalyst but not by its amount⁷⁹. In contrast, the pre-exponential factor of the Arrhenius relationship increases as a function of catalyst amount, which is attributed to the increase in exchange sites for transesterification with increasing catalyst content.

In addition to catalyst amount, the amount and accessibility of reacting groups, chain flexibility, crosslinking density, and statistical distance between reaction groups influence the kinetics of the bond exchange reaction. Longer dicarboxylic acid chain lengths result in fewer crosslinks, enhancing the mobility and interaction of hydroxyl ends and ester groups for transesterification. This also increases the backbone flexibility, allowing more adaptable configuration changes. However, the extended chain length introduces limitations to bond exchange by reducing the relative density of functional groups and increasing the distance for exchangeable ends to participate in the reaction. This interplay of factors underscores the complexity of bond exchange reactions and their influence on macroscopic flow and stress relaxation behaviour and is reflected in the topological freezing temperature results obtained in this study resulting in an increase-plateau-decrease dependence of topological transition on chain length.

6 High temperature behaviour of dicarboxylic acid-epoxy vitrimers

Vitrimers stand apart from conventional thermoset materials due to their possession of exchangeable bonds, endowing them with exceptional adaptability in terms of shape. Nonetheless, their remarkable temperature-dependent behaviour necessitates a thorough investigation into its implications. While the material response around its glass transition and topology temperatures has been studied previously, achieving a comprehensive understanding across the full temperature range mandates an exploration of its behaviour beyond the topology transition point. Particularly, delving into the material behaviour at temperatures surpassing the critical transition points is highly relevant. Central to this exploration is the understanding of the distinctive phenomenon of rapid bond exchange occurring within this specific temperature range and its potential ramifications on a spectrum of material properties. In essence, untangling the intricate interplay of these factors across various temperature regimes significantly enhances the comprehensive grasp of vitrimers.

6.1 Rheological behaviour

6.1.1 The development of vitrimer physical properties from uncured mixture

Figure 6.1 illustrates the curing response of vitrimer C6Z1, capturing both mechanical data and thermal information during the curing process. The temperature profiles for the corresponding DMA and DSC experiments are identical, as evidenced by the identical yellow and orange curves indicating that the heating programs for DSC and rheological tests are the same. These profiles start with a heating ramp of 10°C/min from 30°C to 160°C, followed by a period of isothermal conditioning of 2-hour at 160°C. Notably, after an initial fluctuation stage, characterised by noise in the loss modulus (G'') during the early stages of curing - especially at the onset of crosslinking, which is indicative of the material transition from a viscous state with high energy dissipation to a more solid, elastic state where viscous flow and energy loss are significantly reduced - the material

experienced a rapid increase in both loss modulus (G'') and storage modulus (G') coinciding with the onset of the curing reaction as indicated by the enthalpy curve. However, in contrast to typical thermosetting materials, as the reaction nears completion, which occurs approximately 1 hour after its initiation showing as the end of the increase of enthalpy, both modulus values continued to increase. This suggests that the vitrimer undergoes rearrangement towards a more interconnected stage and denser network without any significant thermal changes. The underlying mechanism for this phenomenon is believed to involve the transesterification reaction facilitated by the catalyst. The duration of this process may vary depending on the temperature to which the material is subjected. A study by Dusk and Matejka¹⁵⁶ revealed that for the Azelaic acid-DGEBA system, achieving a steady state when heated at 110°C requires 60-80 hours, whereas gelation occurs in just 6 hours.

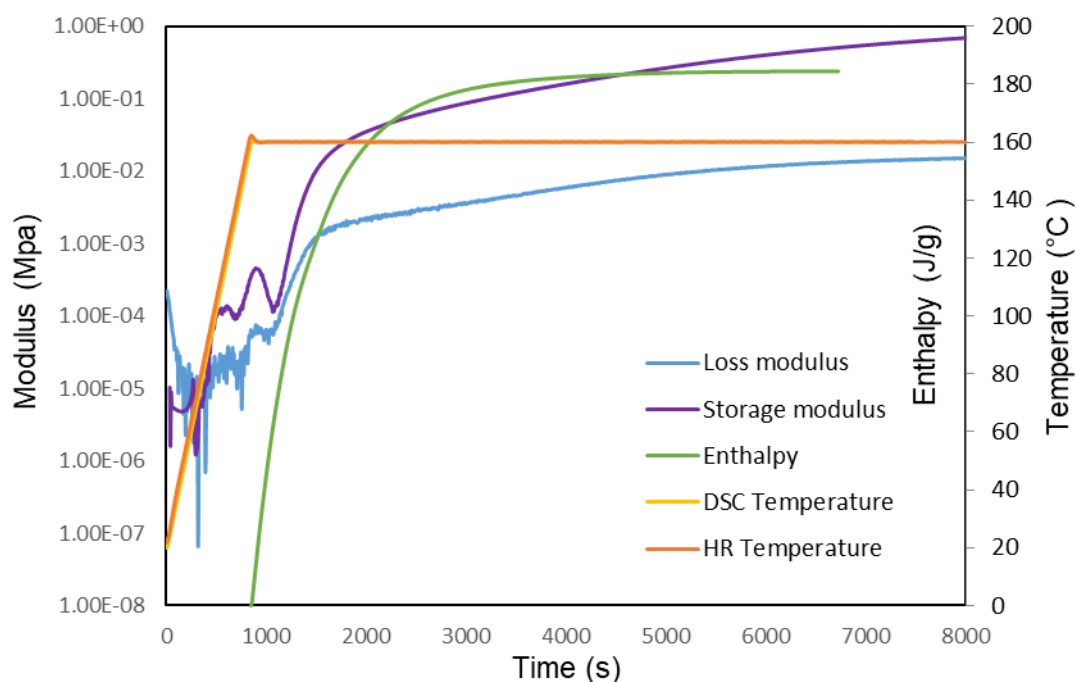


Figure 6.1: The dynamic thermal mechanical development of vitrimer C6Z5

Figure 6.2 illustrates the change of storage and loss modulus as the temperature goes through a heat and cool ramp right after the curing process shown in Figure 6.1. Following the two-hour curing period, the material exhibits intriguing thermo-mechanical behaviour, with both the storage and loss moduli increasing with

temperature. The noise observed during the rheology tests under single frequency oscillation mode, particularly for the loss modulus (G''), can be attributed to the limitations of the rheometer, especially when maintaining a set amplitude over an extended period. In contrast, during the cooling process, both moduli decrease until the temperature approaches the glass transition temperature. This indicates the presence of a temperature range above the glass transition temperature where the material modulus shows a positive correlation with temperature. Specifically, for the C6Z5 formulation, the loss modulus begins to increase at around 115°C, while the storage modulus exhibits a noticeable rise at approximately 70°C during the subsequent cooling phase which indicates the beginning of the material glass transition region.

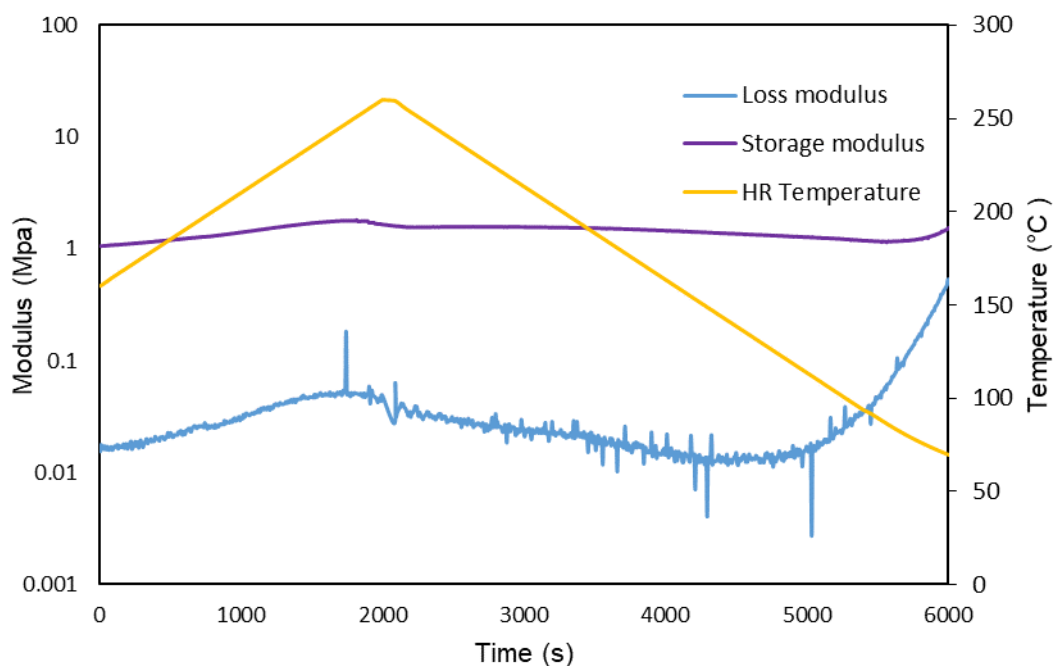


Figure 6.2: Temperature-dependent mechanical behaviour of cured C6Z5

Figure 6.3 illustrates the complex modulus development within the uncured C6Z5 mixture. This involved a sequential procedure that initiated with subjecting the mixture to a temperature ramp of 10°C, beginning from room temperature. This temperature ramp was executed across three distinct temperature points: 160°C, 170°C, and 180°C. Following this temperature ramp, each of the temperature conditions was followed by a consistent isothermal period spanning 2 hours. The

modulus evolution is similar for all three experiments up to about 2000 s. As the thermal profiles begin to diverge, distinct trends emerge in the modulus. The most rapid increase in modulus is observed at 180°C, whilst the slowest increase occurs at 160°C, which is evident around the 2000 - 2500 s time interval. Subsequently, the modulus continues increasing, reaching values of 0.46, 1.30, and 1.83 MPa for the materials cured at 160°C, 170°C, and 180°C, respectively. This shows that the curing temperature not only affects the reaction rate between the dicarboxylic acid and epoxy but also influences the extent and speed of reaching the crosslinking state.

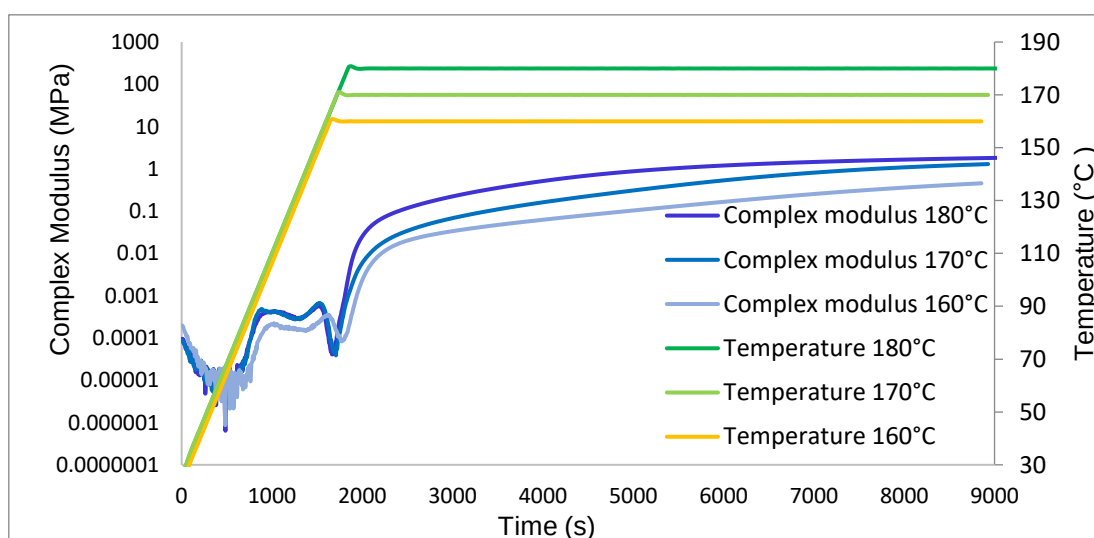


Figure 6.3: Evolution of storage modulus during C6Z5 vitrimer curing at different temperatures

One potential explanation for the trend observed is that the material has a higher modulus at elevated temperatures²³¹. Similar to rubbers, vitrimers are composed of interconnected macromolecules. At equilibrium, the polymer chains in vitrimers are coiled and adopt a random configuration, a state driven by the system inherent entropy²³². This randomness can be visualised as a series of interconnected segments. The orientation between consecutive segments is statistically random, causing the entire chain to follow a random walk behaviour. When an external mechanical force is applied, these polymer chains align in the direction of the applied stress. This alignment is a thermodynamic response, driven by the system desire to minimise its free energy²³³. However, this ordered

state leads to a decrease in the configurational entropy of the polymer chains, as the number of possible microstates the system can occupy is reduced. Upon heating, the kinetic energy of the polymer chains increases, granting them greater mobility. This mobility allows the chains to attempt to revert to their original, entropically favourable configurations. The chains aim to return to a coiled, random state to maximise their entropy. However, this entropic drive is counteracted by the enthalpic contribution from the applied mechanical stress, resulting in a net increase in the material's modulus¹¹³.

Another potential explanation for the behaviour observed could be that crosslink build-up occurs more rapidly at higher curing temperatures, consistent with findings of the dependence in reaction enthalpy at different curing temperature in Figure 4.21-Figure 4.25, that the reaction rate of curing is higher at elevated temperatures, resulting in differences in the rate of modulus increase between 1700 s and 2500 s from the beginning of the temperature. Subsequently, the modulus of the materials continues to increase and approaches toward an equilibrium value during the period of curing is another indication of the existence of the ultimate crosslink stage.

Figure 6.4 illustrates the variation in complex modulus of C6Z5 cured at temperatures of 160°C, 170°C, and 180°C when subjected to a heat-cool ramp, with temperatures transitioning from 200°C to 260°C and then down to 70°C directly following their initial 2-hour curing process, as depicted in Figure 6.3. During the subsequent heat and cool ramp, all materials cured at different temperatures exhibits similar results to those reported in s

Table 6.1. Although the modulus data contain noise due to testing conditions approaching the equipment torque limits, which impacts the consistency of oscillation, the complex modulus still shows a clear trend. It continues to increase as the temperature rises and decreases upon cooling, until the temperature approaches the glass transition temperature, and the material starts entering its glassy region as depicted in Figure 6.4. Specifically, the modulus of the material cured at 170°C and 180°C approaches approximate values at the peak temperature of 14.2 MPa and 5.6 MPa, respectively. Upon cooling, the modulus

values converge, reaching 1.80 MPa at a temperature of 110°C. Conversely, the material cured at 160°C requires more time to reach a peak modulus of 1.8 MPa, with a lower value of 1.2 MPa at 110°C. There is a noticeable difference in the speed of modulus increase towards the highest temperature among the three materials. In addition, after the heating ramp, all materials have a higher modulus at the same temperature compared to the value before the ramp.

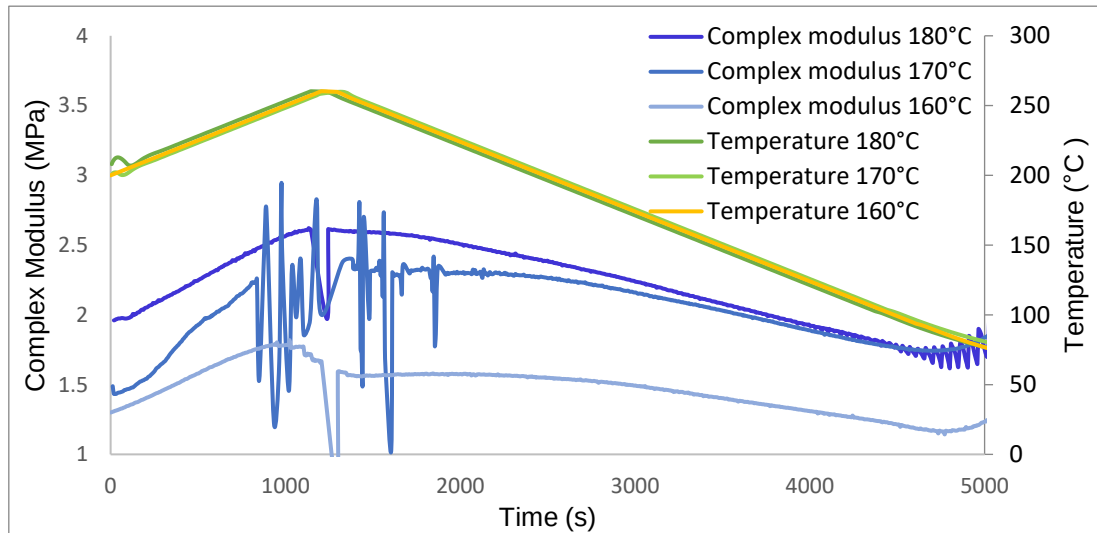


Figure 6.4: Temperature-dependent mechanical behaviour of C6Z5 cured at different temperatures

Table 6.1: Modulus at temperature of 160°C, 170°C and 180°C

Cure temperature (°C)	End of cure Modulus (MPa)	Ramp temperature (°C)	Modulus (MPa)
160	0.46	170	1.11
		180	1.16
		180	1.51
		170	1.48
		160	1.44
170	1.30	180	2.18
		170	2.12
		160	2.07
180	1.82	180	2.29
		170	2.23
		160	2.17

Table 6.1 reports the complex modulus for all three experiments at the end of the cure, together with the values of the modulus during the heat-cool ramp for each

material at temperatures of 160°C, 170°C, and 180°C. The modulus of all materials increases dramatically after being subjected to the highest temperature of 250°C compared to their end of cure value. The material cured at 160°C exhibits the most significant increase of about 210%, followed by increases of about 60% and 25% for the materials cured at 170°C and 180°C, respectively. There is an exponential relationship between crosslink development and temperature; the material cured at 160°C for 2 hours initially would display the lowest crosslink density compared to the other two materials. However, this difference is rapidly compensated by a faster crosslink build-up during heating at higher temperatures.

Despite the application of a temperature ramp, variations in modulus persist among the materials cured at different temperatures. Specifically, the modulus at 160°C after the heating ramp for the materials cured at 160°C and 170°C accounts for 65% and 95% of the value for the material cured at 180°C which is a direct indication of the difference in crosslinking density. Of all three materials, the one cured at 180°C has the longest time at the optimum conditions for crosslinking which allows it to form more crosslinks compared to the other two. The idea of the ultimate state of crosslinks proposed by Důšek and Matejka¹⁵⁶ suggests that when allowed enough time, a vitrimer could reach the equilibrium state in which the maximum crosslinking would be reached. Based on that, the modulus difference appearing at 250°C could be explained as at the end of the heating ramp of the materials cured at 170°C and 180°C the material has enough time to reach a similar state of crosslinking while when cured at 160°C the crosslinking is less established due to the lower initial reaction rate and bond exchange rate.

Apart from the hypothesis of establishment of the crosslinks, part of the results reported here can be attributed to rubber elasticity. Figure 6.5 shows the complex modulus for three materials at the temperature of 180°C, 170°C and 160°C after being subjected to 250°C. The points obtained from each sample follow a linear relationship with respect to temperature. Assuming the crosslinking density remains constant during this period, this effect only accounts for 7% of the

modulus change for material cured at 160°C when the measuring temperature changes from 180°C to 160°C during the cooling ramp and 11% and 12.6% respectively for the ones cured at 170°C and 180°C. As seen in the linear relationship coefficients listed in 250°C

Table 6.2, the increase in the slope of the line indicates that the effect is intensified in the case of material cured at higher temperature as evidence that more crosslinks are formed in those materials. Overall, the rubber elasticity only has a minor contribution to the change in modulus as a function of temperature. When allowed enough time for all three materials to reach the ultimate crosslinking stage during the initial curing, a unified temperature dependent modulus behaviour is expected.

