Self-healing dendrimers based on ionic or hydrogen-bonding supramolecular interactions

by

Thomas Louis Jacques Henri CHAFFRAIX

MEng

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University

October 2014
I am the author of the thesis entitled

Self-healing dendrimers based on ionic or hydrogen-bonding supramolecular interactions

submitted for the degree of  Doctor of Philosophy

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: ................Thomas CHAFFRAIX.................................................................

(Please Print)

Signed: ..........................................................Signature Redacted by Library

Date: ..................06/03/2015..................................................................................
I certify the following about the thesis entitled (10 word maximum)

___Self-healing dendrimers based on ionic or hydrogen-bonding__________________

___supramolecular interactions__________________________________________

submitted for the degree of _____Doctor of Philosophy_____________________

a. I am the creator of all or part of the whole work(s) (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.

b. The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

c. That if the work(s) have been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.

I also certify that any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: .......Thomas CHAFFRAIX.................................................................

(Please Print)

Signed: ............ Signature Redacted by Library ..............................................

Date: ........06/03/2015..............................................................................
Acknowledgements

First and foremost, I would like to thank both my supervisors, Dr Kevin Magniez and Prof Bronwyn Fox for their guidance and the support they both provided throughout the duration of this PhD. Kevin spent days and nights translating, correcting and reviewing the large number of drafts I sent him. The improvement of my writing skills and my ability to plan, schedule and achieve my research goals are without a doubt the fruit of his support and guidance. Thanks Kevin for giving me the support I needed to believe in myself. Bronwyn contributed to my personal development through her constant support, guidance and motivation.

I would like to acknowledge the funding of this PhD project by the Advanced Manufacturing cooperative Research Centre (AMCRC) and more particularly Dr Larry Jordan and Dr Sam Quint for accepting me on board and the numerous discussions regarding the project. The four years I spent within the organisation have been fantastic and more precisely I’d like to thank the AMCRC for giving the opportunity to present my work during several conferences which have been greatly fruitful for me.

This project would not have been possible without the support of Dr Andreea Voda who spent a large number of hours teaching and tutoring me in practical synthetic chemistry, NMR including structure elucidation of my compounds. I’d also like to acknowledge Gail Dyson for her help with NMR studies. I am particularly thankful for the helpful discussions I had with Dr Ludovic Dumee and Dr Alessandra Sutti. I would like to thank Dr Luke Henderson for his help in helping with the structure of the discussion on chemistry and help me bring some scientific cohesion as a whole.

My colleagues and friends Peter, Nicolas, Juliane, Jascha, Adam, Mick, Matt, Sulley, Satya, Cassie, Kyra, Sunna, Christophe, Chrystelle, Ludo and everyone from the Deakin Outdoor and Climbing Club, I would like to thank you for those great moments we have been going through.
A special thank you to Erwan Castanet for his support, discussions and friendship over the past three years, thanks Buddy.

I am grateful for the support and encouragement of my family for providing me every opportunity and believing in me in all aspects of my education. A very special thanks to my grand-mother who passed away in January 2012 and who always believed in me. “Mamie, J'espère que de là haut, tu es fière de moi.”

Last but certainly not least, I would like to extend my appreciation to my partner Kertu for the emotional support provided. Thank you for your sacrifices you have made for me to make this thesis possible.
# Table of Contents

Acknowledgements ........................................................................................................ iv

Table of Contents....................................................................................................... vi

List of Figures........................................................................................................... xi

List of Schemes ......................................................................................................... xvi

List of Tables .............................................................................................................. xvii

List of Abbreviations, Acronyms and Symbols ....................................................... xix

Abstract ..................................................................................................................... xxii

## Chapter One – Introduction to self-healing ......................................................... 1

1.1. Preface.................................................................................................................... 2

1.2. Self-healing concepts .......................................................................................... 3

1.2.1. Capsule-based systems ................................................................................ 3

1.2.2. Vascular networks .......................................................................................... 6

1.2.3. Intrinsic systems ............................................................................................ 7

1.3. Dendrimers .......................................................................................................... 19

1.3.1. Structure ....................................................................................................... 20

1.3.2. Synthesis ...................................................................................................... 20

1.3.3. Applications.................................................................................................. 22

1.4. Research challenges .......................................................................................... 26

1.5. Research questions/research plan ..................................................................... 27

1.6. Thesis outline ..................................................................................................... 29

1.7. References .......................................................................................................... 31
Chapter Two – Materials and Experimental ................................................. 42

2.1. Materials ................................................................................................................... 43
  2.1.1. Starting material and reagents .......................................................................... 43
  2.1.2. Solvents .............................................................................................................. 44

2.2. Experimental ............................................................................................................. 45
  2.2.1. Synthesis of the carboxylic acid terminated dendrimer (H_{20}COOH) .......... 45
  2.2.2. Sodium neutralisation ....................................................................................... 48
  2.2.3. Zinc neutralisation ........................................................................................... 49
  2.2.4. Amidation of the H_{20}COOH ........................................................................... 51

2.3. Characterisation ........................................................................................................ 54
  2.3.1. Fourier Transformation Infra-Red spectroscopy (FTIR) ................................. 54
  2.3.2. Nuclear Magnetic Resonance spectroscopy (NMR) ...................................... 54
  2.3.3. X-ray Photoelectron Spectroscopy (XPS) ...................................................... 55
  2.3.4. Differential Scanning Calorimeter (DSC) ....................................................... 55
  2.3.5. Dynamic Light Scattering (DLS) ..................................................................... 57
  2.3.6. Scanning Electron Microscopy (SEM) ............................................................ 57
  2.3.7. Optical Microscopy .......................................................................................... 57
  2.3.8. Self-healing capability ...................................................................................... 58

2.4. References ................................................................................................................. 61

Chapter Three – Sodium based ionic dendrimer ........................................... 63

3.1. Introduction ............................................................................................................... 64

3.2. Functionalisation of the starting material Boltorn H_{20} ........................................ 65
  3.2.1. Synthesis of H_{20}COOH ................................................................................ 66
3.2.2. Purification of H$_2$O-COOH ................................................................. 66
3.2.3. Characterisation of the starting material H$_2$O and reaction product H$_2$O-COOH 68
3.3. Sodium neutralisation of H$_2$O-COOH ....................................................... 80
  3.3.1. Sodium neutralisation ............................................................................. 80
  3.3.2. Characterisation .................................................................................... 81
3.4. Self-healing behaviour .............................................................................. 91
3.5. Conclusions ............................................................................................. 92
3.6. References .............................................................................................. 93

Chapter Four – Zinc-based metallosupramolecular dendrimer ................. 97

  4.1. Introduction ............................................................................................ 98
  4.2. Zinc neutralisation of H$_2$O-COOH ......................................................... 99
    4.2.1. Neutralisation scheme ........................................................................ 99
    4.2.2. XPS measurement ............................................................................ 100
    4.2.3. In-situ NMR measurement ............................................................... 104
    4.2.4. FTIR characterisation ....................................................................... 106
    4.2.5. DSC measurement ......................................................................... 110
  4.3. Assessment of the self-healing behaviour ........................................... 117
    4.3.1. Self-healing in bulk and film ......................................................... 117
    4.3.2. Self-healing in a blend with PLA .................................................. 123
  4.4. Conclusions ........................................................................................... 125
  4.5. References ............................................................................................... 127
Chapter Five – Hydrogen bonded dendritic supramolecular network

5.1. Introduction

5.2. Synthesis of 1-(2-Aminoethyl)-2-imidazolidone (AEIO)

5.2.1. Synthesis of AEIO

5.2.2. FTIR characterisation

5.2.3. ¹H NMR characterisation

5.2.4. ¹³C NMR characterisation

5.2.5. 2D NMR

5.3. Amidation of H₂O-COOH with AEIO

5.3.1. Synthetic route

5.3.2. NMR characterisation

5.3.3. FTIR characterisation

5.4. Self-healing behaviour

5.5. Conclusions

5.6. References

Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers

6.1. Introduction

6.2. Metallosupramolecular elastomers based on zinc counter ions

6.2.1. FTIR characterisation

6.3. Self-healing ability

6.3.1. Neat zinc-based metallosupramolecular elastomer

6.3.2. Composite Application
Chapter Seven – General conclusions and recommendations for future work

7.1. Summary of the research findings ................................................................. 185
7.2. Recommendations for future work ............................................................... 187

Appendix ........................................................................................................... 189

Appendix A: $^1$H NMR spectrum of Boltorn H$_2$O .............................................. 189
Appendix B: $^{13}$C NMR spectrum of Boltorn H$_2$O .............................................. 190
Appendix C: $^1$H NMR spectrum of H$_2$O-COOH after an excess of sodium hydroxide was added ........................................................................................................ 191
Appendix D: C1s XPS of sodium based ionic dendrimer .................................. 192
Appendix E: C1s XPS spectra of zinc-based metallosupramolecular dendrimer .... 193
Appendix F: DEPT NMR spectrum of H$_2$O-COO – 0.50Zn in the carbonyl region after diffusion ............................................................................................................ 194
Appendix G: FTIR deconvolution of zinc-based metallosupramolecular dendrimer in the carboxylate region ................................................................. 195
Appendix H: $^{13}$C NMR of AEIO ............................................................................ 197
Appendix I: Glass transition temperature of DGEBF, DGEBF/NBR and DGEBF/NBR – 0.25Zn compact samples after curing ..................................................... 198
List of Figures