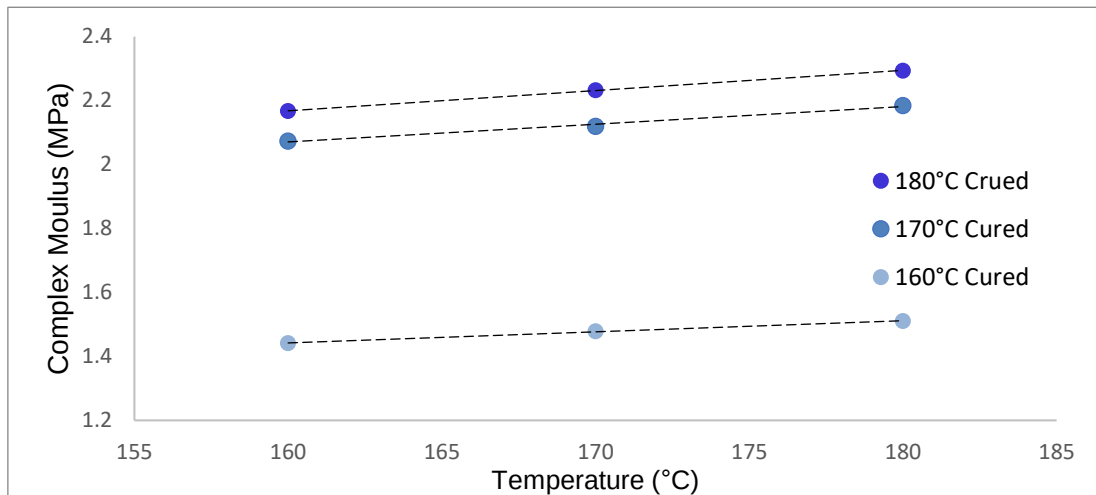


Figure 6.5: Complex modulus of the materials cured under different temperatures after being elevated to 250°C

Table 6.2: The parameters of the linear relationship illustrated in Figure 6.5

Cure temperature (°C)	Slope (MPa/K)	Intercept (MPa)
160	0.0035	1.155
170	0.0055	1.186
180	0.0063	0.886

6.1.2 Multi-frequency oscillation rheological behaviour

This section introduces the multi-frequency oscillation rheological behaviour. By subjecting materials to different oscillation frequency, insights into viscoelastic properties and understanding of their performance under diverse conditions can be gained. This approach is useful for characterising the dynamic behaviour of materials, especially in complex systems like vitrimers.

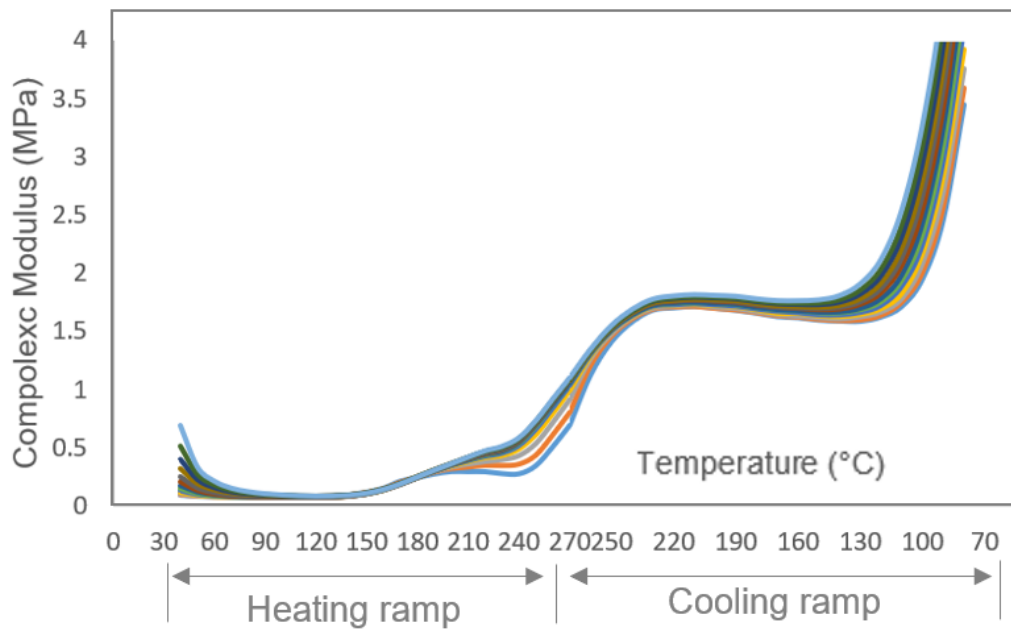


Figure 6.6: The change of modulus of C10Z5 regarding temperature

Figure 6.6 displays the changes in the complex modulus of cured material C10Z5 during a sequential heating-cooling ramp, with a frequency sweep ranging from 0.1 rad/s to 100 rad/s, and three data points per decade. From 30°C to 90°C, the material's modulus decreases, a shift attributed to its transition from a glassy to a rubbery state. This phase sees the material exhibiting varied frequency responses. Subsequently, the material enters a phase where its modulus is indifferent to frequency, as the modulus sharply falls to its lowest at 0.08 MPa. Approaching 150°C, a gradual increase in modulus occurs, linked to crosslink development. The temperature rise sees continued modulus growth, with the material regaining frequency response around 190°C. This upward trend remains during the cooling phase from a high of 270°C to 220°C, concluding with a peak

modulus value of 1.8 MPa. As cooling progresses, a modulus reduction is noted from 220°C, continuing until nearing its glass transition temperature at about 130°C. Concurrently, the modulus's frequency response seems to fade around 240°C in the cooling stage, lasting until the material cools to roughly 190°C. Furthermore, a marked enhancement in the modulus is observed post exposure to elevated temperatures. This can be ascribed to the progressive development of the network structure. It also leads to a rise in the T_g of the materials post the heating ramp, moving from 70°C prior to the ramp to 110°C afterward.

Figure 6.7-Figure 6.15 present a comprehensive investigation into the dynamic mechanical properties of nine distinct cured vitrimers. These vitrimers are prepared by utilising sebacic acid, suberic acid, and adipic acid as dicarboxylic acids, combined with varying concentrations (1%, 2.5%, and 5%) of zinc acetylacetonate hydrate. These formulations are designated as C10Z1, C10Z2.5, C10Z5, C8Z1, C8Z2.5, C8Z5, C6Z1, C6Z2.5, and C6Z5. The experimental analysis entails subjecting these materials to a controlled heating ramp while concurrently performing multiple frequency scans. The mechanical characteristics examined encompass the normalised storage modulus (G'/G^*), the loss modulus (G''/G^*), and the loss tangent ($\tan \delta$).

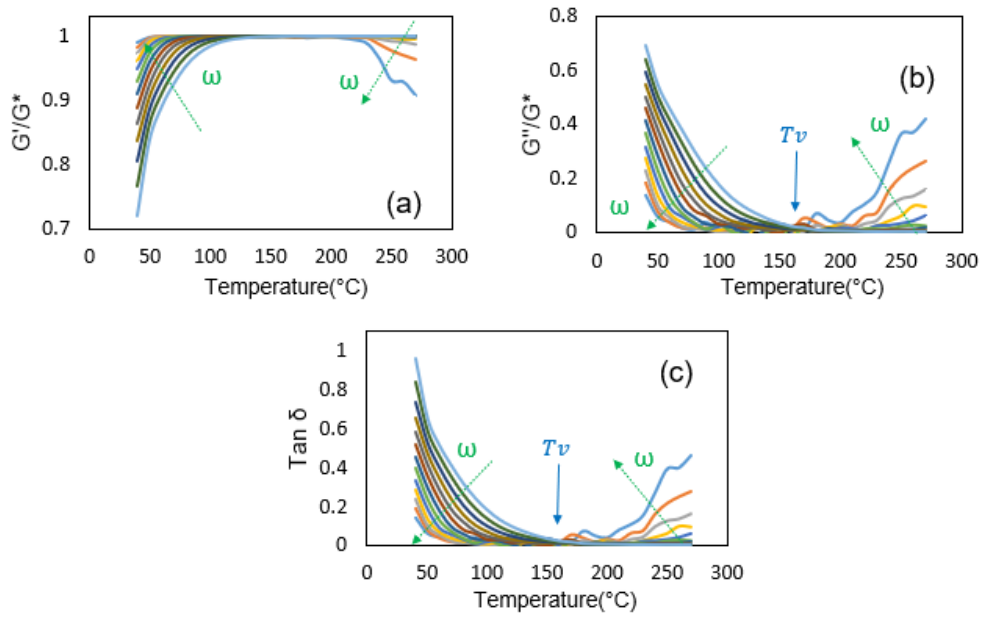


Figure 6.7: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z1 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

Initially, with an increase in frequency, there is a notable elevation in the value of the normalised storage modulus. This aligns with increased molecular mobility and more efficient energy transfer mechanisms operating at elevated frequencies. As the temperature increases, a discernible phase materialises, during which the materials showcase a period devoid of frequency dependence. Within this interval, the molecular mobility attains a state of saturation, resulting in a consistent storage modulus across different frequencies. Of particular significance is the subsequent occurrence of a reversal in the frequency-dependent effect on storage modulus. With increasing frequency, there is a reduction in the storage modulus value. This observation underscores the intricate interplay between molecular mobility, crosslinking, and energy dissipation, collectively shaping the dynamic response of the material.

Initially, as frequency increases, the normalised loss modulus is reduced. Yet, the efficacy of this frequency dependence gradually wanes, culminating in a temperature regime where loss modulus reaches its minimum, signifying an

absence of frequency dependency. Following this, a reversal transpires, and elevated frequencies instigate an increase in the normalised loss modulus.

The loss tangent exhibits comparable behaviour, following the established pattern. Importantly, the temperature at which this reversal is initiated closely corresponds with the previously observed transitions in the storage and loss modulus curves. This consistent phenomenon is present in all materials. At lower temperatures, G'/G^* displays a positive correlation with frequency, while the decrease in normalised loss modulus and $\tan\delta$ signifies a solid-like behaviour of the material at these temperatures. Following the transition phase, a reversal in influence is evident, suggesting a more liquid-like behaviour attributed to an accelerated bond exchange rate, enabling the material to flow. This transition exhibits distinct sensitivity to temperature changes across varying parameters. The transition of G'/G^* spans a broader temperature range, whereas $\tan\delta$ or normalised loss modulus (G''/G^*) transition occurs more abruptly or at a specific temperature. Remarkably, a notable observation arises regarding the frequency-dependent separation of response enhancers, particularly following the transitional phase, as the catalyst content increases. This observation underscores the intricate influence of frequency on material properties, revealing its interplay with catalyst content in a dynamically evolving system.

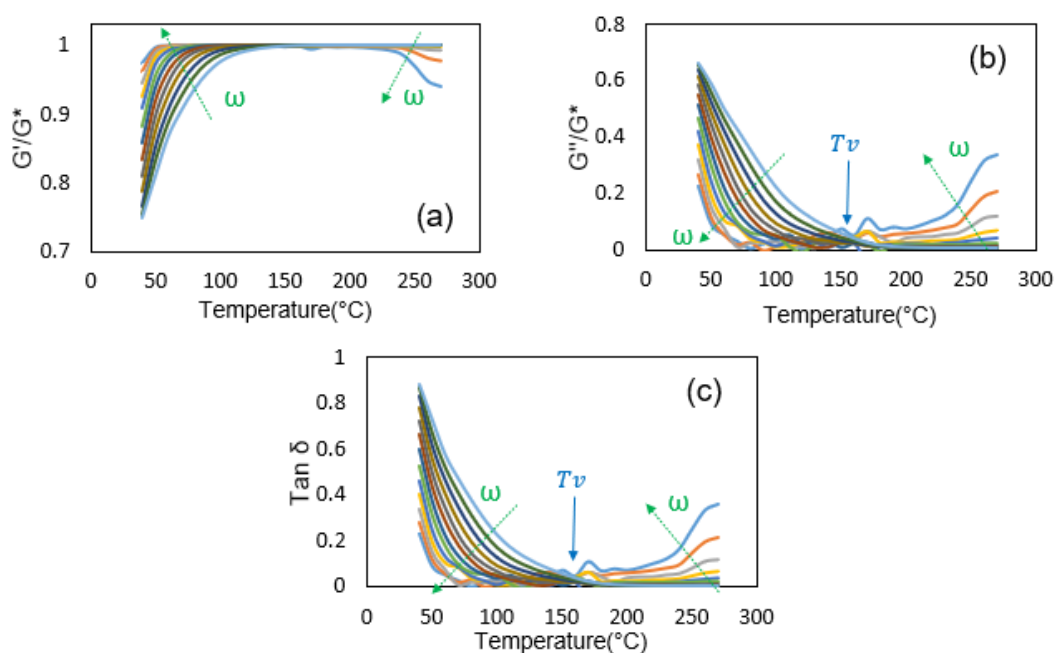


Figure 6.8: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z2.5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

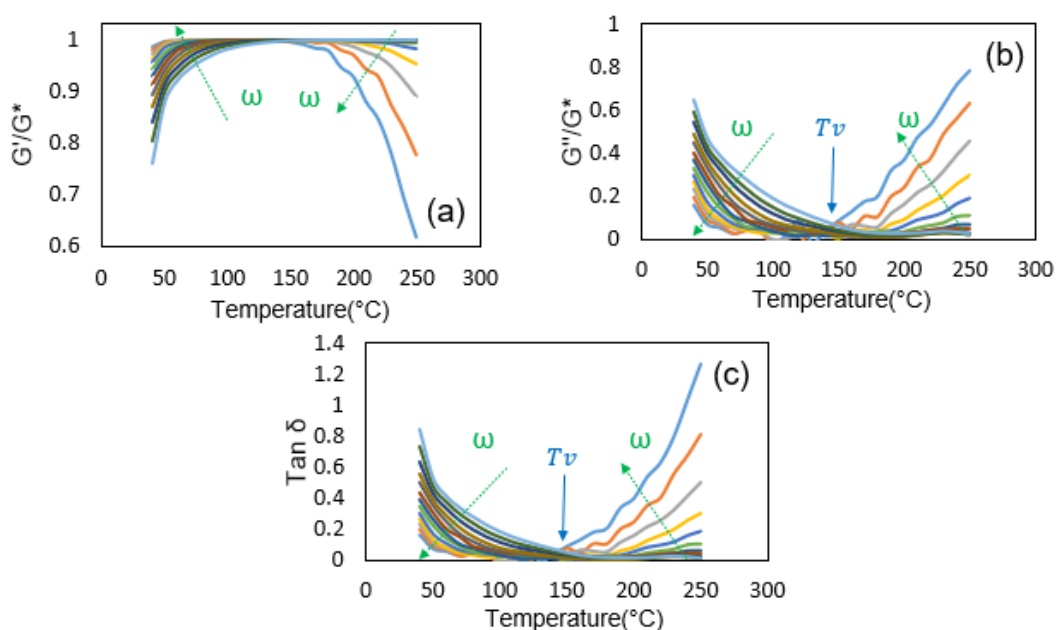


Figure 6.9: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C10Z5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

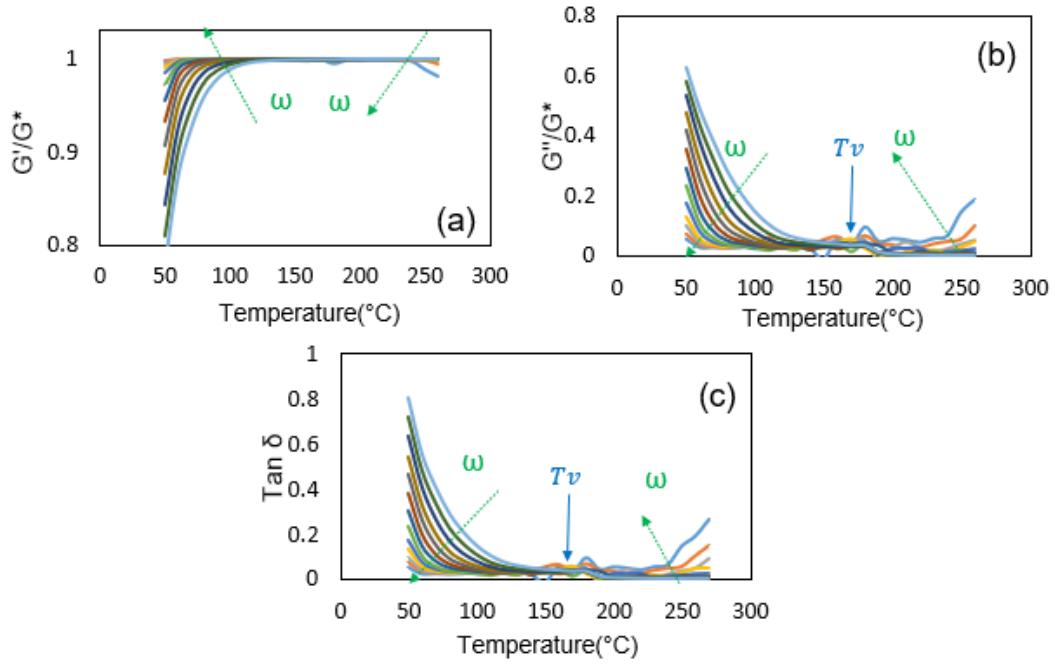


Figure 6.10: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z1 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

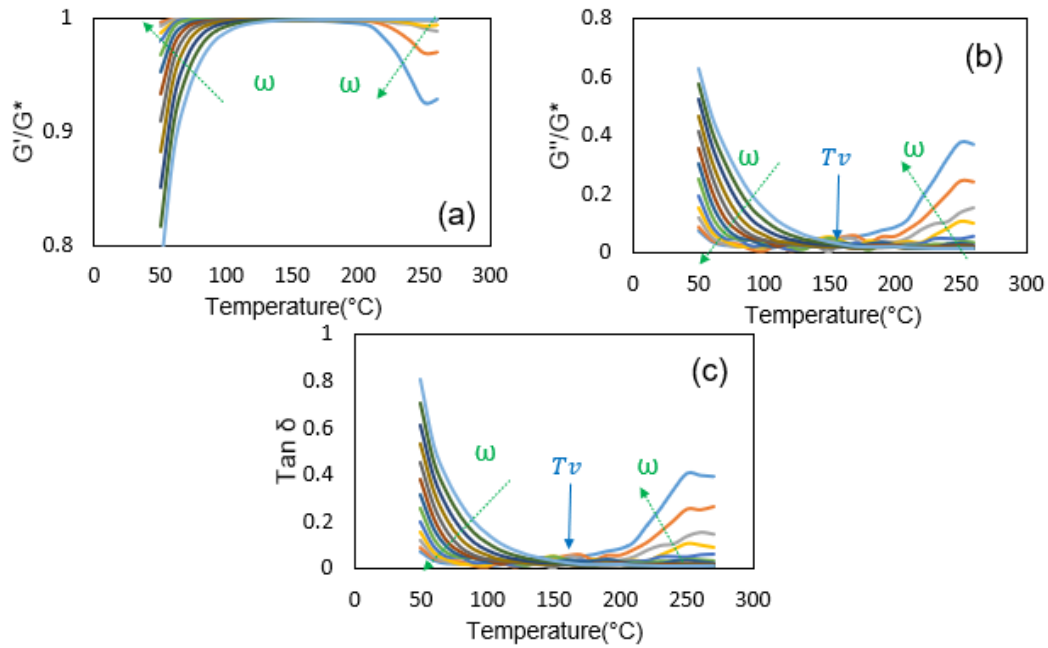


Figure 6.11: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z2.5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

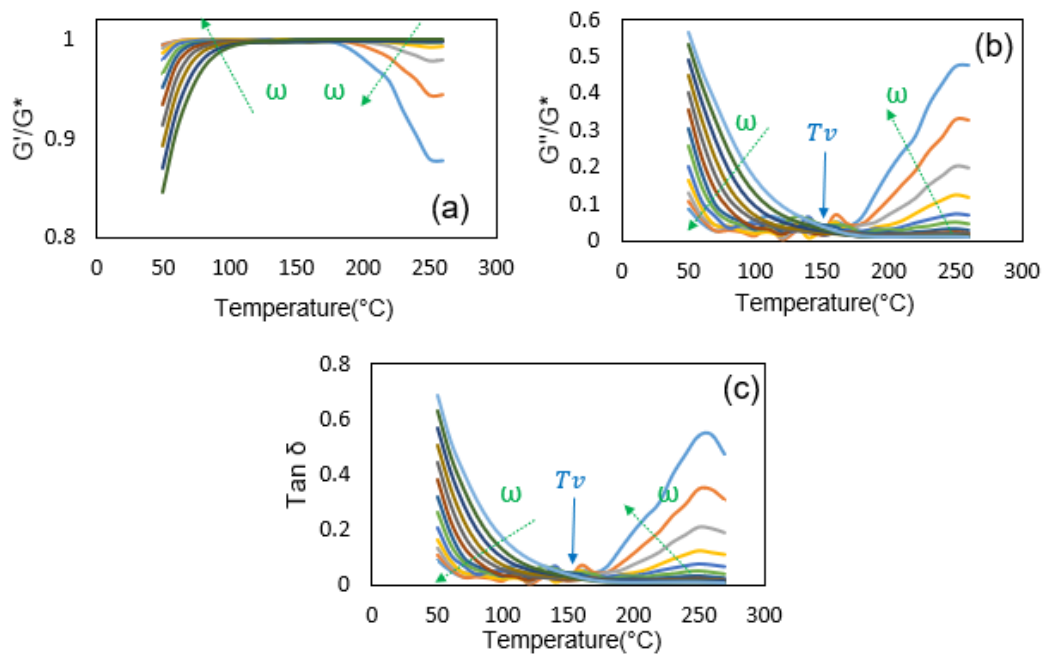


Figure 6.12: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C8Z5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