Figure 1.1: Visual interpretation of an autonomic capsule-based ............................................ 3
Figure 1.2: Visual interpretation of an autonomic vascular network system [6] ................. 6
Figure 1.3: Visual interpretation of an autonomic intrinsic self-healing system [6] ................. 8
Figure 1.4: The various stages of self-healing based on a molecular interdiffusion mechanism [37] ............................................................................................................................................. 9
Figure 1.5: Structural diversity evident in the metallopolymer field [52] ............................... 12
Figure 1.6: Schematic representation of the self-healing process during high-energy impact [73] ........................................................................................................................................... 14
Figure 1.7: Schematic representation of the “ion hopping” mechanism in an ionomer. The circles represent the ionic clusters and the curved line is the polymer chain [74] .......... 15
Figure 1.8: Schematic representation of ion pairs and the region of restricted mobility in the surrounding polymer [78, 65] ........................................................................................................ 17
Figure 1.9: Schematic representation of a dendrimer [101] ................................................... 20
Figure 1.10: The divergent synthesis of dendrimers [102] ...................................................... 21
Figure 1.11: The convergent synthesis of dendrimers [102] ................................................... 22
Figure 2.1: Starting material $H_2O$ on the left and its representation on the right .......... 43
Figure 2.2: Schlenk oxygen exclusion manifold [4] ............................................................... 45
Figure 2.3: Dialysis purification into Milli-Q water ............................................................... 48
Figure 2.4: Neutralised $H_2O-COOH$ products (increasing degree of neutralisation, compounds 3, 4, 5, 6 from left to right). ................................................................................................. 49
Figure 2.5: Freshly prepared Zn(OH)$_2$ ................................................................. 50
Figure 2.6: Solid/liquid diffusion process .............................................................................. 50
Figure 2.7: Heat cycle conventional DSC ............................................................................. 56
Figure 2.8: Modulated heating rate for the first heat ............................................................ 56
Figure 2.9: TDCB geometry (dimensions in mm) [17] ......................................................... 59
Figure 2.10: Schematic representation of a tear specimen during a test ......................... 60
Figure 3.1: Starting material $H_2O$ on the left and its representation on the right .......... 65
Figure 3.2: $^1H$ NMR of $H_2O-COOH$ before dialysis purification into Milli-Q water ........ 67
Figure 3.3: $^1$H NMR of H$_2$O-COOH after dialysis purification into Milli-Q water ..............68
Figure 3.4: $^1$H NMR of H$_2$O-COOH in CD$_3$COCD$_3$ (*) ..........................................................70
Figure 3.5: $^{13}$C NMR H$_2$O-COOH in CD$_3$COCD$_3$ (*) ................................................................72
Figure 3.6: FTIR of H$_2$O starting material and H$_2$O-COOH (a) and zoom of the hydroxyl region (b), carbonyl region (c), C-O stretch region between 1275 and 1075 cm$^{-1}$ (d) and C-O stretch region between 1075 and 925 cm$^{-1}$ (e)....................................................................................74
Figure 3.7: XPS Survey spectra of H$_2$O (a) and H$_2$O-COOH (b) ....................................................76
Figure 3.8: C1s XPS spectrum H$_2$O ..................................................................................................77
Figure 3.9: C1s XPS spectrum H$_2$O-COOH ................................................................................77
Figure 3.10: DSC curves for H$_2$O (red) and H$_2$O-COOH (black)..........................................................79
Figure 3.11: FTIR (ATR mode) representing the carbonyl absorption of..............................................81
Figure 3.12: FTIR peak assignment following various types of interactions in carboxylic and mono-coordinated carboxylate groups (adapted from [32]) ..................................................82
Figure 3.13: $^1$H NMR of sodium based ionic dendrimers in D$_2$O ........................................................83
Figure 3.14: C1s XPS of H$_2$O-COO – 0.50Na ................................................................................85
Figure 3.15: C1s XPS of H$_2$O-COO – Na ......................................................................................85
Figure 3.16: Morphological changes that EMAA ionomers undergo upon heating [39] ........87
Figure 3.17: DLS size distribution of H$_2$O-COOH (a), H$_2$O-COO – 0.25 Na (b), H$_2$O-COO – 0.50 Na (c), H$_2$O-COO – 0.75 Na (d) and H$_2$O-COO – Na (e)........................................................................................89
Figure 3.18: SEM images of H$_2$O-COOH ..........................................................................................90
Figure 3.19: SEM images of H$_2$O-COO – 0.50Na ..........................................................................90
Figure 3.20: H$_2$O, H$_2$O-COOH and H$_2$O-COO – 0.50 Na samples (top to bottom, respectively) just after crack opening (left) and after heat treatment (30 min at 100°C) (right) ........91
Figure 4.1: Example of a zinc-based metallosupramolecular dendrimer sample (H$_2$O-COO-0.75Zn shown here) ....................................................................................100
Figure 4.2: C1s XPS of H$_2$O-COO – 0.25Zn ..................................................................................101
Figure 4.3: C1s XPS of H$_2$O-COO – 0.50Zn ..................................................................................102
Figure 4.4: High resolution Zn2p scan of H$_2$O-COO – 0.50Zn .........................................................103
Figure 4.5: Evolution of the methylene peaks (position 12 and 13) resulting from the diffusion of Zn(OH)$_2$ in a D$_2$O/H$_2$O-COOH solution as a function of time. ................................................104
Figure 4.6: Evolution of the upfield shift of the methylene moieties in position 13 over time
................................................................................................................................................ 105
Figure 4.7: HMBC spectra of H20-COO and H20-COO – 0.50 Zn in D2O after 192h of diffusion
................................................................................................................................................ 106
Figure 4.8: FTIR H20-COO and its zinc-based metallosupramolecular dendrimers .......... 107
Figure 4.9: Potential zinc coordination molecular arrangements in the neutralised H20-COOH dendrimer adapted from [19]................................................................................................ 108
Figure 4.10: Example of deconvolution in the carboxylate region (H20-COO - 0.75Zn is presented here) ................................................................................................................................................ 109
Figure 4.11: MDSC Reversible Heat Flow curve for the first and second Heat cycle of H20-COO – 0.25Zn.................................................................................................................................. 111
Figure 4.12: Order-disorder transition in the ionic domains [26] ......................................... 112
Figure 4.13: Schematic representation of the coordination environments suggested for poly(ethylene imine)/metal ions complexes (top) [30] and the possible coordinations arrangements (A, B, C, D and E) in this work (bottom). ........................................................ 114
Figure 4.14: Highlighted regions A and B of Figure 4.13 showing a tetra-coordinated Zn2+ counter-ion in an inter (A, left) and intra (B, right) molecular type of configuration .......... 115
Figure 4.15: Highlighted regions C, D and E of Figure 4.13 showing a hexa-coordinated zinc counter-ion in an inter (C), an inter/intra- (D) or intra molecular (E) configuration................. 116
Figure 4.16: Self-healing of zinc-based metallosupramolecular dendrimer H20-COO – 0.75Zn ................................................................................................................................................ 118
Figure 4.17: Schematic representation of the association of the carboxylate group with tetra-coordinated Zn2 ions coupled with hydrogen bonding between the carboxylate groups and carboxylic groups absorbing at 1537 cm^{-1} (top) [20] and a possible arrangement in this work (bottom)........................................................................................................................................ 122
Figure 4.18: FTIR spectra PLA, H20-COO – 0.75Zn and PLA/ H20-COO – 0.75Zn blend.............. 124
Figure 4.19: Self-healing test of PLA (top) and PLA/H20-COO – 0.75 Zn blend (bottom) ...... 125
Figure 5.1: Imidazolidone ring ............................................................................................... 132
Figure 5.2: FTIR spectra of AEIO............................................................................................. 134
Figure 5.3: 1H NMR of AEIO in CDCl3 (*) ................................................................................ 135
Figure 5.4: 1H NMR AEIO in D2O (*) ....................................................................................... 137
Figure 5.5: $^{13}$C NMR of AEIO in CDCl$_3$ (*) ................................................................. 138
Figure 5.6: 2D HSQC spectrum of AEIO in D$_2$O .............................................................. 141
Figure 5.7: 2D HMBC spectrum of AEIO in D$_2$O .............................................................. 142
Figure 5.8: Visual representation of one branch of an ideal H$_2$O-COO – AEIO molecule .... 144
Figure 5.9: $^1$H NMR of H$_2$O-COO – AEIO in D$_2$O (*) ................................................... 145
Figure 5.10: $^{13}$C spectrum of H$_2$O-COO – AEIO ............................................................. 146
Figure 5.11: 2D HSQC spectrum of H$_2$O-COO – AEIO region of interest ....................... 148
Figure 5.12: HMBC of H$_2$O-COO – AEIO in the carbonyl region between 180 and 150 ppm . 149
Figure 5.13: 2D HMBC of H$_2$O-COO – AEIO in the carbonyl region between 80 and 30 ppm 150
Figure 5.14: Characteristics region of the H$_2$O-COO – AEIO FTIR spectrum .................... 153
Figure 5.15: Zoom on the carbonyl region (1775 cm$^{-1}$ to 1525 cm$^{-1}$) of H$_2$O-COO – AEIO .... 155
Figure 5.16: Temperature-dependent FTIR spectra of H$_2$O-COO - AEIO .......................... 156
Figure 5.17: Synchronous 2D correlation spectrum of H$_2$O-COO – AEIO in the regions of interest: amide N-H stretch (3800 cm$^{-1}$ to 3100 cm$^{-1}$) and the carbonyl region (1800 cm$^{-1}$ to 1500 cm$^{-1}$) .............................................................................................................................. 159
Figure 5.18: H$_2$O-COO – AEIO sample just after crack initiation (left) and after 5 min at room temperature (right) ........................................................................................................... 160
Figure 6.1: Examples of NBR products [4] ............................................................................. 166
Figure 6.2: Commercially available carboxylated NBR (Nipol DN601) used in this work ..... 167
Figure 6.3: FTIR of zinc-based metallosupramolecular elastomers in the carbonyl region .. 168
Figure 6.4: Crack healing of neat NBR (top) and NBR – 0.75Zn (bottom) ............................. 171
Figure 6.5: Example of deconvolution in the carboxylate region during the self-healing process at t = 1min (NBR - 0.75Zn is presented here) .................................................................................... 172
Figure 6.6: Example of deconvolution in the carboxylate region after complete healing (NBR - 0.75Zn is presented here) ........................................................................................................... 173
Figure 6.7: Compact tension sample cured at 150 degrees showing a very porous structure as a result of zinc catalysed CO$_2$ release. ................................................................................................. 174
Figure 6.8: Compact tension sample of DGEBF + 4wt% NBR ............................................... 175
Figure 6.9: Fracture toughness results for the neat epoxy resin, epoxy resin/DN601 system and epoxy resin/ DN601-25% Zn system ............................................................................................... 176
Figure 6.10: Compact tension sample of DGEBF/NBR – 0.25Zn after heat treatment (overnight at 100 ºC) .................................................................................................................................................. 177

Figure 6.11: SEM image of DGEBF/NBR – 0.25Zn compact tension sample in the crack region. Highlighted are cavities left by pulled out NBR – 0.25Zn globules (size between 150 and 250 nm). A homogeneous fine dispersion of NBR – 0.25Zn globules is visible throughout the sample.................................................................................................................................................. 178

Figure 6.12: Neat NX775 material (top) showing no self-healing and NX 775/NBR – 0.75Zn blend (bottom) showing self-healing........................................................................................................................................ 179

Figure A.1: 1H NMR spectrum of H₂O in CD₃COCD₃ (*) ........................................................................................................................................... 189
Figure B.2: 13C NMR spectrum of H₂O in CD₃COCD₃ (*) ........................................................................................................................................... 190
Figure C.3: 1H NMR spectrum of H₂O-COOH after addition of an excess of sodium hydroxide in CD₃COCD₃ (*)........................................................................................................................................... 191
Figure D.4: C1s XPS spectrum of H₂O-COO – 0.25Na........................................................................................................................................... 192
Figure D.5: C1s XPS spectrum of H₂O-COO – 0.75Na........................................................................................................................................... 192
Figure E.6: C1s XPS spectrum of H₂O-COO – 0.75Zn........................................................................................................................................... 193
Figure E.7: C1s XPS spectrum of H₂O-COO – Zn........................................................................................................................................... 193
Figure F.8: DEPT NMR of H₂O-COO – 0.50Zn after 192h of diffusion into D₂O .......................... 194
Figure G.9: FTIR deconvolution of H₂O-COO – 0.25Zn ........................................................................................................................................... 195
Figure G.10: FTIR deconvolution of H₂O-COO – 0.50Zn ........................................................................................................................................... 195
Figure G.11: FTIR deconvolution of H₂O-COO – Zn ........................................................................................................................................... 196
Figure H.12: 13C NMR of AEIO in D₂O ........................................................................................................................................... 197
Figure I.13: Glass transition temperatures of DGEBF, DGEBF/NBR and DGEBF/NBR – 0.25Zn compact tension samples after curing........................................................................................................................................... 198
List of Schemes

Scheme 1.1: Ruthenium-based Grubbs’ catalyst initiates ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) [4] .................................................................4
Scheme 1.2: Example of rDA and DA reactions [31] ..................................................................8
Scheme 2.1: Synthesis of 2 via esterification ........................................................................ 46
Scheme 2.2: Neutralisation scheme with sodium hydroxide to yield 3, 4, 5, and 6 .......... 48
Scheme 2.3: Neutralisation scheme with Zinc Hydroxyde to yield 7, 8, 9 and 10. An idealised metallo-supramolecular dendrimer sharing a zinc ion is shown on the right hand side .......51
Scheme 2.4: Scheme AEIO synthesis .................................................................................... 52
Scheme 2.5: Amidation of H$_2$O-COOH scheme ........................................................................ 52
Scheme 5.1: Synthesis route (top) and mechanism (bottom) to AEIO .......................... 133
Scheme 5.2: EDC crosslinking reaction scheme [12] .......................................................... 143
List of Tables

Table 1.1: Summary self-healing efficiency based on capsules systems ........................................ 5
Table 1.2: Summary self-healing efficiency based on vascular systems ........................................ 7
Table 1.3: Summary self-healing efficiency based on intrinsic systems ..................................... 18
Table 3.1: Theoretical ($I_{th}$) and experimental ($I_{exp}$) proton integration ................................. 69
Table 3.2: $^1$H NMR chemical shifts and multiplicity of $H_{20}$-COOH peaks in various solvents .. 71
Table 3.3: Relative carbon related functional group percentages measured in $H_20$ and $H_{20}$-COOH after C1s peaks deconvolution ................................................................. 78
Table 3.4: Relative carbon related functional group percentages measured in the various materials after C1s peaks deconvolution ........................................................................... 84
Table 3.5: Glass transition temperatures of $H_{20}$-COOH and sodium ionomers ...................... 86
Table 3.6: Hydrodynamic diameters (nm) of $H_{20}$-COOH and ionomers ................................. 89
Table 4.1: Relative carbon related functional group percentages measured in the various materials after C1s peaks deconvolution ................................................................. 102
Table 4.2: Quantitative analysis of the tetra and hexa ratios present in the various materials from peak deconvolution ......................................................................................... 109
Table 4.3: Glass transition temperatures for $H_{20}$-COOH and its metallosupramolecular dendrimers with zinc counter-ions ................................................................. 110
Table 4.4: Time needed for the two halves to be able to “stick” together and be stretched to twice their original length .......................................................................................... 118
Table 4.5: FTIR dynamic study of self-healing process in $H_{20}$-COO – 0.50Zn ............................ 120
Table 5.1: Integration of each proton peaks of AEIO in CDCl3 .................................................... 136
Table 5.2: $^1$H NMR shifts of AEIO in CDCl3 and D2O ............................................................. 138
Table 5.3: Complete structure assignment of AEIO in D2O for HSQC .................................... 140
Table 5.4: 2D HSQC correlations $^1$H with $^{13}$C signals of $H_{20}$-COO - AEIO ....................... 148
Table 5.5: HMBC correlations for $H_{20}$-COO – AEIO in D2O ................................................. 151
Table 5.6: Complete structure assignment of $H_{20}$-COO - AEIO in D2O ............................... 152
Table 5.7: Evolution of the characteristic bands of absorption involved in the hydrogen bonding of $H_{20}$-COO – AEIO as a function of temperature ............................................. 157
Table 6.1: Difference between theoretical and experimental zinc degree of neutralisation
................................................................................................................................................169
Table 6.2: Quantitative analysis of the tetra and hexa ratios present in the various materials
from peak deconvolution........................................................................................................170
Table 6.3: Compact tension samples of the different systems before the test, after the test
and after heat treatment........................................................................................................177
# List of Abbreviations, Acronyms and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom ($10^{-10}$ m)</td>
</tr>
<tr>
<td>AEIO</td>
<td>1-(2-aminoethyl)-2-imidazolidone</td>
</tr>
<tr>
<td>AR</td>
<td>Analytical reagent</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>br s</td>
<td>Broad singlet</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon NMR</td>
</tr>
<tr>
<td>CD$_3$COCD$_3$</td>
<td>Deuterated acetone</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>Deuterated chloroform</td>
</tr>
<tr>
<td>CFRC</td>
<td>Carbon Fibre Reinforced Composite</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>Deuterated water</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
<tr>
<td>DA</td>
<td>Diels-Alder</td>
</tr>
<tr>
<td>DCB</td>
<td>Double cantilever beam</td>
</tr>
<tr>
<td>DCPD</td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td>DEPT</td>
<td>Distortionless enhancement by polarisation transfer</td>
</tr>
<tr>
<td>DETA</td>
<td>Diethylenetriamine</td>
</tr>
<tr>
<td>DGEBF</td>
<td>Diglycidyl ether of bisphenol F</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(Dimethylamino)pyridine</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EMAA</td>
<td>Ethylene methacrylic acid</td>
</tr>
<tr>
<td>EDC</td>
<td>1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FRC</td>
<td>Fibre reinforced composite</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform Infra-Red</td>
</tr>
<tr>
<td>G</td>
<td>Generation</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Proton NMR</td>
</tr>
<tr>
<td>HBP</td>
<td>Hyperbranched polymers</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear multiple bond coherence</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>I$_{\text{exp}}$</td>
<td>Experimental integration</td>
</tr>
<tr>
<td>IgM</td>
<td>Immunoglobulin M</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>I$_{\text{th}}$</td>
<td>Theoretical integration</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated differential scanning calorimetry</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile butadiene rubber</td>
</tr>
<tr>
<td>NIBS</td>
<td>Non-invasive backscatter</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear overhauser effect spectroscopy</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>PAMAM</td>
<td>Poly(amidoamine)</td>
</tr>
<tr>
<td>PCL</td>
<td>Poly(caprolactone)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane)</td>
</tr>
<tr>
<td>phr</td>
<td>Per hundred resin</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
</tr>
<tr>
<td>PMMA-PAAc</td>
<td>Poly(methyl methacrylate)-block-poly(acrylic acid) copolymers</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
</tbody>
</table>
PU  Polyurethane
RAFT  Reversible addition-fragmentation chain transfer
rDA  retro Diels-Alder
ROMP  Ring-Opening Metathesis Polymerization
RT  Room temperature
s  Singlet
SBR  Styrene butadiene rubber
SEM  Scanning Electron Microscopy
SENB  Single edge notched beam
SMPU  Shape memory polyurethane
st  Stretch
t  Triplet
TDCB  Tapered double cantilever beam
TEA  Triethylamine
T$_g$  Glass transition temperature
TGDDM  N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane
THF  Tetrahydrofuran
TMS  Tetramethylsilane
UV  Ultraviolet
XPS  X-ray photoelectron spectroscopy
Zn  Zinc
1D  One dimensional
2D  Two dimensional
2Dcos  Two dimensional correlation spectroscopy
2M4F  Furan-maleimide derivative
2MEP4F  1,8-Bis(maleimido)-1-ethylpropane-furan derivative
2s  Two singlets
3D  Three dimensional
δ  Chemical shift (NMR)
v  Wavenumber (FTIR)
Abstract

The scope of the thesis was to develop an autonomous self-healing system based on dendrimers. The high degree of branching (3D) and abundant number of surface functionalities displayed by dendrimers was explored to develop an efficient autonomous intrinsic self-healing system having enhanced inter- and intra-molecular interactions. The research strategy presented in this thesis focussed on the development of a range of self-healing dendrimers based on ionic or hydrogen bonded supramolecular networks.

The first stages of the work involved the functionalisation of a second generation hydroxyl terminated dendrimer (H₂O) to yield a carboxylic acid terminated dendrimer (H₂O-COOH). The success of the functionalisation was investigated using a range of techniques inclusive of Fourier Transform Infra-Red (FTIR), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC) and X-Ray Photoelectron Spectroscopy (XPS). The carboxylic acid terminated dendrimer H₂O-COOH was then used as a precursor for the development of the various supramolecular dendritic networks.