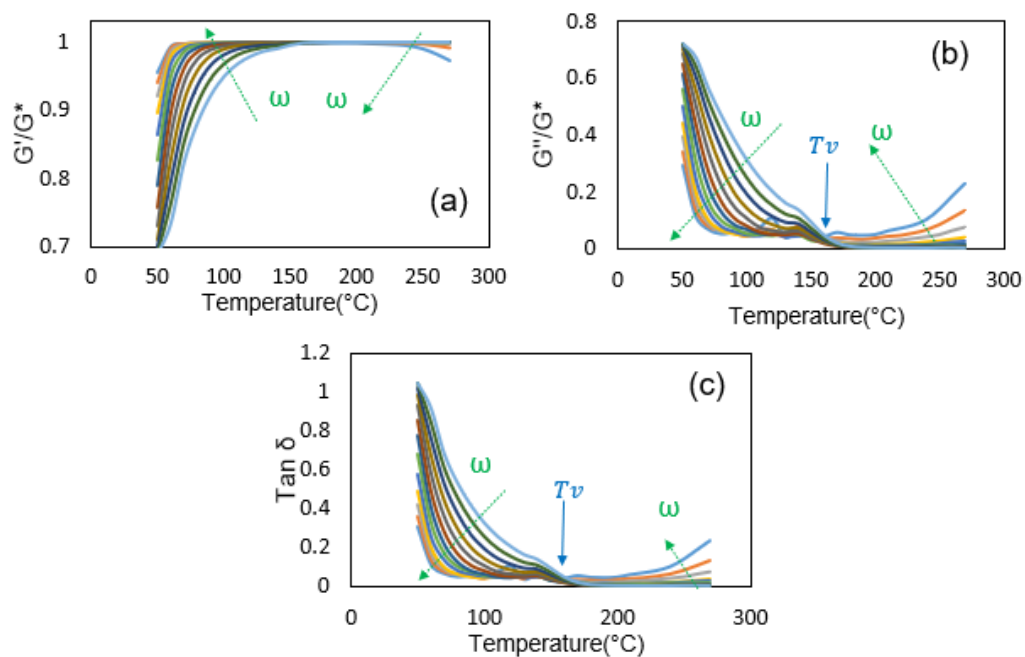


Figure 6.13: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C6Z1 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

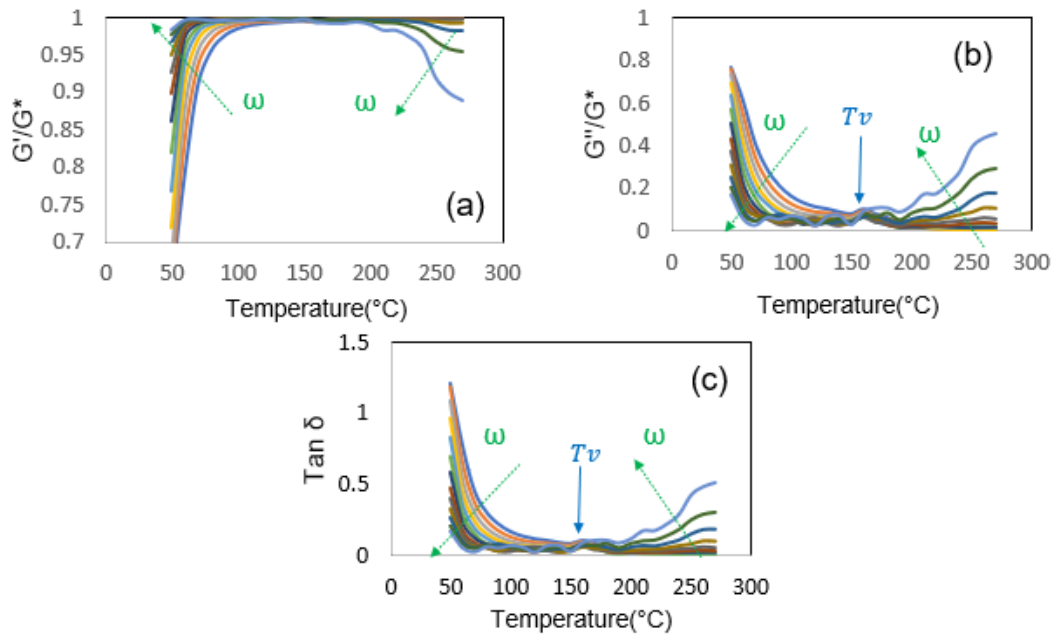


Figure 6.14: Rheological heating scan from 50°C to 270°C with lines for constant frequency converging at a significant temperature for C6Z2.5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

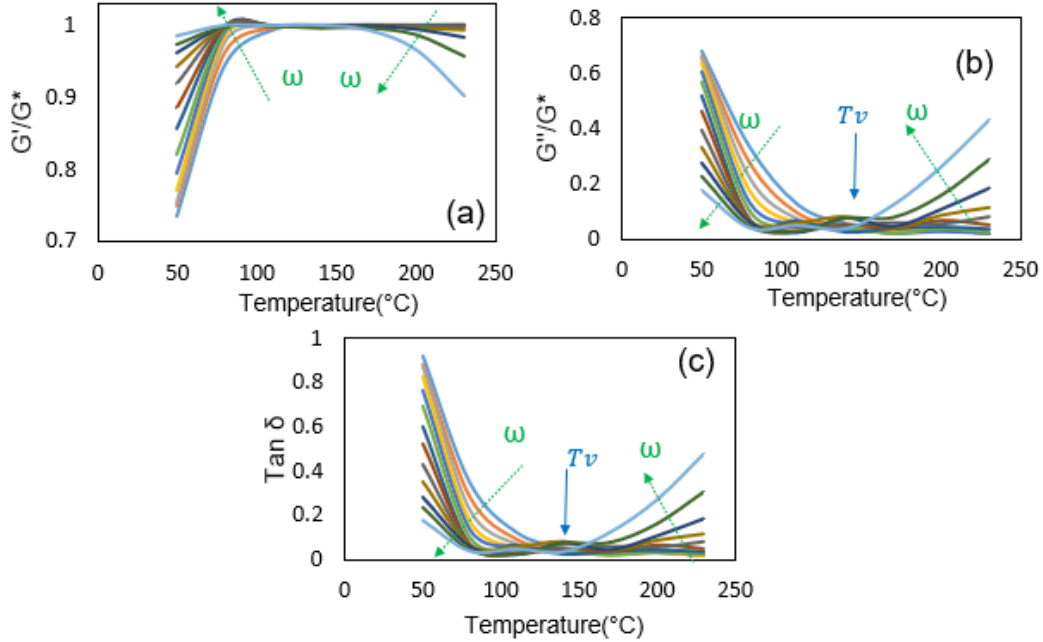


Figure 6.15: Rheological heating scan from 50°C to 230°C with lines for constant frequency converging at a significant temperature for C6Z5 amplified with three functions: (a) G'/G^* , (b) G''/G^* and (c) $\tan \delta$

A significant factor to consider is the duration over which the small amplitude oscillatory shear (SAOS) experiments were conducted; they span a considerably shorter timeframe compared to the static relaxation experiments performed under a predetermined strain. This difference might account for the observed liquid-like behaviour even when the material appears to be in a solid state. Consequently, the threshold viscosity of 10^{12} Pa·s used in the relaxation experiment to delineate between liquid and solid states may not be universally applicable.

Table 6.3: The temperature required for rheological relaxation

Material	Frequency (rad/s)	Relaxation time (s)	Temperature (°C)
C10Z1	0.1	10165	202.6
	100	0.06	608.9
C10Z2.5	0.1	10165	242.4
	100	0.06	536.1
C10Z5	0.1	10165	200.5
	100	0.06	463.7
C8Z1	0.1	10165	259.2
	100	0.06	527.0
C8Z2.5	0.1	10165	250.4
	100	0.06	529.7
C8Z5	0.1	10165	210.2
	100	0.06	488.3
C6Z1	0.1	10165	269.5
	100	0.06	840.9
C6Z2.5	0.1	10165	241.9
	100	0.06	989.6
C6Z5	0.1	10165	157.6
	100	0.06	749.4

Table 6.3 presents the temperatures at which the vitrimeric materials achieve relaxation for both the longest and shortest scanning periods observed during frequency sweep tests. These relaxation times, corresponding to each test frequency, were derived, and integrated into the stress relaxation function (as per Eq.(5-4), utilising parameters from Table 5.2. The data indicates that the temperature required for instantaneous material relaxation at the lowest frequency (0.1 rad/s)—corresponding to the most extended relaxation time—ranges between 157.6°C and 269.5°C. This range is consistent with the test temperature parameters, suggesting that at these temperatures, the materials would remain unresponsive to strain changes at a scanning frequency of 0.1

rad/s. For higher scanning frequencies, however, significantly elevated temperatures are necessary. There is an average temperature increase of 411°C resulting in a range spanning from 463.7°C for C10Z5 to a peak of 989.6°C for C6Z2.5. Notably, relaxation is closely tied to catalyst loading. Materials with a 5% catalyst exhibit an average temperature drop of 92°C to achieve frequency indifference compared to those with a 1% catalyst composition. This indicates that the material should exhibit instantaneous relaxation across all tested frequencies, especially at the temperatures corresponding to a frequency of 100 rad/s. However, in the conducted experiment, the temperature did not exceed the temperature requirement. Instead, a unified modulus across all frequencies was evident at a considerably lower temperature range of 130-230°C. Therefore, the behaviours observed during testing may not be solely attributable to the temperature-dependent relaxation characteristics of vitrimeric materials.

Table 6.4: Transition temperature for vitrimers *via* stress relaxation and rheological experiment.

Sample	G'/G* (°C)		G''/G* (°C)	Tan δ (°C)	T_v (r) (°C)	ΔT_v (°C)
C10Z1	130	210	170	170	123.6	46.4
C10Z2.5	140	210	160	160	113.7	46.3
C10Z5	140	150	150	150	91.4	58.6
C8Z1	130	240	170	170-180	136.3	33.7
C8Z2.5	130	190	150	150	126.3	23.7
C8Z5	130	180	150	150	104.1	45.9
C6Z1	160	230	160	160	104.2	55.7
C6Z2.5	150	190	160	160	83.9	76.1
C6Z5	140	170	140	140	66.1	73.9

The transition temperatures for all materials are recorded in Table 6.4. Increasing the amount of catalyst significantly narrows down the temperature range for the normalised storage modulus transition. For instance, the transition range of material C10 reduces from 80°C (130-210°C) to just 10°C (140-150°C) as the catalyst amount increase from 1% to 5%. Similarly, for C8, the difference is 60°C, reducing the range from 110°C (130-240°C) to 50°C (130-180°C). However, this difference appears to be lower as the dicarboxylic acid chain is shortened, reducing the range from 70°C (160-230°C) to 30°C (140-170°C). This behaviour confirms that the material exhibits a more pronounced response to temperature

with higher catalyst content. The transition occurs at a slightly lower temperature with increasing catalyst content, with an average drop of 20°C from 1% to 5% catalyst for all materials. However, the influence of the catalyst on the transition temperature in the rheological study is much more subtle compared to its impact on the material relaxation behaviour. At the higher end of the temperature ramp, materials containing 5% catalyst display a more pronounced separation compared to those with 1% catalyst. This observation provides compelling evidence linking the observed temperature-dependent behaviour to the rate of bond exchange, a phenomenon influenced by variations in the catalyst concentration. The underlying theoretical framework posits that increased catalyst content induces accelerated bond exchange within the materials even at the same temperatures. Consequently, this increased bond exchange rate gives rise to an intensified response, thereby contributing to the increased thermal-dependant response exhibited by the material.

In a study conducted by Fang *et al.*¹⁸⁹, it was observed that during the transitional temperature range, the material exhibits power law relaxation. This behaviour implies that the material transitions into a hyper-elastic gel state. This conclusion is further supported by the observation that, at this stage, the material displays parallel values of G' (storage modulus) and G'' (loss modulus), with a notably high ratio of G'/G'' . The transition temperatures measured from relaxation are much lower than those obtained from rheological frequency sweeps, with a difference ranging from 73.8 to 23.7°C, as shown in Table 6.4. Furthermore, the difference in T_v obtained by rheological tests shows lower sensitivity to the amount of catalyst present.

6.2 Thermal degradation of vitrimeric materials

Figures 6.16 to 6.18 illustrate the thermal degradation behaviour of materials as a function of temperature, ranging from room temperature to 600°C. Upon heating, these materials generally begin to decompose at around 300°C, marked by a sharp decline in weight, which eventually stabilises at a final weight. The temperatures at which this weight loss stabilises vary: C6 shows the lowest stabilisation temperature at approximately 430-440°C, while C8 and C10 stabilise

around 490°C, and C12 and C14 exhibit the highest stabilisation temperatures at around 500°C. There is also considerable variation in the remaining char of these materials. For instance, in Figure 6.16, C10 demonstrates a notably lower char residue at the end of the reaction, with only 12% remaining, whereas the char for other materials ranges between 16%-22%.

However, this pattern alters for vitrimers with 2.5% and 5% catalyst content. In Figure 6.17, C6, C8, and C10 end with 16% of their initial weight, but C12 only retains 12%, and C14 concludes with 8%. With 5% catalyst, C6 and C8 still show more residual at 600°C, retaining 16% of the initial weight, while C10, C12, and C14 exhibit a value of 12%. This discrepancy could be attributed to differences in the degradation mechanism influenced by the monomer variation. There is a possibility of additional decomposition processes in the vitrimer systems made with dicarboxylic acids containing more methylene groups in their main chain.

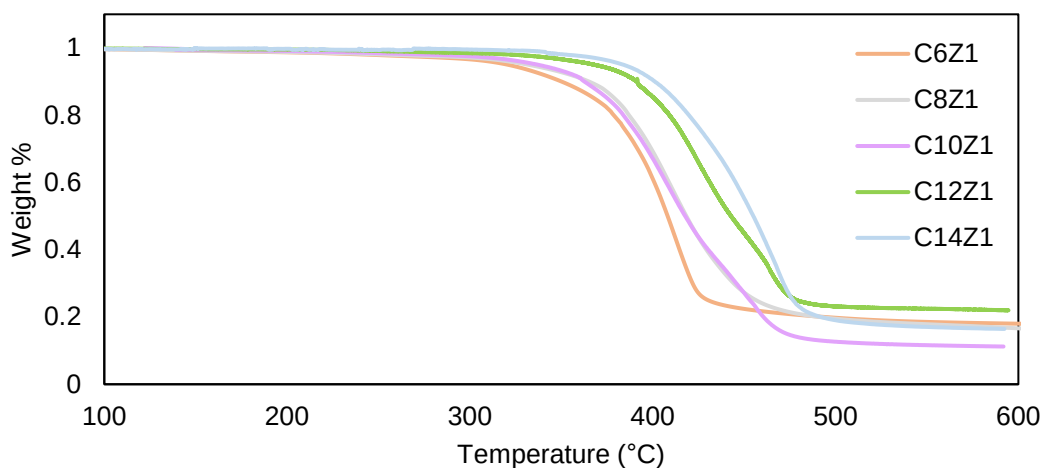


Figure 6.16: Thermal degradation of vitrimers containing 1% catalyst in terms of weight loss

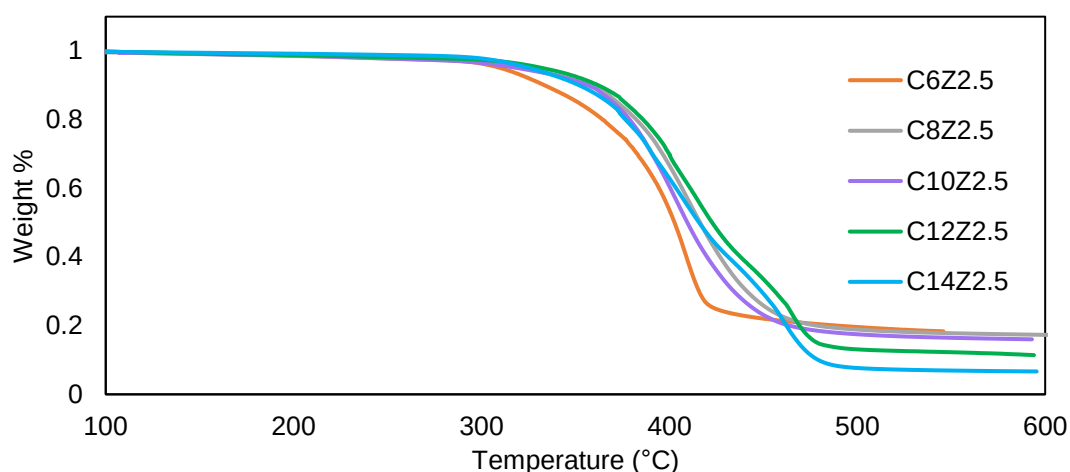


Figure 6.17: Thermal degradation of vitrimers containing 2.5% catalyst in terms of weight loss

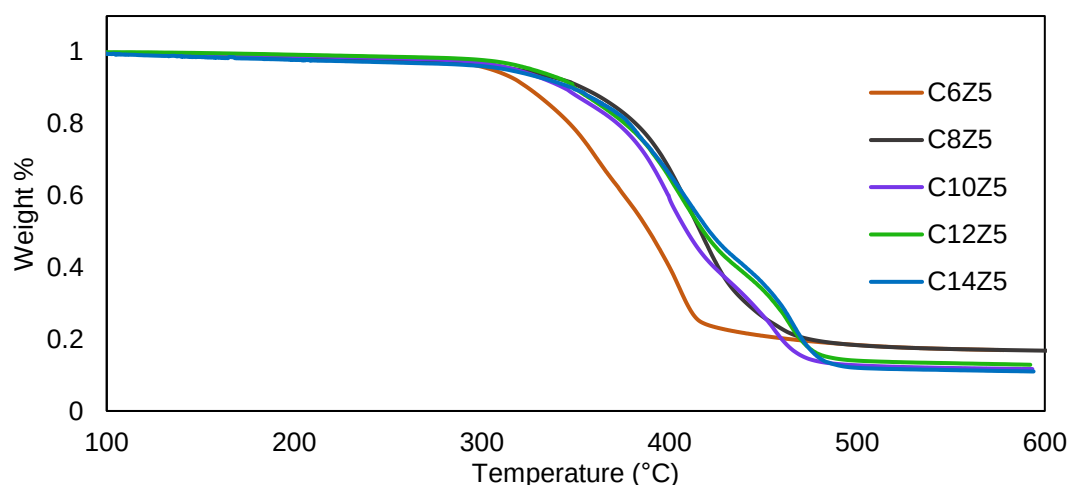


Figure 6.18: Thermal degradation of vitrimers containing 2.5% catalyst in terms of weight loss

Figures 6.19 to 6.21 display the rate of decomposition reactions at various temperatures, revealing distinct patterns in the reaction curves. Vitriimer samples C10, C12, and C14 exhibit a second reaction peak within the temperature range of 460-470°C. In contrast, C6 demonstrates a unique pattern compared to the others. The majority of its reaction occurs before a notable drop in the reaction rate at 410°C, and specifically in C6Z5 (as shown in Figure 6.21), there is a minor peak preceding the major peak at 410°C. For C8, the reaction rate displays a broad yet more symmetric single peak shape, peaking around 410°C. This

indicates a variance in the reaction mechanisms of the vitrimers; while the reactions of C6 predominantly occur at temperatures below 410°C, the degradation of C10, C12, and C14 involves reactions at higher temperatures. The transition in this shift of reaction mechanism could explain the form of the reaction rate for C8, which seems to be influenced by both reaction series.