The development of ionic dendrimers has been first investigated by neutralising the carboxylic acid terminated dendrimer H₂O-COOH with a base. Because the research strategy aimed to understand the effect of valency of the counter-ions, the use of either sodium hydroxide (NaOH) or zinc hydroxide Zn(OH)₂ was investigated in order to yield a range of ionic dendrimers terminated with carboxylate groups associated with either mono-valent sodium (Na⁺) or divalent zinc (Zn²⁺) counter-ions. The degree of neutralisation (e.g. number of surrounding counter-ions) was controlled so that a 25%, 50%, 75% and 100% of the available carboxylic acid functional groups were converted into carboxylate moieties. The chemical properties including spectroscopic (FTIR, NMR and XPS) data confirming formation of these ionomers will be presented. The effects of degree of neutralisation and type of counter-ions on the physical properties and self-healing characteristics of the resulting materials was studied.
Firstly we found that the electrostatic associations between the carboxylate groups and the mono-valent sodium (Na⁺) counter-ions induced a reduction of the chain mobility. This effect was more pronounced with increasing degrees of neutralisation, coinciding with an increase in $T_g$ of the dendrimer. These interactions were also found to be at the origin of back-folding of the dendrimer chain, inhibiting the ion hopping which resulted in a lack of self-healing behaviour displayed by the sodium based ionic dendrimers.

Secondly, concerning the zinc-based metallosupramolecular dendrimer, changes in the state of coordination of the zinc counter-ions (Zn²⁺), namely tetra or hexa type, could be detected via FTIR upon changes in the degree of neutralisation. At low degree of neutralisation, the tetra form was found to be mostly present (~73%), however the percentage of hexa form was found to increase with the increasing degree of neutralisation, to reach up to 55%. The possibility of inter or intra molecular types of interactions, between the zinc counter-ions and carboxylate moieties in the metallosupramolecular dendrimer, was presented. This assumption corroborated with the DSC thermal results showing two distinct ionic domains associated with 2 glass transition temperatures at higher temperatures (~17°C and ~40°C). In thin films, an efficient (e.g. a few minutes) autonomous self-healing of the zinc-based metallosupramolecular dendrimers, following crack opening, was observed at room temperature for the first time. The dynamic changes in the modes of association between zinc counter-ions and carboxylates groups were monitored at the crack interface during repair via FTIR analysis. During repair, a transitional mode of association between the carboxylate and tetra-coordinated zinc ions coupled with hydrogen bonding between carboxylate and carboxylic groups (at 1537 cm⁻¹) was detected at the crack interface. It is believed that this particular transitional mode of association and interaction, which was no longer detected after complete repair of the crack, is responsible for the mechanism of self-healing and successful molecular rearrangement of the zinc-based metallosupramolecular dendrimers. In a separate set of experiment, we also found that the metallosupramolecular dendrimers could possibly be used as a self-healing additive for thermoplastics. By blending one of the zinc-based metallosupramolecular dendrimer with poly(lactic acid) thermoplastic at very low concentration (~5 wt%), some self-healing could be observed using a thermal treatment.
The development of hydrogen bonded supramolecular dendritic networks was then investigated via the attachment of an imidazolidone derivative AEIO onto the carboxylic acid terminated dendrimer. The presence of hydrogen bonding in the $\text{H}_{20}\text{-COO-AEIO}$ material could be detected via 2Dcos (FTIR) experiments revealing the interactions between the N-H moieties and both carbonyl of the amide and imidazolidone functionalities. A fast and effective autonomous self-healing behaviour of the hydrogen-bonded supramolecular was also found to be successful at room temperature.

Finally, some preliminary work was carried out using an engineering carboxylated nitrile butadiene rubber (NBR). This NBR material was converted into the resulting zinc-based metallosupramolecular elastomer using the same approach as previously investigated. These materials were also found to exhibit fast and efficient self-healing behaviour. Very importantly, we demonstrated that zinc-based metallosupramolecular elastomers can be used in combination with epoxy providing dual toughening and self-healing capabilities. In a blend with another high molecular weight NBR (50 wt%), efficient self-healing was also observed in casted films.
Chapter One – Introduction to self-healing
1.1. Preface

The concept of self-healing in material science is inspired from the biological example which provides the ability to human tissue to undergo a healing process after being wounded. The biological process that allows this to happen is complex, but nonetheless Nature does it beautifully. Unlike this fascinating biological example, materials cannot autonomously repair themselves which is why over the past 50 years, scientists have been looking at mimicking this biological example to material science. Materials experience damage and fatigue during their normal utilisation and the concept of eliminating this damage through a self-healing mechanism contributes to an increase of the lifetime and enhanced strength [1]. This is especially important in materials that are intended to perform in a designated manner for significant times where repair is not possible [2].

This PhD research project is concerned with the design of functional polymers towards the development of advanced self-healing materials. This Chapter One will present a thorough literature review in the area of self-healing and will describe the various scientific methodologies used to produce self-healing materials. The area of dendrimer, an exciting class of advanced functional polymeric material will also be described as it is of direct relevance to this project. The gaps in the literature will then be outlined, which will set the scene for the research questions which this work will attempt to address. The scope of this project as well as an outline of this thesis will be provided at the end of Chapter One.
1.2. Self-healing concepts

The translation of the self-healing concept to materials science has been demonstrated scientifically by three conceptual approaches: capsule-based systems, vascular networks, and intrinsic healing. These approaches are described in detail below.

1.2.1. Capsule-based systems

Autonomic self-healing based on a microencapsulated healing agent and a catalytic chemical trigger embedded within a matrix was first reported by White et al. [3]. In this model, the growth and propagation of micro-cracking within the matrix cause the microcapsules to break, releasing a healing agent which is chemically or catalytically activated (Figure 1.1). This process restricts any further propagation and restores entirely or most of the physical properties of the material [3-5].

![Figure 1.1: Visual interpretation of an autonomic capsule-based self-healing concept](image)

The initial work by White et al. [4, 7] used Ring-Opening Metathesis Polymerization (ROMP) of encapsulated DiCycloPentaDiene (DCPD) in the presence of Grubb’s catalyst (Figure 1.2). This technique has since been used by many researchers [4, 7-8]. The effects of size and concentration of the catalyst and microcapsules on fracture toughness and healing efficiency were investigated. White et al. showed significant increase of up to 127 percent in the fracture
toughness of an epoxy resin [7, 9-10]. Moreover, the stability of these microcapsules up to 250°C allows them to be used in many applications where high temperatures are reached [11]. Others have used Poly(DiMethyl Siloxane) (PDMS), an attractive healing agent (due to its chemical stability and low viscosity of its monomers, and its rapid polymerisation at ambient temperature) as an alternative to DCPD. Self-healing efficiency of up to 115% has been reported using encapsulation of two phase separated PDMS monomers [12, 13]. This process however produces ethanol as by-product which is undesirable.

Scheme 1.1: Ruthenium-based Grubbs’ catalyst initiates ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) [4]

A novel catalyst-free chemistry system has been reported by Moore et al. [14]. This system addressed all the aforementioned issues by developing a solvent promoted approach where the solvent carries un-reacted epoxy monomers into the crack where polymerisation takes place and structural integrity can be therefore restored. Encapsulated “green” solvents (chlorobenzene, phenyl acetate and ethyl phenylacetate) in resin systems used by Caruso et al. [10, 14-16] revealed a good healing efficiency of up to 100% with 20wt% of microcapsules. Even if the concept seems attractive, the plasticising effect [17, 18] that these solvents have on the epoxy resin is not negligible. This is a major drawback for the thermo-mechanical property (such as flexural, storage modulus and glass transition) of the resulting material. Mookhoek et al. [19] demonstrated that non-reactive solvents such as o-dichlorobenzene, phenyl acetate, cis-decahydronaphthalene encapsulated into a PMMA matrix can be used as healing agent and don’t need any external intervention. However, the volatility as well as the solvent removal during manufacture were found to be critical for the healing process to occur. Those systems were found to recover 30% of strength with a capsule loading of 15 wt% over
Chapter One – Introduction to self-healing

14 days. More recently, Garcia et al. [20] developed a new water-reactive organic healing agent (octyldimethylsilyloleate) incorporated into an epoxy coating via *in situ* poly(urea-formaldehyde) encapsulation. This catalyst-free approach was found to be effective with a concentration as low as 0.7μL/cm² of healing agent into the epoxy resin resulting in a crack closure and corrosion resistance as shown by the Electrochemical Impedance Spectroscopy (EIS) and Scanning Vibrating Electrode Technique (SVET) experiments.

To sum up, although the capsule-based systems approach has been found to be successful to some extent, it is important to highlight that many of the parameters involved such as storage and chemical stability of the healing agent, mechanical properties (i.e. stiffness and compressive strength) of the microcapsule, release and healing mechanism, must be correctly tailored for this process to be effective [21]. Also of importance is that repeatability is problematic using this approach as the self-healing process can only occur once.

Below is a table (Table 1.1) summarising the healing efficiency of the various capsule-based systems.

**Table 1.1: Summary self-healing efficiency based on capsules systems**

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Testing method</th>
<th>Healing measure</th>
<th>Maximum healing efficiency %)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy/ E-glass FRC</td>
<td>DCPD-Grubbs’</td>
<td>TDCB</td>
<td>Fracture toughness</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Solvent or epoxy resin solvent</td>
<td>TDCB</td>
<td>Fracture toughness</td>
<td>82-100</td>
<td>15, 16</td>
</tr>
<tr>
<td>Epoxy</td>
<td>DCPD Grubbs’</td>
<td>TDCB</td>
<td>Fracture toughness</td>
<td>75-93</td>
<td>4, 8, 9</td>
</tr>
<tr>
<td>Epoxy/CFRC</td>
<td>DCPD Grubbs’</td>
<td>TDCB</td>
<td>Fracture toughness</td>
<td>80</td>
<td>5</td>
</tr>
</tbody>
</table>
1.2.2. Vascular networks

The healing process for vascular networks is somewhat similar to capsule-based systems however, in the case of the vascular network system; the healing agent is introduced after integration of the network within the matrix (Figure 1.2).

The 1D vascular system approach was pioneered by Dry and co-workers [22, 23], in which they qualitatively examined the healing ability with millimetre-diameter glass pipettes preloaded with either cyanoacrylate or a separated two part epoxy system. Williams and co-workers [24, 25] extended on this concept and constructed self-healing 2D networks within composite sandwich panels using a two-part RT310 resin. Toohey et al. [26, 27] went a step further and used direct-ink writing to produce a 3D vascular epoxy network that mimics the structure and functionality of epidermal tissue and this technique reveals a healing efficiency of up to 70%.

<table>
<thead>
<tr>
<th>PMMA</th>
<th>Solvent</th>
<th>TDCB</th>
<th>Strength</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy coating</td>
<td>water-reactive organic silyl ester</td>
<td>EIS and SVET</td>
<td>EIS and SVET</td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS</td>
<td>PDMS-Pt Catalyst</td>
<td>Tear test</td>
<td>Tear strength</td>
<td>115</td>
</tr>
</tbody>
</table>

Figure 1.2: Visual interpretation of an autonomic vascular network system [6]
The main problem with this concept is the inclusion of hollow fibre, a carrier of the self-healing agent, into the matrix. This also implicates the use of a low viscosity resin to facilitate fibre and damage infusion. Moreover, the aspect ratio and the relatively large diameter of the hollow carrier fibres (a few hundreds microns up to a millimetre in diameter) are also problematic [28].

Below is a table (Table 1.2) summarising the main efficiency of vascular network systems.

**Table 1.2: Summary self-healing efficiency based on vascular systems**

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Testing method</th>
<th>Healing measure</th>
<th>Maximum healing efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>Hollow fibres cyanoacrylate</td>
<td>Tensile/flexural</td>
<td>Fracture toughness</td>
<td>Visual rebonding</td>
<td>22,23</td>
</tr>
<tr>
<td>RT310 resin</td>
<td>DCPD Grubbs’ catalyst</td>
<td>Impact/compression</td>
<td>Compressive strength</td>
<td>100</td>
<td>24,25</td>
</tr>
<tr>
<td>Epoxy</td>
<td>DCPD Grubbs’ catalyst</td>
<td>Mode I 4 point bend</td>
<td>Fracture toughness</td>
<td>38-70</td>
<td>26, 27</td>
</tr>
</tbody>
</table>

**1.2.3. Intrinsic systems**

The concept of intrinsic healing differs from what was reported previously because it primarily consists of a matrix that has inherent self-healing properties (Figure 1.3). A number of chemical and physical approaches such as reversible, molecular diffusion, ion hopping and supramolecular networks have been investigated. These methods are described in the following sections.
1.2.3.1. Reversible reactions (remendable process)

Intrinsic systems based on reversible reactions use polymers reversibly transformed from the monomeric state to the cross-linked polymeric state caused by external stimuli. The most widely used reaction scheme for remendable self-healing materials is based on the Diels-Alder (DA) and retro-Diels-Alder (rDA) reactions (Scheme 1.2) [29-31].

Scheme 1.2: Example of rDA and DA reactions [31]

Park et al. used cyclopentadiene as a precursor to produce polymer DCPD, which can undergo the DA reaction as shown in Figure 5. Healing efficiencies of up to 94% have been reported using this polymer in both its bulk form [32] and as a matrix in a carbon fibre reinforced composite [33]. One of the main advantage of this process is its capacity to heal repeatedly with minimal change to material properties as described by Park et al. [32-33]. However, the healing process for this process is mainly based on the thermal activation of the molecular
rearrangement. Temperatures above $T_g$ (up to $150^\circ C$ [32]) are necessary for the healing process to be initiated.

### 1.2.3.2. Molecular diffusion

The elementary steps of all physical self-healing principles are interdiffusion and entanglement of polymer chains [34, 35]. Both properties depend on intermolecular forces, which are closely linked to the chemical nature of the polymer and the length of the molecules. It has been shown that the polymer/polymer interface gradually vanishes and the mechanical strength at the initial interface increases by bringing two pieces of identical or even compatible polymers into contact. Thus, the polymer matrix is actually healed due to molecular diffusion along the polymer/polymer interface [35, 36]. In order to understand this phenomenon, Wool and O’Connor [37] developed, in 1981, a five-stage mechanism to unscramble the complexity of strength recovery at ruptured polymer/polymer interfaces, and provide an explanation for the function of many self-healing concepts (Figure 1.4), being strongly related to molecular interdiffusion.

![Figure 1.4: The various stages of self-healing based on a molecular interdiffusion mechanism [37]](image-url)
Chapter One – Introduction to self-healing

The principle stages of healing according to the mechanism of Wool and O’Connor include the steps of surface rearrangement, surface approach, wetting, diffusion and randomization. The self-healing process of molecular diffusion is divided into 2 different class of polymers: thermoplastic polymers and thermosets.

1.2.3.2.1. Thermoplastic polymers

O’Connor showed that the inclusion of styrene-isoprene-styrene block copolymers and polystyrene [37-39] allowed void closure, surface interaction and molecular entanglement between the damaged faces. Void closure of micro-cracks arising from molecular entanglement of dangling chains using weak polyurethane gel was also successfully investigated by Yamagushi et al. [40, 41]. These systems showed a maximum level of healing of 80% in tear strength.

Self-healing of a thermoset matrix can also be achieved by incorporating a thermoplastic additive. Often, during this process, the material is heated above the melting point of the dispersed thermoplastic phase which then diffuses through the crack plane and, interacts mechanically with the matrix. Hayes et al. [42, 43] showed that the incorporation of poly(bisphenol A-co-epichlorohydrin) (phenoxy), into an epoxy composite allowed for recovery of load bearing after thermal healing at 130°C for 6 h or 160°C for 1 h, and multiple healing cycles were possible. Self-healing was demonstrated with as little as 5wt% of phenoxy, but was found to be optimum at 20wt% resulting in 70% efficiency. Luo et al. [44] also prepared a thermally remendable material by dispersing phase-separated poly(caprolactone) (PCL) in an epoxy matrix. Upon heating, PCL melts and undergoes a volumetric thermal expansion filling the micro-cracks and allowing for healing.

1.2.3.2.2. Thermosets

Others have used cross-linking agents as a mean of providing a self-healing mechanism. For example, using an epoxy matrix with an excess of amine activated by thermal treatment Rahmatullah et al. [45] showed that the matrix can recover from damage, with a maximum efficiency of up to 68%. Fang et al. [46] synthetised self-healing hydrogels based on chitosan
copolymers. Networks based on those hydrogels and containing redox initiators are the source of molecular diffusion at the interface polymer/polymer and can lead to a healing efficiency of 80%.

1.2.3.3. Ionomers

1.2.3.3.1. General information

Ionomers are a class of polymers containing some ionic species or segments attached to their backbone. These materials have been intensively studied during the last 40 years because of the interesting changes of properties observed. The ion incorporation can be achieved by two different approaches: the neutralisation of pendant groups such as carboxylates or sulfonates with or by polymerisation of ionic co-monomer [47]. In the early 1950’s, the first ionic elastomers based on a poly(butadiene-co-acrylonitrile-co-acrylic acid) neutralised with zinc hydroxide was introduced by B.F Goodrich [48]. Those ionic elastomers were found to exhibit enhanced tensile properties and improved adhesion in comparison with conventional copolymers. In the 1960’s DuPont introduced poly(ethylene-co-methacrylic acid) under the trade name Surlyn [49]; these copolymers were partially neutralised with sodium and zinc hydroxide. More recently, different families of ionic elastomers have emerged that possess a wide variety of properties leading to different applications such as perfluorosulfonate ionomers (Nafion from DuPont) [50], perfluorocarboxylate ionomers (Flemion from Asahi Glass) or polybutadiene (Hycar from BF Goodrich).

Ionomers are typically prepared by copolymerisation of a functionalised monomer with an olefinic unsaturated monomer or direct functionalisation of a “preformed” polymer. For example, carboxyl-containing ionomers are obtained by direct copolymerisation of acrylic or methacrylic acid with ethylene, styrene, and similar co-monomers by free radical copolymerisation [37]. The resulting copolymer is generally available as the free acid, which can be neutralised to the degree desired with metal hydroxides, acetates, and similar salts. Another class of ionomers based on metal-ligand interactions, called metallopolymers, was introduced in 1955 [51].
1.2.3.3.2. Metallopolymers

Metallopolymers contain either main group (p-block) metals, d-block transition metals, or lanthanides and actinides (f-block elements) [52]. In addition, a range of different possible structural types exist depending on where the metal centres are incorporated and the nature of the bonding between them. A major subdivision arises from a consideration of the location of the metal centres; these can be either in the main chain or in the side group structure. As a further subdivision, metallopolymers can be linear or dendritic (Figure 1.5) [52].

![Figure 1.5: Structural diversity evident in the metallopolymer field [52]](image)

The introduction of metal complexes into polymeric materials can lead to interesting properties and, particularly, the structural properties of these complexes are of importance in self-healing materials [53].

A polymer network, described by Schubert et al. [54], was synthesized by the crosslinking of terpyridine-functionalized poly(alkyl methacrylates). For this purpose, an iron salt was added, resulting in insoluble and very hard polymer films after drying. The ionic interactions between the charged complexes (i.e. sulphate) and the counterions (iron) are responsible for the self-
healing behaviour of such ionically crosslinked metallopolymer network. Recently, the concept of self-healing metallopolymer networks was improved by the Schubert group using cadmium(II)-bisterpyridine complexes [55] synthesized by the addition of cadmium acetate. In comparison with what has been reported with the iron counterions, the authors could show that these materials (i.e. cadmium based) behave differently due to a different coordination of the metal centre. The acetate moiety was found to coordinate to the cadmium, but this metal–ligand interaction is much weaker resulting in an improved self-healing behaviour in comparison with the iron-based complexes.