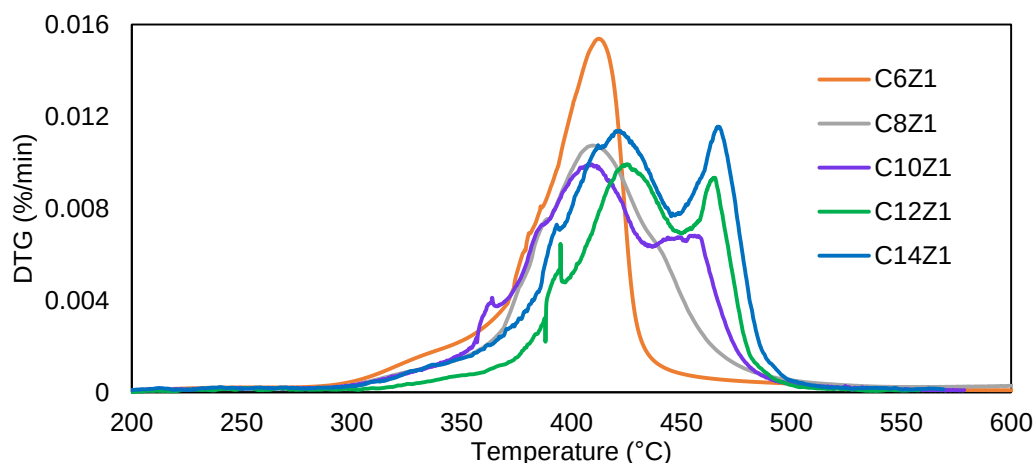


Figure 6.19: Rate of the thermal degradation vs. temperature curves of vitrimers containing 1% catalyst

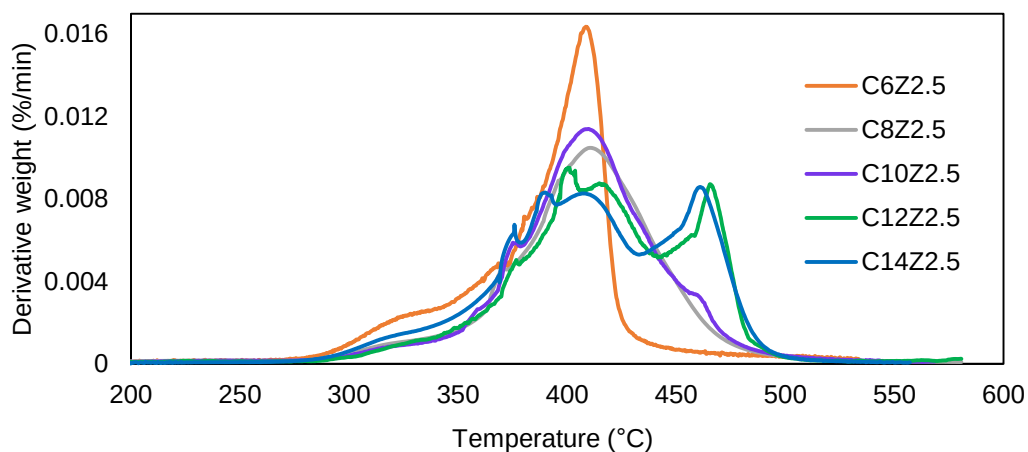


Figure 6.20: Rate of the thermal degradation vs. temperature curves of vitrimers containing 2.5% catalyst

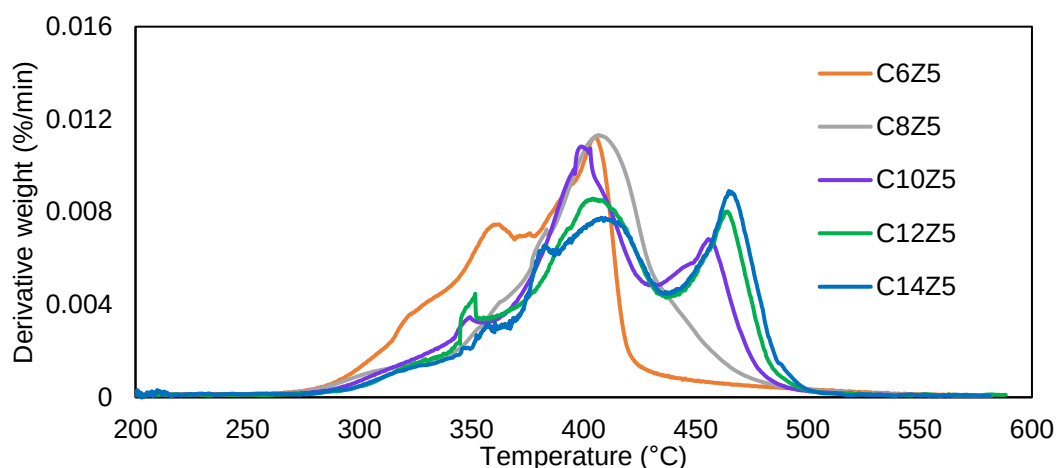


Figure 6.21: Rate of the thermal degradation vs. temperature curves of vitrimers containing 5% catalyst

Figures 6.22 to 6.26 illustrate the progression of thermal degradation as the temperature steadily increases. Specifically, in Figure 6.21, during the initial decomposition stage between 300-380°C, there is a pronounced dependence of the reaction rate on catalyst concentration, with the most significant variance observed at 360°C. A similar dependency is noticeable in C8, as depicted in Figure 6.22. However, as the dicarboxylic acid chain length increases, the discernible difference in reaction rates is primarily evident between vitrimers containing 1% and 5% catalyst. Notably, for vitrimers C10, C12, and C14, those with 5% catalyst demonstrate a more rapid reaction during the initial phase of decomposition.

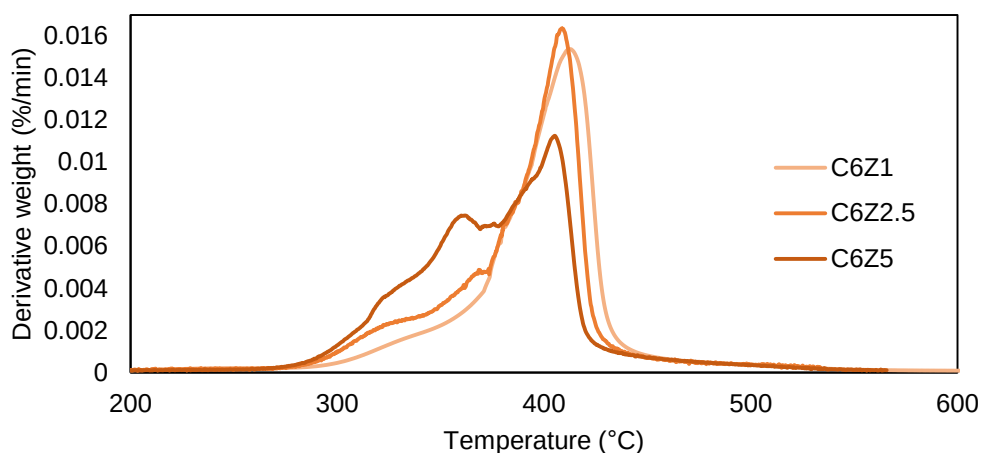


Figure 6.22: Rate of the thermal degradation vs. temperature curves of vitrimer C6

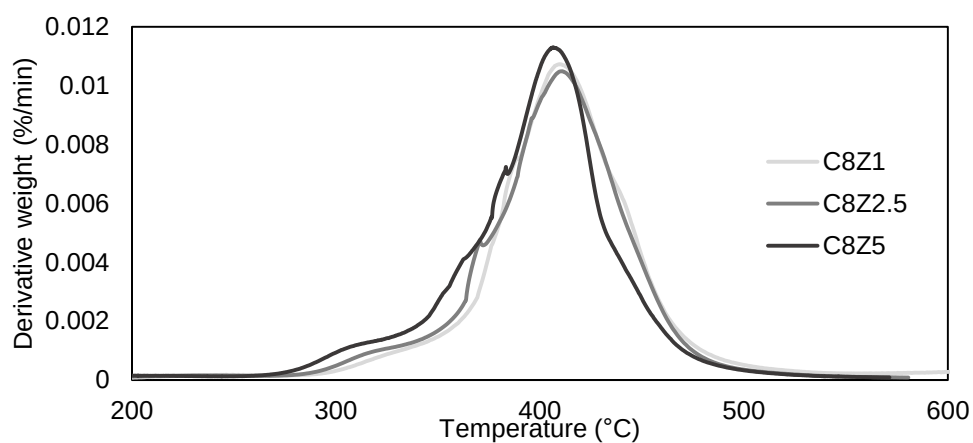


Figure 6.23: Rate of the thermal degradation vs. temperature curves of vitrimer C8

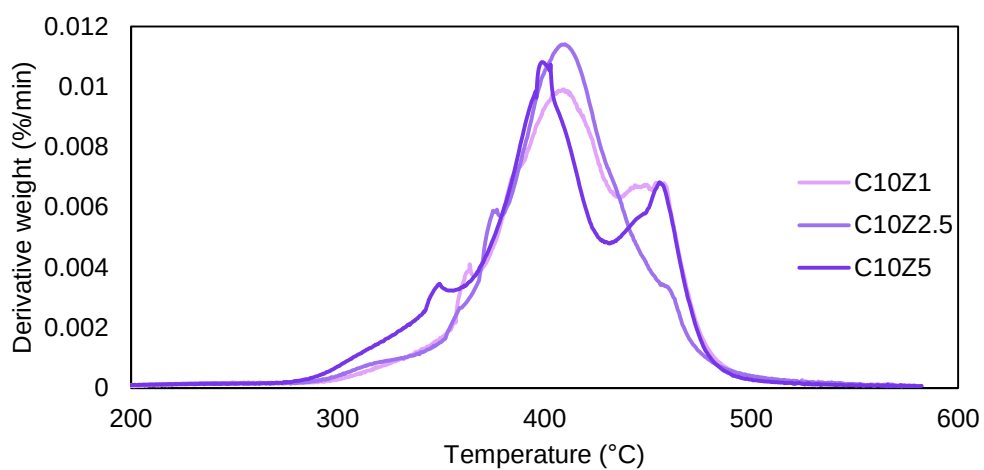


Figure 6.24: Rate of the thermal degradation vs. temperature curves of vitrimer C10

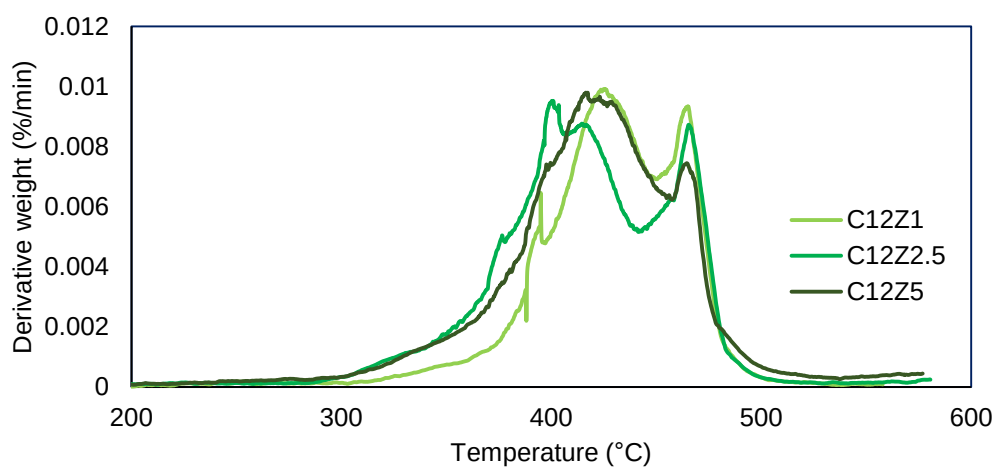


Figure 6.25: Rate of the thermal degradation vs. temperature curves of vitrimer C12

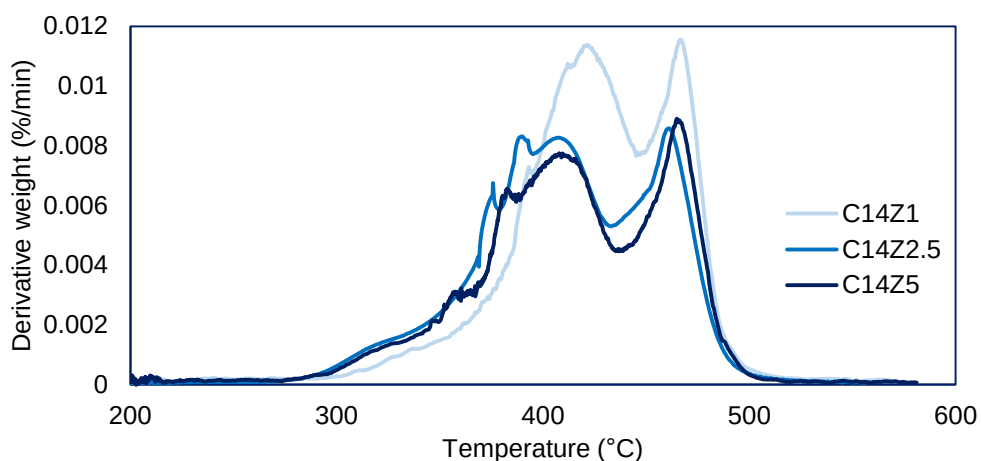


Figure 6.26: Rate of the thermal degradation vs. temperature curves of vitrimer C14

Studies on the thermal degradation mechanism of polyesters indicate that the presence of hydrogen in the beta position to the ester group facilitates the scission of aliphatic fragments predominantly through β -hydrogen scission. This occurs via a six-membered cyclic transition state, involving the transfer of a hydrogen atom from the alkyl group in beta position to the ester group to the ester carbonyl group²³⁴. The initial pyrolysis predominantly yields vinyl and carboxyl-terminated compounds, which subsequently undergo decarboxylation as suggested by^{235,236} as illustrated in Figure 6.27.

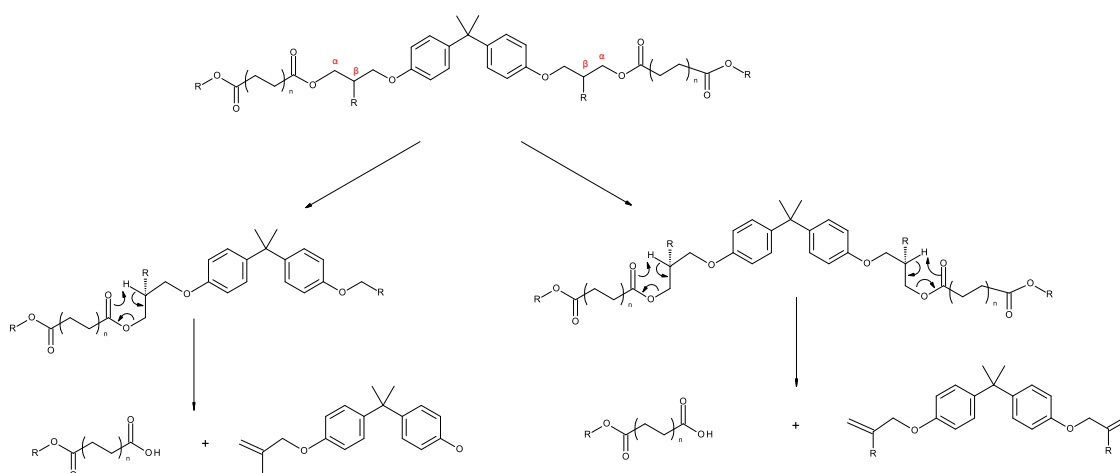


Figure 6.27: Scheme of intramolecular β -hydrogen scission process

These carboxyl-terminated compounds may further degrade into diacid, diolefin, and other short-chain products. In the vitrimer design, the varying factor in

monomer structure is the number of methylene units in the aliphatic chain. As degradation progresses, dicarboxylic acids are formed. A study of the thermal decomposition of a series of linear dicarboxylic acids reveals an increase in decomposition temperature from 200°C for succinic acid (C₄H₆O₄) to 250-300°C for glutaric acid (C₅H₈O₄), and then to 350-400°C for adipic acid (C₆H₁₀O₄)²³⁷. However, the degradation pathway of dicarboxylic acids containing more than seven carbons has not been extensively analysed. Analysis of the decomposition reactions revealed differences between adipic and sebacic acid derivatives. The latter demonstrated a minor yet significant decomposition process at temperatures exceeding 425°C, whereas the former appeared to degrade in a single step²³⁸. This could share similar reaction roots to the observation of the second reaction peaks in the thermal degradation of the vitrimers reported.

Table 6.5 provides a breakdown of temperatures at which 5% and 10% weight losses occur for each material. These data suggest that thermal stability is influenced by dicarboxylic acid chain length, a trend that remains consistent across varying catalyst concentrations. A comparative analysis of the degradation behaviour based on the number of CH₂ groups in the alkylene chains reveals distinct differences. For instance, the temperatures corresponding to 5% (Td5%) and 10% (Td10%) weight losses increase by 43.5°C and 34.1°C, respectively, when transitioning from C6Z1 to C14Z1. However, this differential reduces for materials with 2.5% and 5% catalyst concentrations. The degradation profiles predominantly exhibit a single-step decline, resulting in nearly identical trends for Td5% and Td10%. Literature sources^{239,240} propose that polymer scission predominantly occurs at the propyl group situated between the aromatic rings and the carbon-oxygen bond opposite these rings. A plausible explanation for the observed trends is that an extended dicarboxylic acid chain length reduces the proportion of bonds susceptible to decomposition, leading to an elevated overall degradation temperature. This is consistent with findings on diesters derived from linear dicarboxylic acids, where thermal stability was found to increase with the carbon number²⁴¹. Figure 6.28 shows a trend where shorter methylene chain lengths²⁴² and increased catalyst concentrations correspond to reduced decomposition temperatures. This can be attributed to the dual role of

the catalyst: facilitating vitrimer bond exchange and promoting vitrimer oxidation by reducing the decomposition reaction's activation energy. This observation aligns with findings by M. Giebler *et al.*²⁴³, where networks prepared with 2.5 mol% zinc(II)-acetylacetonate hydrate as a catalyst in an epoxy-anhydride vitrimer system exhibited superior thermal stability compared to those with 5 mol% catalyst.

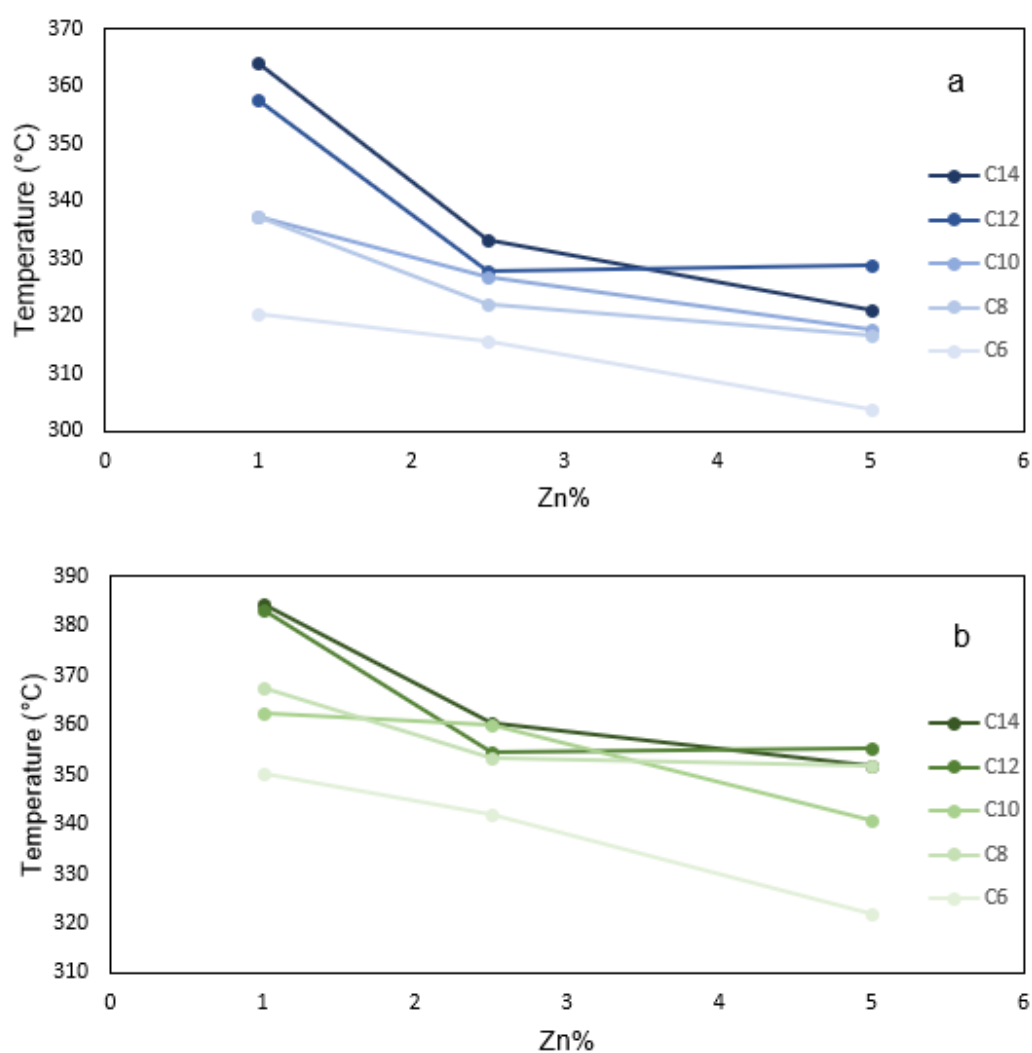


Figure 6.28: (a)Temperature for 5% weight loss of vitrimers, (b) Temperature for 10% weight loss of vitrimers