1.2.3.3.3. Self-healing applications

1.2.3.3.3.1. Composites

Ionomer systems have been used as a reinforcement for composite and nanocomposite applications. Kim and Lee [56] defined the importance of the degree of neutralisation in the increase of tensile strength in carboxylic polyurethane resin. Upon neutralisation with triethylamine, an increase in interchain interactions caused an increase in tensile properties. Matsuda et al. [57] found that the interleaving of an ethylene methacrylic acid copolymer partially ionized with zinc ions into a carbon fibre reinforced composite increased its fracture toughness up to eleven folds (DCB method). In a similar fashion, Choi et al. [58, 59] reported the electrospinning of perfluorosulfonic acid into membranes and their use in composites. The increase of Young’s modulus and limit stress in the reinforced nanocomposites were up to 3.5-fold and 2-fold higher respectively. Another nanocomposite system formed by melt processing from a series of organoclays and poly(ethylene-co-methacrylic acid) ionomers has been studied by Shah et al. [60]. These nanocomposites showed promising improvements in performance and may be particularly interesting for barrier applications [61].

1.2.3.3.3.2. Ballistic

Ionomers have been shown to self-repair after impact and penetration of a high energy projectile [62, 63] but also after sawing, cutting, and puncture [63]. The self-healing process
based on ionomer systems has been investigated using different methods [64]. The presence of intrinsic molecule interactions [65] and ion hopping proved to be the main mechanism responsible for this phenomenon. Fall [66] characterised the viscoelastic properties of a range of EMAA ionomers using a variety of dynamic mechanical and rheological methods. The presence of heat to activate the molecules was found to be the most important parameter for the self-healing process to occur. Castellucci [67] developed a new composite material composed of a conductive network embedded into an EMAA ionomer (Surlyn). This composite was capable of detecting damage through the conductive network and healing could be induced using resistance heating of the embedded conductive network. Kalista and Ward expanded the work on EMAA [68, 69] and demonstrated that a balance between the elastic and viscous flow is required to achieve adequate self-healing. Huber and Hinkley [70] similarly developed a simple method to test the healing properties of EMAA ionomers consisting of a series of compressive penetration tests with a cylindrical probe at different impact rates. Varley et al. [71, 72] reported a new method which allows the penetrant to be completely removed from the impact zone (Figure 1.6), and thus does not interfere with the self-healing process.

![Figure 1.6: Schematic representation of the self-healing process during high-energy impact](image)

EMAA ionomers were found to demonstrate a diverse range of mechanical properties from elastic, elastomeric and molten behaviour after impact. The ability of these ionomers to
exhibit solid-like and liquid-like behaviour were found to be critical for the self-healing process [71-72].

### 1.2.3.3.4. Self-healing mechanism

It has been previously mentioned in section 1.2.3.3. ionomers can display self-healing behaviour under certain circumstances, which is facilitated by ion hopping. A schematic representation of ion hopping mechanism is shown in Figure 1.7 [74] where the ionic species within a given polymer are observed to “hop” from one ionic cluster to another.

![Schematic representation of the “ion hopping” mechanism in an ionomer. The circles represent the ionic clusters and the curved line is the polymer chain [74].](image)

During the process displayed in Figure 1.7, the ions “hop” or diffuse from one cluster to another, allowing for the relaxation of the chain segment of the macromolecule. This mechanism allow the entire polymer to diffuse and flow. It is important to mention that in relation to the self-healing, the “ion hopping” which provides the physical mechanism to allow
the polymer structure to exhibit elastomeric and self-heal has only been showed to occur in the melt state of the ionomer [75]. In the melt state, the clusters are not stable anymore, and the ionic clusters are “degrading” leading to the flow of ions from clusters to clusters as per Figure 1.7. During ballistic impact for example, the energy required to penetrate through the impact zone is sufficient to generate enough energy to allow for the polymer to heat up at the interface (above the melting point) and allowing for the ion hopping to happen [72, 73]. The temperature at the interface has been measured by Thermal IR camera nearing 100 degrees [66] in the particular case of EMAA polymer subjected to a ballistic impact. To our knowledge the ion hopping mechanism responsible for self-healing has not been reported under normal room temperature condition or without thermal stimuli.

In composite applications, Meure et al. [76, 77] showed that polyethylene-co-methacrylic acid (EMAA) ionomers can be used as a self-healing template. They studied the chemical reactions/interactions between the EMAA healing agent and an epoxy resin. It was reported that interfacial strength development during curing and healing are critical to the successful incorporation of healing characteristics into this new type of mendable resin. Covalent bonds, formed into the system during the post-curing, were responsible for the increase of the interfacial strength of the system resulting in an 85% recovery in critical stress intensity and over 100% recovery in sustainable peak load. Self-healing was only observed but needed thermal activation.

1.2.3.3.5. Characterisation

Different morphology of ionic species and structures can be observed but in most cases, ions clusters will form locally. Because of their particular structure, characterisation of those polymers has been challenging and specific model structures have been developed primarily by Eisenberg et al. (Figure 1.8) [78, 65].
Chapter One – Introduction to self-healing

When the concentration of ionic species increases, the morphology of the polymer changes, which forms groups of ionic clusters (multiplets) into the structure [75], resulting in the creation of a network based on physical ionic cross-linking. The mechanical and physical properties of ionomers, such as the glass transition temperature, modulus and viscosity for example [78] are strongly affected by the nature, localisation morphology and concentration of these ionic clusters.

The characterisation of ionomers in solution can be difficult; Keling and Williams [79] described a new method to determine the degree of neutralisation of ionomers based on the absorbance ratio comparison on a FTIR spectrum. Lee et al. [80] described a new technique for the characterisation of ionomers based on plasma treatment and time-of-flight secondary ion mass spectrometry. Ionomers’ structures have also been investigated using X-Ray scattering in a solid state [81, 82].

1.2.3.4. Hydrogen-bonded supramolecular networks

Supramolecular polymers use the “chemistry beyond the covalent bond” to combine reversible, secondary interactions with the attractiveness of conventional polymers [83]. Polymers can be molecularly designed to form strong end group and/or side-group associations via multiple complementary, ionic, reversible hydrogen bonds, resulting in a self-
healing system. The relevant issues for utilizing supramolecular bonds in self-healing polymers are the timescale of the dynamics, relating dynamics of the bond to the timescale of healing, and their strength, resulting in stronger or weaker networks [84]. The design of self-healing polymers based on hydrogen bonding combines highly dynamic properties [85, 86-88] as bonds show a reversible “sticker-like” behaviour enabling connection and reconnection. Supramolecular network formation [88-89] as well as strength are generated by the “stickiness” of the applied supramolecular bonds or by cluster formation [89, 91] between several hydrogen bonding motifs. Sijbesma et al. [91, 92] reported that a strong change in material properties can be achieved with quadruple hydrogen bonds such as the ureido-pyrimidone bond. Depending on the binding sites, linear as well as cross-linked polymers were formed, whereas the absence of unspecific aggregation allowed excellent control over the formed network architecture. Cordier et al. [93] demonstrated self-healing of a rubbery material prepared via supramolecular assembly, and his colleague Montarnal et al. [94] developed a simplified synthesis of the active linker responsive for the self-healing. In their original work published in Nature, they showed the recovery and self-healing of two freshly cut pieces of their rubbery compound through hydrogen bonding.

Table 1.3: Summary self-healing efficiency based on intrinsic systems

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Testing method</th>
<th>Healing measure</th>
<th>Maximum healing efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M4F</td>
<td>DA/rDA reaction</td>
<td>Compact Tension</td>
<td>Fracture toughness</td>
<td>57</td>
<td>29</td>
</tr>
<tr>
<td>2MEP4F</td>
<td>DA/rDA reaction</td>
<td>Compact Tension</td>
<td>Fracture toughness</td>
<td>83</td>
<td>30</td>
</tr>
<tr>
<td>Mendomer 401/CFRC</td>
<td>DA/rDA reaction</td>
<td>Mode I 3 point bend</td>
<td>Strain energy</td>
<td>94</td>
<td>33</td>
</tr>
<tr>
<td>Epoxy/</td>
<td>Meltable polymer</td>
<td>Compact Tension</td>
<td>Fracture toughness</td>
<td>77</td>
<td>40</td>
</tr>
</tbody>
</table>
## 1.3. Dendrimers

In synthetic organic chemistry, the creation and design of dendritic compounds is a relatively new field. The first successful attempt to create and design dendritic structures by organic synthesis was carried out by Vogtle and co-workers [95] in 1978. Donald Tomalia [96, 97] from Dow Chemicals was the first to develop a commercial dendrimer. He developed a new class of amide containing cascade polymers such as a polyamidoamine (PAMAM). Tomalia and co-workers labelled this new class of macromolecules “dendrimers” derived from the Greek words “dendrons” meaning “tree” or “branch” and “meros” meaning “part”. In some cases, dendrimers are denoted “arboroles” [98], or more broadly, “hyperbranched polymers”.

The following sections describe the structure of a dendrimer, the different methods of synthesis and finally the main applications.
1.3.1. Structure

Dendrimers are built from a starting molecule (a core), to which “branches” are added by a repeating series of chemical reactions producing a spherical branching structure (Figure 1.9). As the process repeats, successive layers are added, and the size of the dendrimer can be expanded. The result is a spherical macromolecular structure whose size is similar to albumin and haemoglobin [97], but smaller than such the gigantic IgM antibody multimers complex. Dendrimers possess three distinguished architectural components [99, 100]:

- An initiator core.
- Interior layers (generations G) composed of repeating units, radically attached to the interior core.
- Exterior (terminal functionality) attached to the outermost interior generations.

![Figure 1.9: Schematic representation of a dendrimer [101]](image)

1.3.2. Synthesis

Dendrimers are generally prepared using either a divergent or a convergent method [102]. There is a fundamental difference between the two.
Chapter One – Introduction to self-healing

### 1.3.2.1. Divergent method

In the divergent methods, the dendrimer grows outwards from a multifunctional core molecule. The core molecule reacts with monomer molecules containing one reactive and two unreactive groups giving a first generation dendrimer. Subsequently, the periphery of the first generation dendrimer can be ‘activated’ to allow for another layer of reactive monomers to be grafted. The process is repeated for several generations and a dendrimer is built layer after layer (Figure 1.10). The divergent approach is successful for the production of large quantities of dendrimers. Problems occur from side reactions and incomplete reactions of the end groups that lead to structure defects (asymmetry). To prevent side reactions and to force reactions to completion, large excesses of reagents are required, which can cause some difficulties in the purification of the final product.

![Figure 1.10: The divergent synthesis of dendrimers [102]](image)

### 1.3.2.2. Convergent method

The convergent methods were developed as a response to the weaknesses of the divergent synthesis [104]. In the convergent approach, the dendrimer is constructed stepwise, starting from the end groups and progressing inwards. When the growing branched polymeric arms, called dendrons, are large enough, they are attached to a multifunctional core molecule (Figure 1.11). The convergent method has several advantages. It is relatively easy to purify
the desired product and the occurrence of defects in the final structure is minimised. The first synthetised dendrimers using this method was the famous PAMAM [105, 106].

**Figure 1.11: The convergent synthesis of dendrimers [102]**

The attraction of the convergent method lies in the fact that only a small number of molecules is involved in the reaction steps that form each successive generation. In contrast, increasing numbers of molecules are involved in the reactions in the later stages of a synthesis using the divergent approach. Large excesses of reagents and slight impurities can also be avoided, without sacrificing high yields.

### 1.3.3. Applications

There are many types of dendrimers, each having different functional surface functionalities as well as interior and core, which can be tailored accordingly to suit a number of applications. These specific properties make dendrimers suitable for high technology biomedical and industrial applications [107].
1.3.3.1. Drug delivery

The physical characteristics of dendrimers, including their mono-dispersity, water solubility, encapsulation ability, and large number of functionalisable peripheral groups, make these macromolecules appropriate candidates for evaluation as drug delivery vehicles. The use of dendrimers for the encapsulation of hydrophobic drugs [108-110] and for the delivery of anticancer drugs [111] has been the subject of intense research. Three methods have been reported for using dendrimers as a drug carrier. In the first approach, the drug is covalently attached to the periphery of the dendrimer to form dendrimer prodrugs. In the second, the drug is coordinated to the outer functional groups via ionic interactions. Finally, in the third approach, the dendrimer acts as a uni-molecular micelle by encapsulating a drug through the formation of a dendrimer-drug supramolecular assembly [112, 113]. The use of dendrimers as drug carriers by encapsulating hydrophobic drugs is a potential method for delivering highly active pharmaceutical compounds that may not be in clinical use due to their limited water solubility and resulting suboptimal pharmacokinetics. Dendrimers have been widely explored for controlled delivery of antiretroviral bioactives [114]. The inherent antiretroviral activity of dendrimers enhances their efficacy as carriers for antiretroviral drugs. The dendrimer enhances both the uptake and retention of compounds within cancer cells, a finding that was not anticipated at the onset of studies [115, 116]. The encapsulation increases with dendrimer generation and this method may be useful to “encapsulate” drugs with a relatively high therapeutic dose. Studies based on this dendritic polymer also open up new avenues of research into the further development of drug-dendrimer complexes specific for a cancer and/or targeted organ system. These encouraging results provide further impetus to design, synthesize, and evaluate dendritic polymers for use in basic drug delivery studies [112, 117].

1.3.3.2. Gene delivery

The ability to deliver pieces of DNA to the required parts of a cell presents many challenges. Current research is being performed to find ways to use dendrimers to traffic genes into cells without degrading or deactivating the DNA. To maintain the activity of DNA during
dehydration, the dendrimer/DNA complexes were encapsulated in a water soluble polymer, and then deposited on or sandwiched in functional polymer films with a fast degradation rate to mediate gene transfection. Based on this method, PAMAM dendrimer/DNA complexes were used to encapsulate functional biodegradable polymer films for substrate-mediated gene delivery. Research has shown that the fast degrading functional polymer has great potential for localised transfection [118-120].

1.3.3.3. Sensors

Scientists have also studied dendrimers for use in sensor technologies. Studied systems include proton or pH sensors using poly(propylene imine) [121] cadmium-sulfide/polypropylenimine tetrahexacontaamine dendrimer composites to detect fluorescence signal quenching [122], and poly(propyleneimine) first and second generation dendrimers for metal cation photodetection [123]. There is a great deal of research in this field due to the potential for multiple detection and binding sites in dendritic structures.

1.3.3.4. Toughening agents

The inherent brittleness of epoxy resins has restricted their implementation into structural components requiring certain levels of toughness. For the past decade, improvement in the fracture toughness of composite materials has attracted the attention of the scientific and industrial communities. Some of the work focused on the development of novel resin systems involving the use of hyperbranched polymers or dendrimers as toughening agents. The use of polyester dendrimers (Boltorn) as a toughening agent has been reported in different resin systems. Boogh et al. [124-126] investigated the ability of dendritic hyperbranched polymers to increase interlaminar fracture resistance and reduce the internal stress of epoxy-based composites. The results show an increase of up to 80% with only 10 phr of modifier (Boltorn™-E2 epoxy functional HBP and a hydroxy-functional hyperbranched, Boltorn™-H30). Fröhlich et al. [127] studied a novel reactive core/shell-type hyperbranched block copolyether, which was tailored as a new class of liquid rubbers useful as flexibilisers and toughening agents of anhydride-cured epoxy resins.
For example, Lu et al. [128] reported a new kind of toughening agent using amine-terminated Boltorn hyperbranched polymer. The activation energy of the modified system was found to be around 70-80 kJ.mol$^{-1}$ higher than that of the unmodified system. More recently, Zhang et al. [129] showed that the inclusion of Boltorn H$_{40}$ into N, N', N'-tetraglycidyl-4, 4'-diaminodiphenylmethane (TGDDM) epoxy resin almost doubled its fracture toughness. FTIR showed the formation of hydrogen bonding between the epoxy network and the dendrimer. It has also been reported that the presence of Boltorn hyperbranched polymers has an effect on the cure behaviour of epoxy resin. For instance, Oh et al. [130] showed that epoxy/Boltorn system present higher heat of cure and lower activation energy for cure reaction than epoxy/linear polymer system using differential scanning calorimetry and FTIR results. Ratna and Simon [131] revealed that the presence of hydroxyl groups has a catalytic effect on the curing behaviour.
1.4. Research challenges

The research and development of stimuli-responsive advanced materials has seen significant growth in the last few years and some advances have been made in this field. A large amount of research work has been focused on autonomous self-healing systems based on either micro-capsules or vascular networks. However, these approaches have been scientifically criticised for a number of simple reasons such as storage and long term chemical stability of the contained healing agent and poor mechanical properties (i.e. stiffness and compression strength) of the micro-capsule or vascular networks [23-28]. Moreover, it’s important to highlight that the repeatability is problematic as the self-healing process can only occur once. More recently, the development of more efficient and autonomous intrinsic self-healing systems has been presented in the literature via chemical functionalisation of polymers to promote reversible reactions [29, 30, 33], molecular diffusion [35, 41, 44, 45], ion hopping/clusters [70, 71, 76, 77] or hydrogen-bonding interactions [82-85, 90].

The primary mechanism of self-healing involved in these intrinsic systems relies on inter- and intra-molecular interactions, leading to a spatial re-arrangement of the molecules. In order to promote these types of interactions, their self-healing efficiency has often been facilitated scientifically through solvent swelling (hydrogels) and/or plasticisation of the polymer [92] and the use of an external stimuli (for example heat [82, 83]). Self-healing is efficient in these facilitated cases because a large number of non-equilibrated free groups are available at the interface to interact. Nevertheless, as pointed out by Leibler [93], the number of non-associated free groups available for healing decreases with time as a result of local association of these groups at the vicinity of the fractured surface after equilibrium. It has also been concluded that it is necessary to have non-equilibrated free groups on both of the surfaces to be joined together and self-healing to occur.

It is important to point out that to date very few intrinsic systems have demonstrated true room temperature self-healing potential without using swelling, plasticising or external stimuli (UV or heat).
1.5. **Research questions/research plan**

1) **Is it possible to improve inter-molecular interactions for self-healing purposes using a dendrimer?**

In this project it is proposed that the use of a highly branched polymeric system such as a dendrimer could potentially display better intrinsic self-healing characteristic compared to a linear polymer. The high degree of branching and abundant number of surface functionalities of a dendrimer is appealing because it is believed that it would help in enhancing locally the inter-molecular interactions and therefore increase the mobility of the polymer which is sought after to more effectively achieve self-healing. Most of the reported self-healing polymeric systems are based on linear system often having non-compact structure and irregular architecture, which is not ideal if one wants to facilitate local molecular interactions. The development of an intrinsic self-healing system based on a dendrimer could be more efficient and could potentially address some of the research challenges mentioned previously. To date, very little has been done in this area using dendrimers. Andreeva and Shchukin [132] discussed the possibility of using dendrimers as nano-containers for capsule based self-healing systems for protective coatings applications. It was found that the use of dendrimers in this particular case is beneficial because of the ability to retain the active material into their inner volume for a long period and release it on demand. Blaiszik et al [133] studied the possibility of using aldehyde PAMAM dendrimers solutions as liquid healing agent encapsulated into resin systems.

2) **What is the effect of both the valency and the quantity of surrounding counter-ions on the self-healing behaviour of an ionic dendrimer?**

Previous reports have shown that commercially available linear ionomers can be used as self-healing systems [65-68]. Self-healing is achieved as a result of ion hopping between the counter-ions and terminally charged groups. One commercially available linear ionomers which has been extensively studied is the Surlyn, a poly(ethylene-co-methacrylic acid) polymer. It has been reported that self-healing efficiency was affected when using sodium as
a counter-ion, in blends with Ethylene/Vinyl Alcohol copolymer or epoxidized natural rubber [134].

In this work, the effect of valency on the self-healing properties of an ionic dendrimer will be investigated by comparing a mono-valent (Sodium Na\(^+\)) and a bi-valent (Zinc Zn\(^{2+}\)) type of counter-ion. Further to that, the number of counter-ions ionically linked to the charged dendrimer molecule will be varied to understand the effects on the self-healing characteristics of the resulting materials.

3) Is it possible to achieve self-healing based on supra-molecular dendritic networks?

Systems based on hydrogen-bonding supra-molecular networks have already been reported to be effective as reported by Cordier et al. [93, 94]. However, the need of swelling into a solvent like water to promote the inter-molecular interactions responsible for the healing process to take place makes this approach less appealing for an everyday use.