Table 6.5: 5% and 10% weight loss temperature for all vitrimeric materials

Material	T _{d5%} (°C)	T _{d10%} (°C)	Average T _{d5%} (°C)	Average T _{d10%} (°C)	Td5% Standard Deviation (°C)	Td10% Standard Deviation (°C)
C6Z1	321.5	349.7	320.6	350.3	1.3	0.7
	319.1	351.0				
	321.0	350.2				
C6Z2.5	310.4	333.6	315.7	342.2	5.4	7.6
	321.2	348.1				
	315.5	344.9				
C6Z5	305.9	324.6	303.8	322.1	5.4	6.0
	297.6	315.3				
	307.8	326.5				
C8Z1	332.7	363.3	337.4	367.6	8.5	5.8
	332.2	365.3				
	347.2	374.2				
C8Z2.5	321.6	357.4	322.0	353.5	5.0	3.2
	324.5	353.2				
	315.1	349.7				
	326.7	353.9				
C8Z5	312.5	344.8	316.6	351.7	3.1	5.0
	319.7	353.8				
	316.1	351.8				
	318.3	356.5				
C10Z1	336.3	363.0	337.2	362.4	0.9	0.7
	338.0	361.6				
	337.4	362.6				
C10Z2.5	333.1	362.1	327.0	360.0	7.1	3.0
	319.2	356.5				
	328.6	361.3				
C10Z5	321.3	342.8	317.5	341.0	4.3	4.0
	312.9	336.4				
	318.4	343.8				
C12Z1	368.7	391.8	357.7	383.5	10.0	7.4
	349.3	377.8				
	355.0	380.8				
C12Z2.5	333.0	362.3	327.9	354.6	11.9	13.2
	335.8	363.1				
	310.2	335.0				
	332.8	357.8				
C12Z5	331.0	363.1	329.0	355.4	3.3	6.8
	325.2	352.6				
	330.7	350.5				
C14Z1	386.9	402.6	364.1	384.4	23.5	16.8

Material	T _{d5%} (°C)	T _{d10%} (°C)	Average T _{d5%} (°C)	Average T _{d10%} (°C)	Td5% Standard Deviation (°C)	Td10% Standard Deviation (°C)
C14Z2.5	340.0	369.3	333.2	360.7	7.5	8.1
	365.4	381.5				
	333.7	362.2				
	340.4	367.9				
C14Z5	325.5	351.9	321.0	351.7	4.9	2.5
	313.6	348.0				
	323.8	352.9				
	322.4	352.4				
	323.9	353.4				

Overall, the epoxy-dicarboxylic acid formulations undergo significant changes in mechanical properties during the curing process. The initial rapid increase in modulus followed by a more gradual increase under isothermal condition suggests the building of the crosslinks at the early stage of the curing process and ongoing rearrangements towards a denser network without significant thermal changes¹⁸⁹. This behaviour is due to the esterification and the subsequent transesterification reaction facilitated by the catalyst. Increasing the cure temperature results in higher modulus at the end of the cure for the same amount of time. This can be attributed to the dual impact of temperature on the reaction speed and the crosslinking extent. A higher curing temperature accelerates the crosslinking rate and concurrently diminishes the duration needed for the material to attain its ultimate crosslinked state¹⁹⁰.

The investigation into the cured material complex modulus during a stepwise heat-cool ramp across various frequencies unveils a marked, temperature-sensitive modulus trajectory and a range of temperature where the material shows frequency-independent modulus behaviour¹⁸⁹. As the temperature rises, the material transitions from a glassy to a rubbery state, leading to a reduction in modulus. This transition also displays varied responses to changing frequencies, eventually reaching a stage where the modulus remains mostly unchanged regardless of frequency. However, as temperature continues to increase, the modulus begins to increase, due to the emergence and growth of crosslinks and the material reverts to a frequency-dependent behaviour. In cooling for a high temperature, a decrease in modulus is observed, intensifying as the material

approaches its glass transition temperature. After exposure to higher temperatures, a notable increase in modulus is observed, potentially linked to the ongoing evolution of the network structure, subsequently elevating the material glass transition temperature post-heating. The cause of the frequency independence of modulus is likely due to the influence of structural relaxation and bond exchange induced relaxation¹⁹⁵. During the span of the frequency-independent temperature range the effect of the two relaxations can potentially counteract each other. The catalyst content has a significant influence on the span of the transition temperature and the sensitivity of the response frequency. The range of the transition is reduced with increasing catalyst, whilst the sensitivity on frequency also increases. This can potentially be attributed to the fact that the influence of temperature on bond exchange rate is stronger with higher load of catalyst.

When exposed to higher temperatures, the materials exhibit consistent thermal degradation patterns. Formulations with shorter methylene chain lengths and higher catalyst concentrations display lower decomposition temperatures. This is attributed to the fact that catalyst not only aids in the exchange of vitrimer bonds but also enhances vitrimer decomposition in nitrogen atmosphere by lowering the activation energy needed for the decomposition reaction. Moreover, formulation with longer dicarboxylic acid chains possess fewer decomposition-prone bonds, culminating in elevated overall degradation temperatures. This observation is in agreement with prior findings pertaining to the thermal stability of diesters derived from linear dicarboxylic acids.

7 Limitation and general impact of the research.

7.1 Limitations of the research

The cure analysis carried in this work covered a breadth of formulation, which led to limited tests of repeatability of DSC results. Although duplicated dynamic tests indicate good reproducibility, ideally a minimum of three DSC tests should have been carried out for each experimental condition and formulation. This would have allowed more robust comparisons of kinetics parameters between formulations as well as elimination of potential errors in experimental work. Similar limitations in terms of reproducibility also apply to the rheological experiments of this study.

The kinetics framework used is well suited for mechanisms that involve a single conversion variable and in the particular case of the isoconversional methods and the autocatalytic model adopted a single mechanism. The experimental results show the dominance of a single mechanisms and the superposition tests carried out the relative validity of the single conversion variable assumption. However, there are secondary mechanisms that result in variations of total enthalpy across experiments in the same formulation and the superposition of dynamic and isotherm data show differences that are around 9%. Incorporation of additional mechanisms and underlying variables would have increased the accuracy of kinetics models.

In examining materials made with different catalyst levels, the study is limited by the range of formulations tested. A more extensive exploration of various catalyst amounts would allow a more comprehensive understanding. Furthermore, the inability to produce reference materials without any catalyst, due to the necessity of a catalyst for epoxy ring opening, leaves a gap in understanding the unique nature of exchangeable bonds and conventional thermosetting polymers.

In the study of the relationship between monomer structure and vitrimer properties, the focus is confined to the change in the dicarboxylic acid component. The potential influence of the type and structure of the epoxy, which holds significant promise for fine-tuning material properties, is not considered

here. Further exploration could encompass the functionality of the monomers and the study of branched carboxylic acids or monomers, offering a more rounded insight into material behaviour and properties.

7.2 General impact of the research

The understanding of the transesterification bond exchange mechanism and its impact on the properties of vitrimers developed in this work has significant practical implications. By understanding the intricacies of vitrimers, researchers and industry professionals can potentially develop formulations that are not only more efficient but also highly adaptable to a range of conditions and applications. A focus point of this research is the elucidation of the transesterification bond exchange mechanism in CANs vitrimers. This mechanism, often overlooked or not fully understood in previous studies, is foundational for the dynamic behaviour of these materials.

This study delves into the practical realm by quantifying the significance of variables such as catalyst concentration and dicarboxylic acid chain length. The results highlight the negligible influence of catalyst-induced bond exchange on the glass transition behaviour, given the timescales of standard experimental measurements. This investigation further unravels the complex interplay between temperature, catalyst concentration, dicarboxylic acid chain length, and bond exchange kinetics in associative CANs vitrimers. These critical findings not only provide enhanced understanding of vitrimer properties but also have substantial implications for the design and application of these materials. By manipulating the parameters of formulation, researchers and material scientists can engineer vitrimers with specific characteristics. For example, controlled flow rates and material viscosity can be achieved by the incorporation of additional bond exchange mechanisms²⁴⁴, as well as additional functionalities of the material, when difunctional norbornene monomers are introduced to the system, photocurable vitrimers were obtained by thiol-ene reaction²⁴⁵. Advancements in monomer and catalyst design in vitrimers have led to notable applications, such as self-healing materials in the automotive industry for car parts that repair themselves after damage²⁴⁶. In electronics, specially designed vitrimers are used

for flexible circuits and screens, supporting the development of advanced flexible devices²⁴⁷. Additionally, vitrimers designed for recyclability are contributing to sustainable material solutions, promoting a circular economy⁷. One of the standout findings of this research is the enhanced thermal stability observed in materials with longer acid chains. This suggests a strategy on how materials can be designed for applications that necessitate high thermal resistance. However, the dynamic nature of the ester bonds may restrict the extend of such superior mechanical property. To address the problem, further work need to consider the incorporation of thermally more stable bonds such as boronic esters²⁴⁸, aromatic sulphide crosslinks^{76,249}.

The elucidation of the kinetics of the epoxy-dicarboxylic acid reaction and the development of the corresponding cure kinetics models has practical implication with respect to the processing of these materials. The models can be used to optimise cure profiles in order to minimise process time and cost and in the case of large, thick components, minimise the risk of significant temperature overshoots. The wide range of formulations covered in cure kinetics analysis also allows material selection considerations to be taken into account in process design. This can potentially provide information relevant to processability and manufacturing cost during the stage of material selection for a specific application of a vitrimeric system.

8 Conclusions and recommendation for further work

8.1 Conclusions

The key conclusions of this study are as follows:

- The curing of DGEBA and dicarboxylic acids primarily involves addition esterification and a slower transesterification, resulting in crosslinked vitrimer structures. These reactions are temperature-dependent and maintain consistent mechanisms across both dynamic and isothermal conditions.

- The apparent activation energy of the epoxy- dicarboxylic acid reaction decreases from 121 to 74 kJ · mol⁻¹ as the carbon chain length increases from 6 carbons to 14, due to increased monomer flexibility.
- The diffusion limitation modified autocatalytic model describes the cure kinetics of epoxy- dicarboxylic acid systems with an average 84% goodness of fit.
- The T_g of epoxy-dicarboxylic acid vitrimers decreases with increasing dicarboxylic acid methylene repetitions from 36°C for the dicarboxylic acid with 6 units to lowest of 6°C for 14 units due to the reduction in crosslink density and increased chain flexibility.
- T_g is not affected by catalyst concentration as the bond exchange relaxation is extremely slow at the temperature range of T_g .
- Increasing the concentration of the catalyst speeds up bond exchange and reduces the topological freezing temperature (T_v) with an average reduction of 30°C to 65°C when the catalyst concentration increases from 1% to 5%.
- There is a distinct pattern in the relationship between chain length and T_v , including an increase from an average of 80°C, to a plateau of 120°C and 110°C, and then a decrease to 90°C and 80°C for the material using 6,8,10,12 and 14 carbons in the dicarboxylic acid chain. This pattern underscores the balance between crosslink density, functional group density, chain flexibility, and the distance between functional groups and bond exchange rate.
- The modulus of epoxy-dicarboxylic acid vitrimer during the curing process, increases with rising temperature, indicating faster crosslinking. At elevated temperatures, the modulus increases further due to rubber elasticity and additional crosslinking.
- Vitrimer structures with longer dicarboxylic acid chains exhibit enhanced thermal stability and higher degradation temperatures. The concentration of the catalyst plays a role in determining decomposition temperatures, given its dual function in vitrimer bond exchange and aiding oxidation.
- There is a temperature range above the glass transition in which the materials exhibit frequency independent modulus due to the superposition of bond exchange induced relaxation and structural relaxation. The span of this range

period is reduced by about 70°C when for increasing catalyst concentration from 1% to 5%.

8.2 Recommendation for further work

The comprehensive understanding of the transesterification bond exchange mechanism in CANs vitrimers, as developed in this work, is promising in terms of formulation tailoring and optimisation. To realise this impact, future work should address practical application of these findings. The potential for tailoring vitrimer properties, as highlighted in the study, should be explored in depth. By manipulating variables such as catalyst concentration and dicarboxylic acid chain length, the development of vitrimers with specific, desirable characteristics can be achieved.. However, it is crucial to consider the thermal and dynamic mechanical performance of these vitrimers, especially for aerospace applications. Their use in primary structural components of aerospace might be constrained due to limitations like glass transition temperature (T_g) and reduced performance in hot/wet conditions. Although they could still be viable for interior or secondary components in aerospace, meeting the industry specific demands necessitates further testing and optimization. Consequently, immediate applications in sectors like electronics, automotive interiors, or consumer goods, where the material thermal stability and tailorability align well with less stringent requirements, appear more feasible. Additionally, ongoing research should aim to enhance the hot/wet performance of these vitrimers and modify their polymer structure, thereby extending their applicability to aerospace and other high-performance domains.

To overcome the limitations identified in the study with DSC analysis, a more extensive experimental campaign for kinetics characterisation is necessary. This will bolster the robustness of the curing kinetics analysis, providing more reliable and consistent results. In terms of kinetics modelling, future work should aim to apply models than involve multiple mechanisms as well as more than one degree of cure variable.

Furthermore, the study of materials made with different catalyst levels should be expanded to include a wider range of formulations. Despite the necessity of a

catalyst for epoxy ring opening, alternative methods or materials should be explored to allow comparison with a non-catalysed system to gain a deeper understanding of the unique nature of exchangeable bonds and conventional thermosetting polymers.

The investigation into the rheological behaviour of vitrimers should be expanded in terms of the formulations examined as well as the number of repeat experiments carried out. This will allow a more comprehensive examination of the relationship between dicarboxylic acid structure, catalyst, and the frequency-independent transition temperature is thoroughly explored.

The study of the relationship between monomer structure and vitrimer properties should be broadened to include the potential influence of the type and structure of the epoxy. Increasing the length of the epoxy molecule can achieve effects equivalent to increasing the length of the dicarboxylic acid, whereas providing branching can result in more intensified effects governed by cross-linking. Overall, altering the epoxy pre-polymer structure will provide an additional design variable in the context of material tailoring.

References

1. Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* (80-.). **334**, 965–968 (2011).
2. Scheutz, G. M., Lessard, J. J., Sims, M. B. & Sumerlin, B. S. Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets. *J. Am. Chem. Soc.* **141**, 16181–16196 (2019).
3. Podgórski, M. *et al.* Toward stimuli-responsive dynamic thermosets through continuous development and improvements in covalent adaptable networks (CANs). *Adv. Mater.* **32**, (2020).
4. Long, R., Qi, H. J. & Dunn, M. L. Modeling the mechanics of covalently adaptable polymer networks with temperature-dependent bond exchange reactions. *Soft Matter* **9**, 4083–4096 (2013).
5. Alabiso, W. & Schlögl, S. The impact of vitrimers on the industry of the future: Chemistry, properties and sustainable forward-looking applications. *Polymers*. **12**, (2020).
6. Luo, Zoriana Demchuk, Xiao Zhao, Tomonori Saito, Ming Tian, Alexei P. Sokolov, Peng-Fei Cao, Elastic vitrimers: Beyond thermoplastic and thermoset elastomers. *Matter* vol. 5 1391–1422 (2022).
7. Jie Zheng, Zhuang Mao Png, Shi Hoe Ng, Guo Xiong Tham, Enyi Ye, Shermin S. Goh, Xian Jun Loh, Zibiao Li, Vitrimers: Current research trends and their emerging applications. *Mater. Today* **51**, 586–625 (2021).
8. Zhu, J.-B., Watson, E. M., Tang, J. & Chen, E. Y.-X. A synthetic polymer system with repeatable chemical recyclability. *Science* (80-.). **360**, 398–403 (2018).
9. Jensen, J. P. & Skelton, K. Wind turbine blade recycling: Experiences, challenges and possibilities in a circular economy. *Renew. Sustain. Energy*

Rev. **97**, 165–176 (2018).

10. Abbas-Abadi, M. S. The effect of process and structural parameters on the stability, thermo-mechanical and thermal degradation of polymers with hydrocarbon skeleton containing PE, PP, PS, PVC, NR, PBR and SBR. *J. Therm. Anal. Calorim.* **143**, 2867–2882 (2021).
11. Shi Changxia, McGraw Michael, L.Li, Zi Chen, Cavallo, Luigi Falivene, Laura Chen, Eugene Y.X. High-performance pan-tactic polythioesters with intrinsic crystallinity and chemical recyclability. *Sci. Adv.* **6**, (2020).
12. Ebewele, R. O. *Polymer Science and Technology*. (CRC Press, 2000). doi:10.1201/9781420057805.
13. Crne, M., Park, J. O. & Srinivasarao, M. Electrospinning physical gels: the case of stereocomplex PMMA. *Macromolecules* **42**, 4353–4355 (2009).
14. Fanari, F., Carboni, G., Grosso, M. & Desogus, F. Thermogravimetric analysis of different semolina doughs: Effect of mixing time and gluten content. *Chem. Eng. Trans.* **75**, 343–348 (2019).
15. Tsai, H.-Y., Nakamura, Y., Fujita, T. & Naito, M. Strengthening epoxy adhesives at elevated temperatures based on dynamic disulfide bonds. *Mater. Adv.* **1**, 3182–3188 (2020).
16. Denissen, W., Winne, J. M. & Du Prez, F. E. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **7**, 30–38 (2016).
17. Winne, J. M., Leibler, L. & Du Prez, F. E. Dynamic covalent chemistry in polymer networks: a mechanistic perspective. *Polym. Chem.* **10**, 6091–6108 (2019).
18. Adzima, B. J., Aguirre, H. A., Kloxin, C. J., Scott, T. F. & Bowman, C. N. Rheological and chemical analysis of reverse gelation in a covalently cross-linked diels-alder polymer network. *Macromolecules* **41**, 9112–9117 (2008).
19. Kloxin, C. J., Scott, T. F., Adzima, B. J. & Bowman, C. N. Covalent

- adaptable networks (CANs): A unique paradigm in cross-linked polymers. *Macromolecules* **43**, 2643–2653 (2010).
20. Scott, T. F., Schneider, A. D., Cook, W. D. & Bowman, C. N. Chemistry: Photoinduced plasticity in cross-linked polymers. *Science*. **308**, 1615–1617 (2005).
 21. Nicolaÿ, R., Kamada, J., Van Wassen, A. & Matyjaszewski, K. Responsive gels based on a dynamic covalent trithiocarbonate cross-linker. *Macromolecules* **43**, 4355–4361 (2010).
 22. Amamoto, Y., Otsuka, H., Takahara, A. & Matyjaszewski, K. Self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. *Adv. Mater.* **24**, 3975–3980 (2012).
 23. Hall, D. G. Boronic acid catalysis. *Chem. Soc. Rev.* **48**, 3475–3496 (2019).
 24. Brooks, W. L. A. & Sumerlin, B. S. Synthesis and Applications of Boronic Acid-Containing Polymers: From Materials to Medicine. *Chem. Rev.* **116**, 1375–1397 (2016).
 25. Black, S. P., Sanders, J. K. M. & Stefankiewicz, A. R. Disulfide exchange: Exposing supramolecular reactivity through dynamic covalent chemistry. *Chem. Soc. Rev.* **43**, 1861–1872 (2014).
 26. Deng, G. Li, Fuya Yu, Hongxia, Liu, Fuyong, Liu, Chenyang, Sun, Weixiang Dynamic hydrogels with an environmental adaptive self-healing ability and dual responsive Sol-Gel transitions. *ACS Macro Lett.* **1**, 275–279 (2012).
 27. Xu, X., Flores, J. D. & McCormick, C. L. Reversible imine shell cross-linked micelles from aqueous RAFT-synthesized thermoresponsive triblock copolymers as potential nanocarriers for ‘pH-triggered’ drug release. *Macromolecules* **44**, 1327–1334 (2011).
 28. Bhagavan, N. V. & Ha, C.-E. Protein and amino acid metabolism. *Essentials Med. Biochem.* 169–190 (2011). doi:10.1016/b978-0-12-095461-2.00015-1.

29. Obadia, M. M., Mudraboyina, B. P., Serghei, A., Montarnal, D. & Drockenmuller, E. Reprocessing and recycling of highly cross-linked ion-conducting networks through transalkylation exchanges of C-N bonds. *J. Am. Chem. Soc.* **137**, 6078–6083 (2015).
30. Obadia, M. M., Jourdain, A., Cassagnau, P., Montarnal, D. & Drockenmuller, E. Tuning the viscosity profile of ionic vitrimers incorporating 1,2,3-triazolium cross-links. *Adv. Funct. Mater.* **27**, 1–10 (2017).
31. Ma, J., Porath, L.E., Haque, M.F. Ultra-thin self-healing vitrimer coatings for durable hydrophobicity. *Nat. Commun.* **12**, 1–10 (2021).
32. Yang, Y., Wang, H., Zhang, S., Wei, Y., He, X., Wang, J., Zhang, Y., & Ji, Y. (2021). Vitrimer-based soft actuators with multiple responsiveness and self-healing ability triggered by multiple stimuli. *Matter*, 4(10), 3354–3365. <https://doi.org/10.1016/j.matt.2021.08.009>
33. Hewitt RW. *Epoxy Resins*. *Plast World* **28**, Issue 8, pp. 70-71 (Routledge, 1970).
34. Pascault, J. P. & Williams, R. J. J. *Epoxy polymers: new materials and innovations*. *epoxy polymers: new materials and innovations* pp. 325-344 (Wiley, 2010). doi:10.1002/9783527628704.
35. Kaufman, H. S. Handbook of epoxy resins. Henry Lee and Kris Neville. *J. Appl. Polym. Sci.* **14**, 253–253 (1970).
36. Hao Jiang, Lin Sun, Yurong Zhang, Fanting Meng, Wanxi Zhang, Chengji Zhao, Estrogenic activity research of a novel fluorinated bisphenol and preparation of an epoxy resin as alternative to bisphenol A epoxy resin. *Eur. Polym. J.* **108**, 507–516 (2018).
37. Tsarevsky, N. V., Bencherif, S. A. & Matyjaszewski, K. Graft copolymers by a combination of atp and two different consecutive click reactions. *Macromolecules* **40**, 4439–4445 (2007).

38. Libor Matějka, Svatopluk Pokorný, K. D. Acid curing of epoxy resins. A comparison between the polymerization of diepoxide-diacid and monoepoxide-cyclic anhydride systems. 1979–2176 (1985) doi:10.1002/macp.1985.021861006.
39. Matějka, L. & Dušek, K. Specific features of the kinetics of addition esterification of epoxide with the carboxyl group. *Polym. Bull.* **15**, 215–221 (1986).
40. Schechter, L., Wynstra, J. & Kurkijy, R. Chemistry of styrene oxide. comparison with phenyl glycidyl ether in model compound reactions. *Ind. Eng. Chem.* **49**, 1107–1109 (1957).
41. Blank, W. & He, Z. Catalysis of the epoxy-carboxyl reaction. *Int. Waterborne, High-Solids* **74**, 33–41 (2001).
42. Merfeld, G. Molaison, Chris, Koeniger, Rainer, Acar, A. Ersin, Mordhorst, Steve, Suriano, Joe, Irwin, Pat, Warner, Ron Singh, Gray, Ken, Smith, Mark, Kovalski, Kevin, Garrett, Greg, Finley, Steve, Meredith, Debora, Spicer, Mike, Naguy, Tom, Acid/epoxy reaction catalyst screening for low temperature (120 °C) powder coatings. *Prog. Org. Coatings* **52**, 98–109 (2005).
43. Lee, S. Do, Sanda, F. & Endo, T. Thermal latency and structure-activity relationship of aminimides in the polymerization of epoxide. *J. Polym. Sci. Part A Polym. Chem.* **35**, 689–694 (1997).
44. Suyama, K. & Shirai, M. Photobase generators: Recent progress and application trend in polymer systems. *Prog. Polym. Sci.* **34**, 194–209 (2009).
45. Ricciardi, F., Romanchick, W. A. & Joullié, M. M. 1,3-dialkylimidazolium salts as latent catalysts in the curing of epoxy resins. *J. Polym. Sci. Polym. Lett. Ed.* **21**, 633–638 (1983).
46. Kugler, S., Wierzbicka, E., Ossowicz-Rupniewska, P. & Łopinski, J. Composition and properties of protective coatings made of biologically-

- derived polyester reactive binder. *Polymers*. **13**, (2021).
47. Altuna, F. I., Hoppe, C. E. & Williams, R. J. J. Epoxy vitrimers: The effect of transesterification reactions on the network structure. *Polymers*. **10**, (2018).
 48. Heyd M, Kohnert A, Tan TH, Nusser M, Kirschhöfer F, Brenner-Weiss G, Franzreb M, Berensmeier S. Development and trends of biosurfactant analysis and purification using rhamnolipids as an example. *Anal. Bioanal. Chem.* **391**, 1579–1590 (2008).
 49. Luxia Yu, Chengpu Zhu, XiaoHao Sun, Jacob Salter, HengAn Wu, Yinghua Jin, Wei Zhang, and Rong Long. Rapid fabrication of malleable fiber reinforced composites with vitrimer powder. *ACS Appl. Polym. Mater.* **1**, 2535–2542 (2019).
 50. Altuna, F. I., Hoppe, C. E. & Williams, R. J. J. Shape memory epoxy vitrimers based on DGEBA crosslinked with dicarboxylic acids and their blends with citric acid. *RSC Adv.* **6**, 88647–88655 (2016).
 51. Legrand, A. & Soulié-Ziakovic, C. Silica–epoxy vitrimer nanocomposites. *Macromolecules* **49**, 5893–5902 (2016).
 52. Shi, Qian, Yu, Kai, Kuang, Xiao, Mu, Xiaoming, Dunn, Conner K., Dunn, Martin L., Wang, Tiejun, Jerry Qi, H. Recyclable 3D printing of vitrimer epoxy. *Mater. Horizons* **4**, 598–607 (2017).
 53. Tuan Liu, Liangdong Zhang, Ruoshi Chen, Liwei Wang, Bing Han, Yan Meng, and Xiaoyu Li. Nitrogen-free tetrafunctional epoxy and its DDS-cured high-performance matrix for aerospace applications. *Ind. Eng. Chem. Res.* **56**, 7708–7719 (2017).
 54. Tuan Liu, Cheng Hao, Shuai Zhang, Xiaoning Yang, Liwei Wang, Jiarui Han, Yuzhan Li, Junna Xin, and Jinwen Zhang. A Self-healable high glass transition temperature bioepoxy material based on vitrimer chemistry. *Macromolecules* **51**, 5577–5585 (2018).

55. Adrien Demongeot, Ramon Groote, Han Goossens, Theo Hoeks, François Tournilhac, and Ludwik Leibler. Cross-linking of poly(butylene terephthalate) by reactive extrusion using Zn(II) epoxy-vitrimer chemistry. *Macromolecules* **50**, 6117–6127 (2017).
56. Zhou, Y., Goossens, J. G. P., Sijbesma, R. P. & Heuts, J. P. A. Poly(butylene terephthalate)/Glycerol-based Vitrimers via Solid-State Polymerization. *Macromolecules* **50**, 6742–6751 (2017).
57. Zhou, Y., Groote, R., Goossens, J. G. P., Sijbesma, R. P. & Heuts, J. P. A. Tuning PBT vitrimer properties by controlling the dynamics of the adaptable network. *Polym. Chem.* **10**, 136–144 (2019).
58. Tran, T. N., Rawstron, E., Bourgeat-Lami, E. & Montarnal, D. Formation of cross-linked films from immiscible precursors through sintering of vitrimer nanoparticles. *ACS Macro Lett.* **7**, 376–380 (2018).
59. Han, H. & Xu, X. Poly(methyl methacrylate)–epoxy vitrimer composites. *J. Appl. Polym. Sci.* **135**, 1–5 (2018).
60. Zhang Biao, Yuan Chao, Zhang Wang, Dunn Martin L., Qi H. Jerry, Liu Zhuangjian, Yu Kai, Ge Qi. Recycling of vitrimer blends with tunable thermomechanical properties. *RSC Adv.* **9**, 5431–5437 (2019).
61. Zhiqiang Chen, Yu-Chen Sun, Jintian Wang, H. Jerry Qi, Tiejun Wang, and Hani E. Naguib. Flexible, reconfigurable, and self-healing tpu/vitrimer polymer blend with copolymerization triggered by bond exchange reaction. *ACS Appl. Mater. Interfaces* **12**, 8740–8750 (2020).
62. Huagao Fang, Wujin Ye, Kangjie Yang, Kai Song, Haibing Wei, Yunsheng Ding. Vitrimer chemistry enables epoxy nanocomposites with mechanical robustness and integrated conductive segregated structure for high performance electromagnetic interference shielding. *Compos. Part B Eng.* **215**, 108782 (2021).
63. Jinye Zhang, Shichang Luo, Yunlong Ma, Ruiyang Li, Yinghua Jin, Li Qiu, Wei Zhang. Monolithic polyimine vitrimer/graphene aerogel composites.

Chinese Chem. Lett. **34**, 107363 (2023).

64. Yang Yang, Pei Zhiqiang, Zhang Xiqi, Tao Lei, Wei Yen, Ji Yan. Carbon nanotube-vitrimer composite for facile and efficient photo-welding of epoxy. *Chem. Sci.* **5**, 3486–3492 (2014).
65. Huimin Wang, Yang Yang, Mingchao Zhang, Qi Wang, Kailun Xia, Zhe Yin, Yen Wei, Yan Ji, and Yingying Zhang. Electricity-triggered self-healing of conductive and thermostable vitrimer enabled by paving aligned carbon nanotubes. *ACS Appl. Mater. Interfaces* **12**, 14315–14322 (2020).
66. Zhanbin Feng, Jing Hu, Hongli Zuo, Nanying Ning, Liqun Zhang, Bing Yu, and Ming Tian. Photothermal-induced self-healable and reconfigurable shape memory bio-based elastomer with recyclable ability. *ACS Appl. Mater. Interfaces* **11**, 1469–1479 (2019).
67. Li Zhen, Yang Yang, Wang Zhenhua, Zhang Xiaoyong, Chen Qiaomei, Qian Xiaojie. Polydopamine nanoparticles doped in liquid crystal elastomers for producing dynamic 3D structures. *J. Mater. Chem. A* **5**, 6740–6746 (2017).
68. Luan, C., Yao, X., Zhang, C., Fu, J. & Wang, B. Integrated self-monitoring and self-healing continuous carbon fiber reinforced thermoplastic structures using dual-material three-dimensional printing technology. *Compos. Sci. Technol.* **188**, 107986 (2020).
69. Abry, J. C., Bochard, S., Chateauminois, A., Salvia, M. & Giraud, G. In situ detection of damage in CFRP laminates by electrical resistance measurements. *Compos. Sci. Technol.* **59**, 925–935 (1999).
70. Yu, K., Shi, Q., Dunn, M. L., Wang, T. & Qi, H. J. Carbon fiber reinforced thermoset composite with near 100% recyclability. *Adv. Funct. Mater.* **26**, 6098–6106 (2016).
71. Wang Sheng, Ma Songqi, Li Qiong, Xu Xiwei, Wang Binbo, Yuan Wangchao, Zhou Shenghua, You Shusen, Zhu Jin. Facile: In situ preparation of high-performance epoxy vitrimer from renewable resources

- and its application in nondestructive recyclable carbon fiber composite. *Green Chem.* **21**, 1484–1497 (2019).
72. Aoki Ryosuke, Yamaguchi Ayaka, Hashimoto Tamotsu, Urushisaki Michio, Sakaguchi Toshikazu, Kawabe Kazumasa, Kondo Keiichi, Iyo Hirohumi. Preparation of carbon fibers coated with epoxy sizing agents containing degradable acetal linkages and synthesis of carbon fiber-reinforced plastics (CFRPs) for chemical recycling. *Polym. J.* **51**, 909–920 (2019).
 73. Li Qiong. Ma Songqi. Wang Sheng. Yuan Wangchao. Xu Xiwei. Wang Binbo. Huang Kaifeng. Zhu Jin. Facile catalyst-free synthesis, exchanging, and hydrolysis of an acetal motif for dynamic covalent networks. *J. Mater. Chem. A* **7**, 18039–18049 (2019).
 74. Ruiz De Luzuriaga Alaitz, Martin Roberto, Markaide Nerea, Rekondo Alaitz, Cabañero Germán, Rodríguez Javier, Odriozola Ibon. Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Mater. Horizons* **3**, 241–247 (2016).
 75. Wang, Y., Jin, B., Ye, D. & Liu, Z. Fully recyclable carbon fiber reinforced vanillin-based epoxy vitrimers. *Eur. Polym. J.* **162**, 110927 (2022).
 76. Hongwei Si, Lin Zhou, Yeping Wu, Lixian Song, Ming Kang, Xiuli Zhao, Mao Chen. Rapidly reprocessable, degradable epoxy vitrimer and recyclable carbon fiber reinforced thermoset composites relied on high contents of exchangeable aromatic disulfide crosslinks. *Compos. Part B Eng.* **199**, 108278 (2020).
 77. Zhang, H., Cui, J., Hu, G. & Zhang, B. Recycling strategies for vitrimers. *Int. J. Smart Nano Mater.* **13**, 367–390 (2022).
 78. Otera, J. Transesterification. *Chem. Rev.* **93**, 1449–1470 (1993).
 79. Capelot, M., Unterlass, M. M., Tournilhac, F. & Leibler, L. Catalytic control of the vitrimer glass transition. *ACS Macro Lett.* **1**, 789–792 (2012).

80. Kumar, A. & Connal, L. A. Biobased transesterification vitrimers. *Macromol. Rapid Commun.* **44**, (2023).
81. Jiarui Han, Tuan Liu, Shuai Zhang, Cheng Hao, Junna Xin, Baohua Guo, and Jinwen Zhang. Hyperbranched polymer assisted curing and repairing of an epoxy coating. *Ind. Eng. Chem. Res.* **58**, 6466–6475 (2019).
82. Zhang, B., Kowsari, K., Serjouei, A., Dunn, M. L. & Ge, Q. Reprocessable thermosets for sustainable three-dimensional printing. *Nat. Commun.* **9**, (2018).
83. Capelot, M., Montarnal, D., Tournilhac, F. & Leibler, L. Metal-catalyzed transesterification for healing and assembling of thermosets. *J. Am. Chem. Soc.* **134**, 7664–7667 (2012).
84. Legrand, A. & Soulié-Ziakovic, C. Silica-epoxy vitrimer nanocomposites. *Macromolecules* **49**, 5893–5902 (2016).
85. Jiarui Han, Tuan Liu, Shuai Zhang, Cheng Hao, Junna Xin, Baohua Guo, and Jinwen Zhang. Mechanically robust and recyclable epdm rubber composites by a green cross-linking strategy. *ACS Sustain. Chem. Eng.* **7**, 11712–11720 (2019).
86. Rani, M., Keshu, Yadav, J. & Shanker, U. Green synthesized Zn-based catalysts. in *Zinc-based nanostructures for environmental and agricultural applications*, pp. 93–121 (Elsevier, 2021). doi:10.1016/B978-0-12-822836-4.00008-2
87. Reza Tayebie, S. Javad Ahmadi, Esmaeil Rezaei Seresht, Farzad Javadi, Mohammad A. Yasemi, Morteza Hosseinpour, and Behrouz Maleki. Commercial zinc oxide: a facile, efficient, and eco-friendly catalyst for the one-pot three-component synthesis of multisubstituted 2-aminothiophenes via the gewald reaction. *Ind. Eng. Chem. Res.* **51**, 14577–14582 (2012).
88. Hussien, N. A., Al Malki, J. S., Al Harthy, F. A. R., Mazi, A. W. & Al Shadadi, J. A. A. Sustainable eco-friendly synthesis of zinc oxide nanoparticles using banana peel and date seed extracts, characterization, and cytotoxicity

- evaluation. *Sustainability* **15**, 9864 (2023).
89. Faiza A.M. Alahdal, Mohsen T.A. Qashqoosh, Yahiya Kadaf Manea, Mansour A.S. Salem, Amjad M.T. Khan, Saeeda Naqvi. Eco-friendly synthesis of zinc oxide nanoparticles as nanosensor, nanocatalyst and antioxidant agent using leaf extract of *P. austroarabica*. *OpenNano* **8**, 100067 (2022).
 90. Demongeot, A., Mognier, S. J., Okada, S., Soulié-Ziakovic, C. & Tournilhac, F. Coordination and catalysis of Zn^{2+} in epoxy-based vitrimers. *Polym. Chem.* **7**, 4486–4493 (2016).
 91. Self, J. L., Dolinski, N. D., Zayas, M. S., Read De Alaniz, J. & Bates, C. M. Brønsted-acid-catalyzed exchange in polyester dynamic covalent networks. *ACS Macro Lett.* **7**, 817–821 (2018).
 92. Wang Jinyun, Chen Shubin, Lin Tengfei, Ke Jinhuang, Chen Tianxiang, Wu Xiao, Lin Cong. A catalyst-free and recycle-reinforcing elastomer vitrimer with exchangeable links. *RSC Adv.* **10**, 39271–39276 (2020).
 93. Jacob J. Lessard, Luis F. Garcia, Charles P. Easterling, Michael B. Sims, Kyle C. Bentz, Scarlett Arencibia, Daniel A. Savin, and Brent S. Sumerlin. Catalyst-free vitrimers from vinyl polymers. *Macromolecules* **52**, 2105–2111 (2019).
 94. Cromwell, O. R., Chung, J. & Guan, Z. Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds. *J. Am. Chem. Soc.* **137**, 6492–6495 (2015).
 95. Cuminet Florian, Berne Dimitri, Lemouzy Sébastien, Dantras Éric, Joly-Duhamel Christine, Caillol Sylvain, Leclerc Éric, Ladmira Vincent. Catalyst-free transesterification vitrimers: activation via α -difluoroesters. *Polym. Chem.* 2651–2658 (2022). doi:10.1039/d2py00124a
 96. Van Lijsebetten, F., Holloway, J. O., Winne, J. M. & Du Prez, F. E. Internal catalysis for dynamic covalent chemistry applications and polymer science. *Chem. Soc. Rev.* **49**, 8425–8438 (2020).

97. Cuminet, F., Caillol, S., Dantras, É., Leclerc, É. & Ladmiral, V. Neighboring group participation and internal catalysis effects on exchangeable covalent bonds: application to the thriving field of vitrimer chemistry. *Macromolecules* **54**, 3927–3961 (2021).
98. Shuaipeng Wang, Na Teng, Jinyue Dai, Jingkai Liu, Lijun Cao, Weiwei Zhao, Xiaoqing Liu. Taking advantages of intramolecular hydrogen bonding to prepare mechanically robust and catalyst-free vitrimer. *Polymer*. **210**, 123004 (2020).
99. Zhang, H., Majumdar, S., van Benthem, R. A. T. M., Sijbesma, R. P. & Heuts, J. P. A. Intramolecularly catalyzed dynamic polyester networks using neighboring carboxylic and sulfonic acid groups. *ACS Macro Lett.* **9**, 272–277 (2020).
100. El-Zaatari, B. M., Ishibashi, J. S. A. & Kalow, J. A. Cross-linker control of vitrimer flow. *Polym. Chem.* **11**, 5339–5345 (2020).
101. Schoustra, S. K., Dijksman, J. A., Zuilhof, H. & Smulders, M. M. J. Molecular control over vitrimer-like mechanics – tuneable dynamic motifs based on the Hammett equation in polyimine materials. *Chem. Sci.* **12**, 293–302 (2021).
102. Debnath, S., Kaushal, S. & Ojha, U. Catalyst-free partially bio-based polyester vitrimers. *ACS Appl. Polym. Mater.* **2**, 1006–1013 (2020).
103. Blake, P. G. & Shraydeh, B. F. The thermal decomposition of fluorinated esters. *Int. J. Chem. Kinet.* **13**, 463–471 (1981).
104. Schmeer, G. & Sturm, P. A quantum chemical approach to the water assisted neutral hydrolysis of ethyl acetate and its derivatives. *Phys. Chem. Chem. Phys.* **1**, 1025–1030 (1999).
105. Bégué, J. & Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry Of Fluorine.*, pp. 1-22, (Wiley, 2008). doi:10.1002/9780470281895.
106. Ng Kok Wei Joseph, Lim Jacob Song Kiat, Gupta Nupur, Dong Bing Xue, Hu

- Chun Po, Hu Jingdan, Hu Xiao Matthew. A facile alternative strategy of upcycling mixed plastic waste into vitrimers. *Commun. Chem.* **6**, 1–12 (2023).
107. Soman, B., Go, Y. K., Shen, C., Leal, C. & Evans, C. M. Impact of dynamic covalent chemistry and precise linker length on crystallization kinetics and morphology in ethylene vitrimers. *Soft Matter* **18**, 293–303 (2022).
 108. Krishnan, B. P., Saalwaechter, K., Adjedje, V. K. B. & Binder, W. H. Design, synthesis and characterization of vitrimers with low topology freezing transition temperature. *Polymers* **14**, 1–16 (2022).
 109. Spiesschaert Yann, Taplan Christian, Stricker Lucas, Guerre Marc, Winne Johan M., Du Prez Filip E. Influence of the polymer matrix on the viscoelastic behaviour of vitrimers. *Polym. Chem.* **11**, 5377–5385 (2020).
 110. Chen Chin-Wen, Liu Ping-Hui, Lin Fan-Jie, Cho Chia-Jung, Wang Li-Yuan, Mao Hsu-I., Chiu Yu-Cheng, Chang Shang-Hung, Rwei Syang-Peng, Kuo Chi-Ching. Influence of different molecular weights and concentrations of poly(glycidyl methacrylate) on recycled poly(ethylene terephthalate): a thermal, mechanical, and rheological study. *J. Polym. Environ.* **28**, 2880–2892 (2020).
 111. Dijkstra, K. & Gaymans, R. J. Nylon-6/rubber blends: 8. Influence of the molecular weight of the matrix on the impact behaviour. *Polymer* **35**, 332–335 (1994).
 112. Oshinski, A. J., Keskkula, H. & Paul, D. R. The role of matrix molecular weight in rubber toughened nylon 6 blends: Room temperature Izod impact toughness. *Polymer*. **37**, 4909–4918 (1996).
 113. He Changfei, Christensen Peter R., Seguin Trevor J., Dailing Eric A., Wood Brandon M., Walde Rebecca K., Persson Kristin A., Russell Thomas P., Helms Brett A. Conformational entropy as a means to control the behavior of poly(diketoenamine) vitrimers in and out of equilibrium. *Angew. Chemie - Int. Ed.* **59**, 735–739 (2020).

114. Lukas Odenwald, Florian P. Wimmer, Nina K. Mast, Max G. Schußmann, Manfred Wilhelm, and Stefan Mecking. Molecularly defined polyolefin vitrimers from catalytic insertion polymerization. *J. Am. Chem. Soc.* **144**, 13226–13233 (2022).
115. Chen, M., Zhou, L., Wu, Y., Zhao, X. & Zhang, Y. Rapid stress relaxation and moderate temperature of malleability enabled by the synergy of disulfide metathesis and carboxylate transesterification in epoxy vitrimers. *ACS Macro Lett.* **8**, 255–260 (2019).
116. Zheng Hua, Liu Qing, Lei Xingfeng, Chen Yanhui, Zhang Baoliang, Zhang Qiuyu. Performance-modified polyimine vitrimers: flexibility, thermal stability and easy reprocessing. *J. Mater. Sci.* **54**, 2690–2698 (2019).
117. Hu, W.-G. & Schmidt-Rohr, K. Polymer ultradrawability: the crucial role of α -relaxation chain mobility in the crystallites. *Acta Polym.* **50**, 271–285 (1999).
118. Azcune, I., Huegun, A., Ruiz de Luzuriaga, A., Saiz, E. & Rekondo, A. The effect of matrix on shape properties of aromatic disulfide based epoxy vitrimers. *Eur. Polym. J.* **148**, (2021).
119. Bouyahyi, M., Pepels, M. P. F., Heise, A. & Duchateau, R. ω -Pentadecalactone polymerization and ω -pentadecalactone/ $\hat{\mu}$ -caprolactone copolymerization reactions using organic catalysts. *Macromolecules* **45**, 3356–3366 (2012).
120. Meng, F., Saed, M. O. & Terentjev, E. M. Elasticity and relaxation in full and partial vitrimer networks. *Macromolecules* **52**, 7423–7429 (2019).
121. Ricarte, R. G. & Shanbhag, S. Unentangled vitrimer melts: interplay between chain relaxation and cross-link exchange controls linear rheology. *Macromolecules* **54**, 3304–3320 (2021).
122. Jiancheng Luo, Zoriana Demchuk, Xiao Zhao, Tomonori Saito, Ming Tian, Alexei P. Sokolov, Peng-Fei Cao, Elastic vitrimers: Beyond thermoplastic and thermoset elastomers. *Matter* **5**, 1391–1422 (2022).

123. Huanbo Wang, Yuan Fu, Yue Liu, Jinpeng Li, Xianzu Sun, Tian Liu. Synthesis of facilely healable and recyclable imine vitrimers using biobased branched diamine and vanillin. *Eur. Polym. J.* **196**, 112309 (2023).
124. Zhou, Z., Su, X., Liu, J. & Liu, R. Synthesis of vanillin-based polyimine vitrimers with excellent reprocessability, fast chemical degradability, and adhesion. *ACS Appl. Polym. Mater.* **2**, 5716–5725 (2020).
125. Hu, S., Chen, X. & Torkelson, J. M. Biobased reprocessable polyhydroxyurethane networks: full recovery of crosslink density with three concurrent dynamic chemistries. *ACS Sustain. Chem. Eng.* **7**, 10025–10034 (2019).
126. Delliere, P. & Guigo, N. Exploring new horizons for bio-based poly(furfuryl alcohol) by exploiting functionalities offered by side reactions. *ACS Macro Lett.* **11**, 1202–1206 (2022).
127. Min Liu, Fei Gao, Xinru Guo, Qianqian Liang, Jinlong He, Jiang Zhong, Cong Lin, Faman Lin, Liang Shen. Room temperature-curable, easily degradable, and highly malleable and recyclable vanillin-based vitrimers with catalyst-free bond exchange. *Polym. Test.* **115**, 107740 (2022).
128. Saalwächter, K., Soman, B. & Evans, C. M. Crystallinity and perfection in ethylene vitrimers probed by combined calorimetry, scattering, and time-domain NMR. *Front. Soft Matter* **3**, (2023).
129. Barabanova, A. I., Afanas'ev, E. S., Molchanov, V. S., Askadskii, A. A. & Philippova, O. E. Unmodified silica nanoparticles enhance mechanical properties and welding ability of epoxy thermosets with tunable vitrimer matrix. *Polymers (Basel)*. **13**, (2021).
130. Huang, Z., Wang, Y., Zhu, J., Yu, J. & Hu, Z. Surface engineering of nanosilica for vitrimer composites. *Compos. Sci. Technol.* **154**, 18–27 (2018).
131. Lin Wang, Yingjun Liu, Na Hao, Yunhe Qiao, Wanting Zeng, Liping Wei, Aihua Du. Combining multiple hydrogen bonds and boronic ester chemistry

- towards mechanically robust and creep resisting elastomer vitrimer. *Polymer (Guildf)*. **265**, 125595 (2023).
132. Hong Gao, Yingchun Sun, Miaomiao Wang, Zhen Wang, Guoqiang Han, Ling Jin, Peng Lin, Youyi Xia, and Kui Zhang. Mechanically robust and reprocessable acrylate vitrimers with hydrogen-bond-integrated networks for photo-3d printing. *ACS Appl. Mater. Interfaces* **13**, 1581–1591 (2021).
 133. Kim, G., Caglayan, C. & Yun, G. J. Epoxy-based catalyst-free self-healing elastomers at room temperature employing aromatic disulfide and hydrogen bonds. *ACS Omega* **7**, 44750–44761 (2022).
 134. Breuillac, A., Kassalias, A. & Nicolaÿ, R. Polybutadiene vitrimers based on dioxaborolane chemistry and dual networks with static and dynamic cross-links. *Macromolecules* **52**, 7102–7113 (2019).
 135. Brutman, J. P., Fortman, D. J., De Hoe, G. X., Dichtel, W. R. & Hillmyer, M. A. Mechanistic study of stress relaxation in urethane-containing polymer networks. *J. Phys. Chem. B* **123**, 1432–1441 (2019).
 136. Zhao, S. & Abu-Omar, M. M. Catechol-Mediated Glycidylation toward Epoxy Vitrimers/Polymers with Tunable Properties. 123. Zhao, S. & Abu-Omar, M. M. Catechol-mediated glycidylation toward epoxy vitrimers/polymers with tunable properties. *Macromolecules* **52**, 3646–3654 (2019).
 137. Hayashi, M., Yano, R. & Takasu, A. Synthesis of amorphous low: Tg polyesters with multiple COOH side groups and their utilization for elastomeric vitrimers based on post-polymerization cross-linking. *Polym. Chem.* **10**, 2047–2056 (2019).
 138. Hayashi, M. & Yano, R. Fair investigation of cross-link density effects on the bond-exchange properties for trans-esterification-based vitrimers with identical concentrations of reactive groups. *Macromolecules* **53**, 182–189 (2020).
 139. Brutman, J. P., Delgado, P. A. & Hillmyer, M. A. Polylactide vitrimers. *ACS*

Macro Lett. **3**, 607–610 (2014).

140. Taplan, C., Guerre, M., Winne, J. M. & Du Prez, F. E. Fast processing of highly crosslinked, low-viscosity vitrimers. *Mater. Horizons* **7**, 104–110 (2020).
141. Poutrel, Q. A., Blaker, J. J., Soutis, C., Tournilhac, F. & Gresil, M. Dicarboxylic acid-epoxy vitrimers: Influence of the off-stoichiometric acid content on cure reactions and thermo-mechanical properties. *Polym. Chem.* **11**, 5327–5338 (2020).
142. Domínguez, J. C., Grivel, J. C. & Madsen, B. Study on the non-isothermal curing kinetics of a polyfurfuryl alcohol bioresin by DSC using different amounts of catalyst. *Thermochim. Acta* **529**, 29–35 (2012).
143. Adroja, P. P., Ghumara, R. Y. & Parsania, P. H. Dynamic DSC curing kinetic study of epoxy resin of 1,3-bis(4-hydroxyphenyl) prop-2-en-1-one using aromatic diamines and phthalic anhydride. *J. Appl. Polym. Sci.* **130**, 572–578 (2013).
144. Wang, Q., He, T., Xia, P., Chen, T. & Huang, B. Cure processing modeling and cure cycle simulation of epoxy-terminated poly(phenylene ether ketone). I. DSC characterization of curing reaction. *J. Appl. Polym. Sci.* **66**, 789–797 (1997).
145. Liang, G. & Chandrashekhara, K. Cure kinetics and rheology characterization of soy-based epoxy resin system. *J. Appl. Polym. Sci.* **102**, 3168–3180 (2006).
146. Bogetti, T. A. & Gillespie, J. W. Process-induced stress and deformation in thick-section thermoset composite laminates. *J. Compos. Mater.* **26**, 626–660 (1992).
147. Wang, Q., He, T., Xia, P., Chen, T. & Huang, B. Cure processing modeling and cure cycle simulation of epoxy-terminated poly(phenylene ether ketone). III. Determination of the time of pressure application. *J. Appl. Polym. Sci.* **66**, 1745–1750 (1997).

148. Hossain, A., Bhattacharyya, A. & Reiser, O. Copper's rapid ascent in visible-light photoredox catalysis. *Science* (80-.). **364**, (2019).
149. Defense documentation center. *Appl. Ergon.* **7**, 52 (1976).
150. Tsanaktsidou E, Kammona O, Labude N, Neuss S, Krüger M, Kock L, Kiparissides C. Biomimetic cell-laden meha hydrogels for the regeneration of cartilage tissue. *Polymers*. **12**, 1598 (2020).
151. Fei, X.; Zhao, F.; Wei, W.; Luo, J.; Chen, M.; Liu, X. Tannic acid as a bio-based modifier of epoxy/anhydride thermosets. *Polymers*. **8**, (2016).
152. Pire, M., Norvez, S., Iliopoulos, I., Le Rossignol, B. & Leibler, L. Imidazole-promoted acceleration of crosslinking in epoxidized natural rubber/dicarboxylic acid blends. *Polymer*. **52**, 5243–5249 (2011).
153. Pire Myriam, Lorthioir Cédric, Oikonomou Evdokia K., Norvez Sophie, Iliopoulos Ilias, Le Rossignol Benoît ,Leibler Ludwik. Imidazole-accelerated crosslinking of epoxidized natural rubber by dicarboxylic acids: a mechanistic investigation using NMR spectroscopy. *Polym. Chem.* **3**, 946 (2012).
154. Montarnal, D., Tournilhac, F., Hidalgo, M. & Leibler, L. Epoxy-based networks combining chemical and supramolecular hydrogen-bonding crosslinks. *J. Polym. Sci. Part A Polym. Chem.* **48**, 1133–1141 (2010).
155. Hoppe, C. E., Galante, M. J., Oyanguren, P. A. & Williams, R. J. J. Epoxies modified by palmitic acid: from hot-melt adhesives to plasticized networks. *Macromol. Mater. Eng.* **290**, 456–462 (2005).
156. Dusek, K. & Matejka, L. Transesterification and gelation of polyhydroxy esters formed from diepoxides and dicarboxylic acids. *Adv. Chem. Ser.* 15–26 (1984) doi:10.1021/ba-1984-0208.ch002.
157. White, J. E., Earls, J. D., Sherman, J. W., López, L. C. & Dettloff, M. L. Step-growth polymerization of 10,11-epoxyundecanoic acid. Synthesis and properties of a new hydroxy-functionalized thermoplastic polyester.

- Polymer*. **48**, 3990–3998 (2007).
158. Libor Matějka, S. P. & K. D. Network formation involving epoxide and carboxyl groups. *Polym. Bull.* **29**, 119–126 (1987).
 159. Hardis, R., Jessop, J. L. P., Peters, F. E. & Kessler, M. R. Cure kinetics characterization and monitoring of an epoxy resin using DSC, Raman spectroscopy, and DEA. *Compos. Part A Appl. Sci. Manuf.* **49**, 100–108 (2013).
 160. Vyazovkin, S. & Sbirrazzuoli, N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromol. Rapid Commun.* **27**, 1515–1532 (2006).
 161. Wadsö, I. & Goldberg, R. N. Standards in isothermal microcalorimetry (IUPAC Technical Report). *Pure Appl. Chem.* **73**, 1625–1639 (2001).
 162. Sergey Vyazovkin, Alan K. Burnham, José M. Criado, Luis A. Pérez-Maqueda, Crisan Popescu, Nicolas Sbirrazzuoli. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **520**, 1–19 (2011).
 163. Thomas, A., Moinuddin, K., Tretsiakova-McNally, S. & Joseph, P. A kinetic analysis of the thermal degradation behaviours of some bio-based substrates. *Polymers*. **12**, 1830 (2020).
 164. Perkin Elmer. Thermogravimetric analysis (TGA). *Perkin Elmer* 3–19 (2004) doi:10.1198/tech.2005.s328.
 165. Menard, K. P. Dynamic Mechanical Analysis. (CRC Press, 2008). doi:10.1201/9781420053135.
 166. Stuart, B. H. Infrared Spectroscopy: fundamentals and applications. (Wiley, 2004). doi:10.1002/0470011149.
 167. Nakamura, T., Homma, K. & Tachibana, K. Impedance spectroscopy of manganite films prepared by metalorganic chemical vapor deposition. *J. Nanosci. Nanotechnol.* **11**, 8408–8411 (2011).

168. Mewis, J. & Wagner, N. J. *Colloidal suspension rheology*. (Cambridge University Press, 2011). doi:10.1017/CBO9780511977978.
169. Pfeifer, H. Principles of nuclear magnetic resonance microscopy. *Zeitschrift für Phys. Chemie* **176**, 132–132 (1992).
170. Clarke, R. W., McGraw, M. L., Newell, B. S. & Chen, E. Y. X. Thermomechanical activation achieving orthogonal working/healing conditions of nanostructured tri-block copolymer thermosets. *Cell Reports Phys. Sci.* **2**, 100483 (2021).
171. Liu, J., Li, J. J., Luo, Z. H. & Zhou, Y. N. Fast room-temperature self-healing vitrimers enabled by accelerated associative exchange kinetics. *Chem. Eng. J.* **452**, 139452 (2023).
172. Li, M., Jiang, L., He, J.-J. & Sun, J.-H. Kinetic triplet determination and modified mechanism function construction for thermo-oxidative degradation of waste polyurethane foam using conventional methods and distributed activation energy model method. *Energy* **175**, 1–13 (2019).
173. Kovash, C. S., Pavlacky, E., Selvakumar, S., Sibi, M. P. & Webster, D. C. Thermoset coatings from epoxidized sucrose soyate and blocked, bio-based dicarboxylic acids. *ChemSusChem* **7**, 2289–2294 (2014).
174. Milchert, E. & Smagowicz, A. The influence of reaction parameters on the epoxidation of rapeseed oil with peracetic acid. *JAOCs, J. Am. Oil Chem. Soc.* **86**, 1227–1233 (2009).
175. Yang Xuejuan, Wang Chunpeng, Li Shouhai, Huang Kun, Li Mei, Mao Wei, Cao Shan, Xia Jianling. Study on the synthesis of bio-based epoxy curing agent derived from myrcene and castor oil and the properties of the cured products. *RSC Adv.* **7**, 238–247 (2017).
176. Kissinger, H. E. Reaction kinetics in differential thermal analysis. *Anal. Chem.* **29**, 1702–1706 (1957).
177. Liu Jie, Luo Lan, Hu Yadi, Wang Fang, Zheng Xuejing, Tang Keyong.

Kinetics and mechanism of thermal degradation of vegetable-tanned leather fiber. *J. Leather Sci. Eng.* **1**, 9 (2019).

178. Alvarado Flores, J.J.; Rutiaga Quiñones, J.G.; Ávalos Rodríguez, M.L.; Alcaraz Vera, J.V.; Espino Valencia, J.; Guevara Martínez, S.J.; Márquez Montesino, F.; Alfaro Rosas. Thermal degradation kinetics and ft-ir analysis on the pyrolysis of pinus pseudostrobus, pinus leiophylla and pinus montezumae as forest waste in western mexico. *Energies* **13**, 969 (2020).
179. Al-Yaari, M. & Dubdub, I. Pyrolytic behavior of polyvinyl chloride: kinetics, mechanisms, thermodynamics, and artificial neural network application. *Polymers (Basel)*. **13**, 4359 (2021).
180. Mashouf Roudsari, G., Mohanty, A. K. & Misra, M. Study of the curing kinetics of epoxy resins with biobased hardener and epoxidized soybean oil. *ACS Sustain. Chem. Eng.* **2**, 2111–2116 (2014).
181. Ma Zhihang, Wang Xiao, Li Junru, Li Xinlin, Zhang Chuanwei, Zhang Ruyi, Gu Yan, Zhang Pengfei. Isoconversional models toward the curing kinetics of self-healable epoxy resin TGDDM and acid anhydride. *J. Appl. Polym. Sci.* **139**, (2022).
182. Espinosa, J. P., Hanazumi, V., Stefani, P. M. & Ruseckaite, R. A. Curing behavior and properties of high biosourced epoxy resin blends based on a triepoxy monomer and a tricarboxylic acid hardener from 10-undecenoic acid. *Polym. Test.* **81**, 106208 (2020).
183. Jaillet, F., Desroches, M., Auvergne, R., Boutevin, B. & Caillol, S. New biobased carboxylic acid hardeners for epoxy resins. *Eur. J. Lipid Sci. Technol.* **115**, 698–708 (2013).
184. Ding, C., Shuttleworth, P. S., Makin, S., Clark, J. H. & Matharu, A. S. New insights into the curing of epoxidized linseed oil with dicarboxylic acids. *Green Chem.* **17**, 4000–4008 (2015).
185. Menager, C., Guigo, N., Vincent, L. & Sbirrazzuoli, N. Polymerization kinetic pathways of epoxidized linseed oil with aliphatic bio-based

- dicarboxylic acids. *J. Polym. Sci.* **58**, 1717–1727 (2020).
186. Mustata, F. & Tudorachi, N. Curing kinetics and thermal characterization of epoxy resin cured with amidodicarboxylic acids. *Appl. Therm. Eng.* **125**, 285–296 (2017).
 187. Snijkers, F., Pasquino, R. & Maffezzoli, A. Curing and viscoelasticity of vitrimers. *Soft Matter* **13**, 258–268 (2017).
 188. Solène Guggari, Fiona Magliozzi, Samuel Malburet, Alain Graillet, Mathias Destarac, and Marc Guerre. Vanillin-based epoxy vitrimers: looking at the cystamine hardener from a different perspective. *ACS Sustain. Chem. Eng.* **11**, 6021–6031 (2023).
 189. Huagao Fang, Wujin Ye, Yunsheng Ding, and H. Henning Winte. Rheology of the critical transition state of an epoxy vitrimer. *Macromolecules* **53**, 4855–4862 (2020).
 190. Altuna F. I., Casado U., Dell'Erba I. E., Luna L., Hoppe C. E., Williams R. J.J. Epoxy vitrimers incorporating physical crosslinks produced by self-association of alkyl chains. *Polym. Chem.* **11**, 1337–1347 (2020).
 191. Russo, C., Fernández-Francos, X. & De la Flor, S. Rheological and mechanical characterization of advanced applications. *Polymers.* **11**, (2019).
 192. Perego, A., Lazarenko, D., Cloitre, M. & Khabaz, F. Microscopic dynamics and viscoelasticity of vitrimers. *Macromolecules* **55**, 7605–7613 (2022).
 193. Tanaka, F. & Edwards, S. F. Viscoelastic properties of physically crosslinked networks. Part 3. Time-dependent phenomena. *J. Nonnewton. Fluid Mech.* **43**, 289–309 (1992).
 194. Meng, F., Saed, M. O. & Terentjev, E. M. Rheology of vitrimers. *Nat. Commun.* **13**, (2022).
 195. Shi, X., Ge, Q., Lu, H. & Yu, K. The nonequilibrium behaviors of covalent adaptable network polymers during the topology transition. *Soft Matter* **17**,

2104–2119 (2021).

196. Tuan Liu, Cheng Hao, Liwei Wang, Yuzhan Li, Wangcheng Liu, Junna Xin, and Jinwen Zhang. Eugenol-derived biobased epoxy: shape memory, repairing, and recyclability. *Macromolecules* **50**, 8588–8597 (2017).
197. Pritchard, R. H., Redmann, A. L., Pei, Z., Ji, Y. & Terentjev, E. M. Vitrification and plastic flow in transient elastomer networks. *Polymer* **95**, 45–51 (2016).
198. Gupta, A. & Thevamaran, R. Requisites on viscoelasticity for exceptional points in passive elastodynamic metamaterials. (2022).
199. Lang, M. & Müller, T. Analysis of the gel point of polymer model networks by computer simulations. *Macromolecules* **53**, 498–512 (2020).
200. Hricovíniová, Z. Surfactants of biological origin: The role of Mo(VI) and microwaves in the synthesis of xylan-based non-ionic surfactants. *Carbohydr. Polym.* **144**, 297–304 (2016).
201. Málek, J. The kinetic analysis of non-isothermal data. *Thermochim. Acta* **200**, 257–269 (1992).
202. Senum, G. I. & Yang, R. T. Rational approximations of the integral of the Arrhenius function. *J. Therm. Anal.* **11**, 445–447 (1977).
203. Cole, K. C. A new approach to modeling the cure kinetics of epoxy amine thermosetting resins. 1. mathematical development. *Macromolecules* **24**, 3093–3097 (1991).
204. Hubert, P., Johnston, A., Poursartip, A. & Nelson, K. Cure kinetics and viscosity models for Hexcel 8552 epoxy resin. *Int. SAMPE Symp. Exhib.* **46 II**, 2341–2354 (2001).
205. Lee, L. J. Modeling and computer simulation of reactive processing. in *Comprehensive Polymer Science and Supplements* 575–617 (Elsevier, 1989). doi:10.1016/B978-0-08-096701-1.00238-X.
206. Konuray, A. O., Fernández-Francos, X. & Ramis, X. Analysis of the reaction

- mechanism of the thiol-epoxy addition initiated by nucleophilic tertiary amines. *Polym. Chem.* **8**, 5934–5947 (2017).
207. Jing F, Zhao R, Li C, Xi Z, Wang Q, Xie H. Influence of the epoxy/acid stoichiometry on the cure behavior and mechanical properties of epoxy vitrimers. *Molecules* **27**, (2022).
 208. Yang, Z., Wang, Q. & Wang, T. Dual-triggered and thermally reconfigurable shape memory graphene-vitrimer composites. *ACS Appl. Mater. Interfaces* **8**, 21691–21699 (2016).
 209. Starink, M. J. The determination of activation energy from linear heating rate experiments: A comparison of the accuracy of isoconversion methods. *Thermochim. Acta* **404**, 163–176 (2003).
 210. Frensdorff, H. K. Dependence of activation energy for viscous activation for viscous,. *Journal of applied polymer science*, Vol. Vi, Issue No. 23, pp. 29–30. (1962)
 211. Sergey Vyazovkin, Alan K. Burnham, Loic Faveregeon, Nobuyoshi Koga, Elena Moukhina, Luis A. Pérez-Maqueda, Nicolas Sbirrazzuoli. ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics. *Thermochim. Acta* **689**, 178597 (2020).
 212. Ozawa, T. Applicability of Friedman plot. *J. Therm. Anal.* **31**, 547–551 (1986).
 213. Starink, M. J. Analysis of hydrogen desorption from linear heating experiments: Accuracy of activation energy determinations. *Int. J. Hydrogen Energy* **43**, 6632–6641 (2018).
 214. El-Thaher, N., Mussone, P., Bressler, D. & Choi, P. Kinetics study of curing epoxy resins with hydrolyzed proteins and the effect of denaturants urea and sodium dodecyl sulfate. *ACS Sustain. Chem. Eng.* **2**, 282–287 (2014).
 215. Sbirrazzuoli, N., Vyazovkin, S., Mititelu, A., Sladic, C. & Vincent, L. A study of epoxy-amine cure kinetics by combining isoconversional analysis with

- temperature modulated dsc and dynamic rheometry. *Macromol. Chem. Phys.* **204**, 1815–1821 (2003).
216. Sbirrazzuoli, N. Advanced isoconversional kinetic analysis for the elucidation of complex reaction mechanisms: A new method for the identification of rate-limiting steps. *Molecules* **24**, (2019).
 217. Sheng, X., Lee, J. K. & Kessler, M. R. Influence of cross-link density on the properties of ROMP thermosets. *Polymer*. **50**, 1264–1269 (2009).
 218. Morancho, J. M., Ramis X., Fernández-Francos X., Konuray O., Salla J. M. Serra. Dual curing of an epoxy resin with dicarboxylic acids. *J. Therm. Anal. Calorim.* **142**, 607–615 (2020).
 219. Montserrat, S., Cortés, P., Calventus, Y. & Hutchinson, J. M. Effect of crosslink length on the enthalpy relaxation of fully cured epoxy-diamine resins. *Journal of Polymer Science, Part B: Polymer Physics* vol. 38 456–468 (2000).
 220. Song, Z., Wang, Z. & Cai, S. Mechanics of vitrimer with hybrid networks. *Mech. Mater.* **153**, 103687 (2021).
 221. Scheutz, G. M., Lessard, J. J., Sims, M. B. & Sumerlin, B. S. Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets. *J. Am. Chem. Soc.* **141**, 16181–16196 (2019).
 222. Amber M. Hubbard, Yixin Ren, Dominik Konkolewicz, Alireza Sarvestani, Catalin R. Picu, Gary S. Kedziora, Ajit Roy, Vikas Varshney, and Dhriti Nepal. Vitrimer transition temperature identification: coupling various thermomechanical methodologies. *ACS Appl. Polym. Mater.* **3**, 1756–1766 (2021).
 223. Amber M. Hubbard, Yixin Ren, Alireza Sarvestani, Dominik Konkolewicz, Catalin R. Picu, Ajit K. Roy, Vikas Varshney, and Dhriti Nepal. Recyclability of vitrimer materials: impact of catalyst and processing conditions. *ACS Omega* **7**, 29125–29134 (2022).

224. Tangthana-Umrung, K., Poutrel, Q. A. & Gresil, M. Epoxy homopolymerization as a tool to tune the thermo-mechanical properties and fracture toughness of vitrimers. *Macromolecules* **54**, 8393–8406 (2021).
225. Joji Kadota, Dražen Pavlović, Jean-Pierre Desvergne, Brigitte Bibal, Frédéric Peruch, and Alain Deffieux. Ring-opening polymerization of L-lactide catalyzed by an organocatalytic system combining acidic and basic sites. *Macromolecules* **43**, 8874–8879 (2010).
226. Wu Jianqiao, Gao Liang, Guo Zhongkai, Zhang Hao, Zhang Baoyan, Hu Jun, Li Min Hui. Natural glycyrrhizic acid: Improving stress relaxation rate and glass transition temperature simultaneously in epoxy vitrimers. *Green Chem.* **23**, 5647–5655 (2021).
227. Yang Yang, Zhang Shuai, Zhang Xiqi, Gao Longcheng, Wei Yen, Ji Yan. Detecting topology freezing transition temperature of vitrimers by AIE luminogens. *Nat. Commun.* **10**, 1–8 (2019).
228. Lessard, J. J., Stewart, K. A. & Sumerlin, B. S. Controlling dynamics of associative networks through primary chain length. *Macromolecules* **55**, 10052–10061 (2022).
229. Zhao, S. & Abu-Omar, M. M. Catechol-mediated glycidylation toward epoxy vitrimers/polymers with tunable properties. *Macromolecules* (2019) doi:10.1021/acs.macromol.9b00334.
230. Jourdain, Rawnaq Asbai, Omaina Anaya, Mohamed M. Chehimi, Eric Drockenmuller, and Damien Montarnal. Rheological properties of covalent adaptable networks with 1,2,3-triazolium cross-links: the missing link between vitrimers and dissociative networks. *ACS Appl. Mater. Interfaces* (2020) doi:10.1021/acs.macromol.9b02204.
231. Morgan, G. J., Champion, R. P. & Derham, C. J. Stress-induced phenomena in elastomers, and their influence on design and performance of o-rings. in *Elastomers and Components* 153–164 (Elsevier, 2006).

doi:10.1533/9781845691134.2.153.

232. Roy, A., Babuska, T., Krick, B. & Balasubramanian, G. Machine learned feature identification for predicting phase and young's modulus of low-, medium- and high-entropy alloys. *SSRN Electron. J.* (2020) doi:10.2139/ssrn.3546579.
233. Silvello A., Cavaliere P., Yin S., Lupoi R., Garcia Cano I., Dosta S. Microstructural, mechanical and wear behavior of hvof and cold-sprayed high-entropy alloys (heas) coatings. *J. Therm. Spray Technol.* **31**, 1184–1206 (2022).
234. Sivasamy, P., Palaniandavar, M., Vijayakumar, C. T. & Lederer, K. The role of β -hydrogen in the degradation of polyesters. *Polym. Degrad. Stab.* **38**, 15–21 (1992).
235. Terzopoulou, Z. *et al.* Thermal degradation of biobased polyesters: Kinetics and decomposition mechanism of polyesters from 2,5-furandicarboxylic acid and long-chain aliphatic diols. *J. Anal. Appl. Pyrolysis* **117**, 162–175 (2016).
236. Bikiaris, R. D. *et al.* Thermal Stability and Decomposition Mechanism of Poly(alkylene succinate)s. *Macromol* **2**, 58–77 (2022).
237. Moldoveanu, S. C. *Techniques and Instrumentation in Analytical Chemistry*. (Elsevier, 2010). doi:10.1016/S0167-9244(09)02817-0.
238. Heidarzadeh, N. *et al.* Thermal degradation of random copolyesters based on 1,4-butanediol, terephthalic acid and different aliphatic dicarboxylic acids. *Thermochim. Acta* **654**, 101–111 (2017).
239. Erickson, K. L. Thermal decomposition mechanisms of epoxies and polyurethanes. *Int. SAMPE Symp. Exhib.* **51**, (2006).
240. Levchik, S. V. & Weil, E. D. A review on thermal decomposition and combustion of thermoplastic polyesters. *Polym. Adv. Technol.* **15**, 691–700 (2004).

235. Ravotti, R., Fellmann, O., Fischer, L. J., Worlitschek, J. & Stamatiou, A. Investigation of the thermal properties of diesters from methanol, 1-pentanol, and 1-decanol as sustainable phase change materials. *Materials*. **13**, 1–18 (2020).
241. Ravotti, R., Fellmann, O., Fischer, L. J., Worlitschek, J. & Stamatiou, A. Investigation of the thermal properties of diesters from methanol, 1-pentanol, and 1-decanol as sustainable phase change materials. *Materials (Basel)*. **13**, 1–18 (2020).
242. Lee, S. J., Choi, M. Y. & Lim, A. R. Effect of methylene chain length on the thermodynamic properties, ferroelastic properties, and molecular dynamics of the perovskite-type layer crystal $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{MnCl}_4$ ($n = 2, 3$, and 4). *ACS Omega* **6**, 15392–15399 (2021).
243. Giebler, M., Sperling, C., Kaiser, S., Duretek, I. & Schlögl, S. Epoxy-anhydride vitrimers from aminoglycidyl resins with high glass transition temperature and efficient stress relaxation. *Polymers*. **12**, 1–14 (2020).
244. Guerre, M., Taplan, C., Nicolaÿ, R., Winne, J. M. & Du Prez, F. E. Fluorinated Vitrimer Elastomers with a Dual Temperature Response. *J. Am. Chem. Soc.* **140**, 13272–13284 (2018).
245. Lyon, G. B. *et al.* Remoldable Thiol-Ene Vitrimers for Photopatterning and Nanoimprint Lithography. *Macromolecules* **49**, 8905–8913 (2016).
246. Chakma, P. & Konkolewicz, D. Dynamic Covalent Bonds in Polymeric Materials. *Angew. Chemie - Int. Ed.* **58**, 9682–9695 (2019).
247. Dahlke, J., Zechel, S., Hager, M. D. & Schubert, U. S. How to Design a Self-Healing Polymer: General Concepts of Dynamic Covalent Bonds and Their Application for Intrinsic Healable Materials. *Adv. Mater. Interfaces* **5**, (2018).
248. Röttger, M. *et al.* High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science (80-.)*. **356**, 62–65 (2017).

249. Schenk, V. *et al.* Exploring the Limits of High-Tg Epoxy Vitrimers Produced through Resin-Transfer Molding. *ACS Appl. Mater. Interfaces* **15**, 46357–46367 (2023).

Appendix

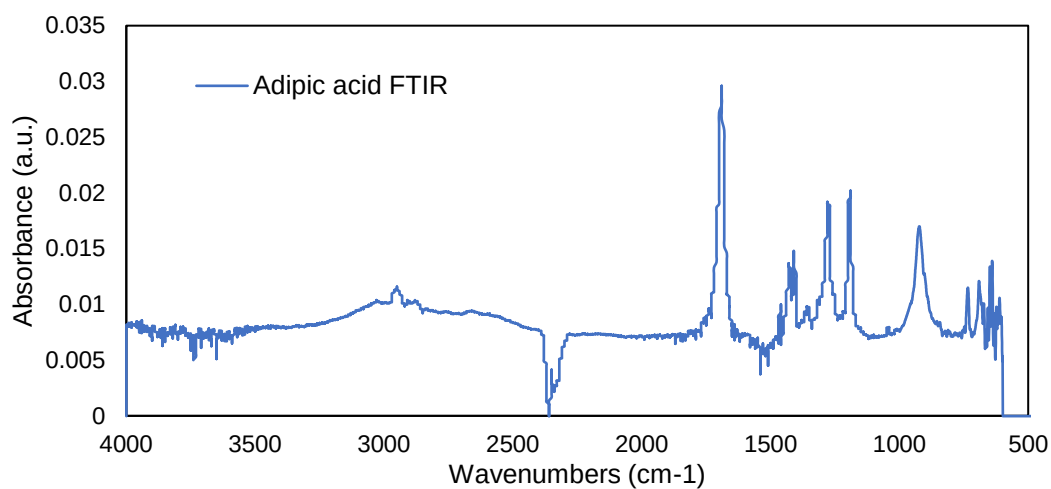


Figure A.1: FTIR spectra of adipic acid

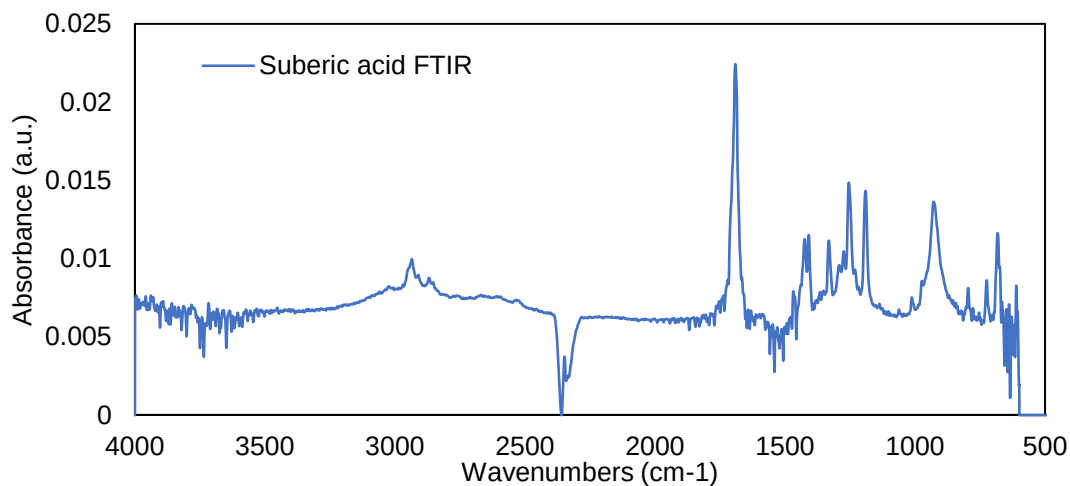


Figure A.2: FTIR spectra of suberic acid

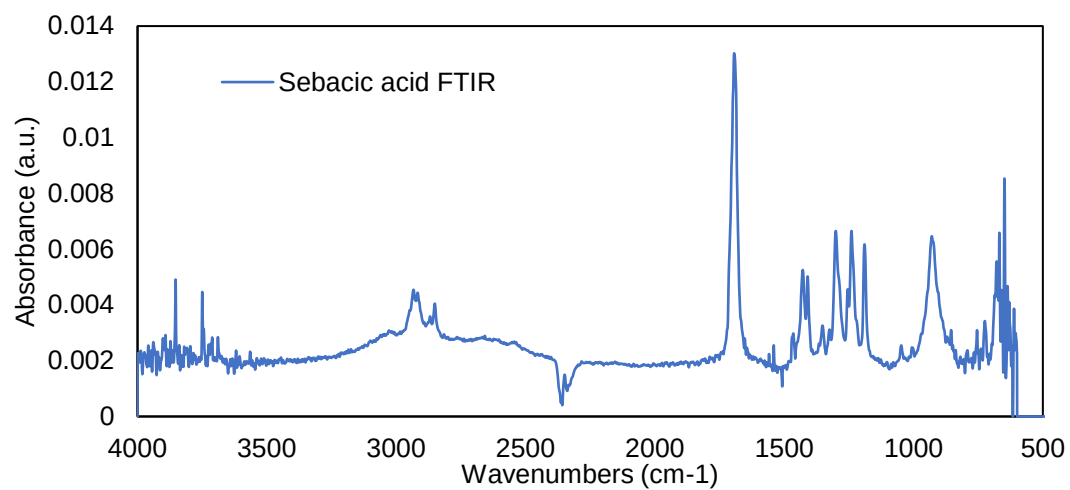


Figure A.3: FTIR spectra of sebacic acid

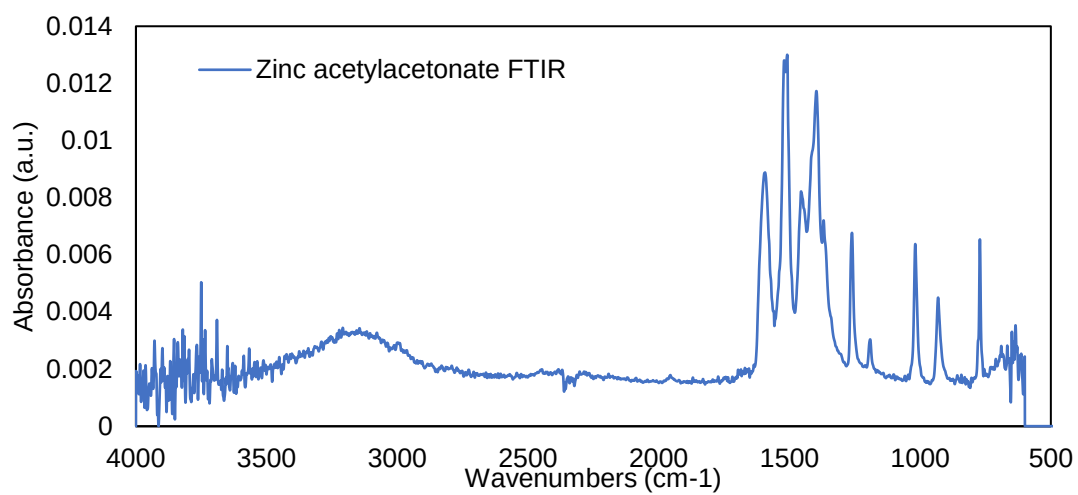


Figure A.4: FTIR spectra of zinc acetylacetonate