In this project, the same chemical approach developed by Cordier will be used on our dendrimer. It is believe that the high degree of branching and abundant local number of surface functionalities of the dendrimer will be helpful in promoting the hydrogen-bonding mechanism between the associative imidazolidone groups. The self-healing behaviour of the supramolecular dendritic networks will be investigated.
1.6. Thesis outline

This thesis consists of seven chapters.

Experimental procedures for this project are presented in Chapter Two inclusive of a description of the Schlenk method technique and a diagram of the apparatus. Lists of NMR shifts are also provided.

In Chapter Three, the synthesis and characterisation of the carboxylic terminated dendrimer, which was used as a precursor for the development of the ionic and hydrogen bonded - supramolecular networks, will be presented. This Chapter will provide details on the elucidation of the molecular structures, through combination of FTIR, NMR and XPS techniques. The neutralisation of the carboxylic terminated dendrimer to yield a range of ionomers having mono-valent counter ions (Na⁺) will be described. Their chemical properties including spectroscopic data confirming formation of the ionomers will be presented. Self-healing properties of films casted from these ionomers will be analysed and interpreted.

In Chapter Four, the neutralisation of the carboxylic terminated dendrimer to yield a range of ionomers having divalent counter-ions (Zn²⁺) will be described. The formation of ionic supramolecular networks created thanks to the ionic bonding between the zinc and carboxylate functions of the dendrimer was studied with a combination of spectroscopic (FTIR and XPS) and thermal (conventional and modulated) techniques. Self-healing properties of films casted from these ionomers will be analysed and interpreted.

Chapter Five describes the formation of a supramolecular dendritic network based on hydrogen bonding via functionalisation of the carboxylic terminated dendrimer with imidazolidone groups. Characterisation of the formed product will be described using FTIR and NMR techniques. The nature of the inter-molecular interactions through space will be investigated using two-dimensional nuclear magnetic resonance (NOESY). The self-healing properties will be verified.
Finally, Chapter Six will extend on the methodology applied in the previous Chapters and will discuss some preliminary work on the self-healing of ionic or hydrogen bonded supramolecular networks based on acrylonitrile butadiene natural rubber carrying a carboxylic functionality. Their functionalisation and characterisation will be detailed as well their self-healing ability.

Finally, Chapter Seven will summarise the work and will conclude some recommendations to pave the way for future potential developments.
1.7. References


Chapter One – Introduction to self-healing


Chapter One – Introduction to self-healing


Chapter One – Introduction to self-healing


Chapter One – Introduction to self-healing


Chapter One – Introduction to self-healing


Chapter Two – Materials and Experimental
2.1. Materials

2.1.1. Starting material and reagents

2.1.1.1. Starting material

This work will be mainly focussed on the use of a second generation commercial hyperbranched polyester Boltorn H$_{20}$ [1] (Perstorp Specialty Chemicals AB, Sweden) H$_{20}$ is dendrimer terminated with 16 hydroxyl groups (Figure 2.1).

![Diagram of Boltorn H$_{20}$](image)

**Figure 2.1: Starting material H$_{20}$ on the left and its representation on the right**

The structure elucidation of the H$_{20}$ using NMR, FTIR has already been published [2, 3]. The H$_{20}$ was dried under vacuum at 60°C overnight prior to any reaction in this work. NMR chemical shifts from [3] are listed below:
NMR: ¹H NMR (270 MHz, CD₃COCD₃); δ (ppm) = 1.18-1.33 (t, 36H, CH₃), 3.42-3.76 (m, 64H, CH₂ – O – CH₂ + R – CH₂OH), 4.14-4.39 (m, 24H, R – CH₂OR);
¹³C NMR (100 MHz, CD₃COCD₃); δ (ppm) = 16.60 (C10), 18.01 (C7), 48.61 (C1), 50.43 (C6), 64.57 (C11), 65.07 (C8), 65.72 (C4), 70.31 (C2), 72.71(C3), 173.44 (C9), 174.64 (C5);
FTIR (ATR-germanium): ν (cm⁻¹) = 3600 – 3200 (st, free –OH alcohol), 3000 – 2800 (st, CH₃/CH₂), 1735 (st, C=O ester), 1470  (b, C-H), 1300 – 1240 (st, C-O), 1070 (st, C-O alcohol), 1040 (st, C-O ether).

2.1.1.2. Main reagents

Triethylamine (TEA) ≥99.5%, 4-(Dimethylamino)pyridine (DMAP) ≥99%, succinic anhydride ≥99%, zinc chloride (ZnCl₂), ACS reagent, ≥97%, diethylenetriamine 99%, 4 Å molecular sieves were purchased from Sigma-Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) 95+% was purchased from Matrix Scientific and urea (AR grade) from Ajax Finechem. Sodium Hydroxide (NaOH) pellets were purchased from Merck KGaA. Zinc hydroxide was synthetised in house using zinc chloride and sodium hydroxide following the method described in section 2.3.1.

2.1.2. Solvents

Tetrahydrofuran (THF) (AR grade), ethyl acetate (AR grade), methanol (AR grade), acetone (AR grade), and ethanol (AR grade) were purchased from Chem-Supply and were used without further purification. THF was dried over molecular sieves prior to the esterification of the starting material.
Acetone-d₆ (CD₃COCD₃), chloroform-d (CDCl₃) and deuterated water (D₂O) were purchased from Cambridge Isotope Laboratories.
2.2. Experimental

2.2.1. Synthesis of the carboxylic acid terminated dendrimer (H_{20}COOH)

2.2.1.1. Apparatus

The dendrimer carboxylic equivalent was carried out using the Schlenk oxygen exclusion method in the presence of Nitrogen (N_{2}). A dual manifold high vacuum line was used as shown in Figure 2.2. The bottom part of the manifold represents the vacuum chamber and the top the inert gas chamber. Reaction vessels, attachments and stirring equipment were flamed dried under vacuum prior to synthesis. Each vessel was purged with N_{2} three times before the introduction of reagents.

![Figure 2.2: Schlenk oxygen exclusion manifold [4]](image-url)
2.2.1.2. Synthesis scheme

The functionalisation of H$_2$O using succinic anhydride and DMAP in pyridine to yield a carboxylic acid terminated H$_2$O has been reported in [5, 6]. This facile method was also chosen in this project to functionalise the H$_2$O starting material.

The esterification of the alcohol functionalities of the H$_2$O was achieved via esterification with succinic anhydride using TEA and DMAP as coupling agent in dry THF at room temperature (Scheme 2.1). We used THF instead of pyridine [5, 6] because THF is easier to remove under vacuum.

![Scheme 2.1: Synthesis of 2 via esterification](image)

The reaction protocol was as follow: 0.50 g of dried H$_2$O (0.29 mmol) was dissolved in 10.0 mL of anhydrous THF in a two-necked round-bottom flask, and then an excess of succinic anhydride (0.55 g, 5.50 mmol) was added in the presence of 25 mg of DMAP (0.20 mmol) and 5 mL of TEA. All additions were conducted under nitrogen atmosphere and the mixture was stirred at ambient temperature overnight. During the reaction, a homogenous and transparent solution was first formed, which then turned to a highly viscous solution. The final product was decanted to eliminate the THF. The obtained product which will be referred as H$_2$O-COOH in this thesis was washed 3 times with 20 mL of THF and then 3 times 20 mL of ethyl acetate in order to remove the excess DMAP. Purification of the product H$_2$O-COOH via dialysis into Milli-Q water was carried out (see next section 2.1.3). An average yield of 62% was obtained after esterification.
NMR: $^1$H NMR (270 MHz, CD$_3$COCD$_3$); $\delta$ (ppm) = 1.18-1.33 (m, 36H, CH$_3$), 2.54-2.56 (2s, 80H, O – CH$_2$ – CH$_2$ – COOH), 3.42-3.76 (m, 16H, CH$_2$ – O – CH$_2$ + R – CH$_2$OH), 4.14-4.39 (m, 56H, R – CH$_2$OR);

$^{13}$C NMR (100 MHz, CD$_3$COCD$_3$); $\delta$ (ppm) = 17.17 (C7), 46.63 (C6), 48.54 (C1), 63.51 (C12), 64.22 (C13), 65.32 (C8), 65.74 (C4), 68.97 (C2), 70.65 (C3), 171.70 (C5), 173.25 (C14).

FTIR (ATR-germanium): $\nu$ (cm$^{-1}$) = 3600 – 3300 (b, H-bonded –OH carboxylic acid), 3300 – 2500 (st, free –OH carboxylic acid), 3000 – 2800 (st, CH$_3$/CH$_2$), 1735 (st, C=O ester), 1710 (st, C=O carboxylic acid), 1470 (b, C-H), 1300 – 1240 (st, C-O), 1220 (st, C-O carboxylic acid), 1040 (st, C-O ether), 960 (b, O-H carboxylic acid)

### 2.2.1.3. Purification

Dialysis of H$_2$O-COOH into Milli-Q water was carried out using large cassettes (Thermo Fisher, G2 2k) (Figure 2.3) with a cut off molecular weight of 2000 g.mol$^{-1}$. The esterification product was re-dissolved into 20 ml of Milli-Q water and the solution was transferred into the flexible membrane of the cassette. The cassette was then transferred into a large beaker filled with Milli-Q water. The Milli-Q water was changed every second day for a duration of approximately 2 weeks. During that time the water miscible TEA (M$_W$ = 101.2 g.mol$^{-1}$) freely diffused across the membrane whilst the carboxylic acid terminated dendrimer H$_2$O-COOH (theoretical M$_W$ of 3305 g.mol$^{-1}$) stayed trapped within the membrane. After dialysis the product was syringed out from the membrane. This technique was found to be much easier than a conventional purification by column separation. The quality of the dialysed compound was found to be similar to that of a column separated compound (Chapter Two section 2.2.2.).


2.2.2. Sodium neutralisation

The carboxylic acid terminated dendrimer $\text{H}_2\text{O}_n\text{-COOH}$ was neutralised to yield a range of ionic dendrimers (Scheme 2.2).

\[ \begin{align*}
\text{H}_2\text{O}_n\text{-COOH} & \xrightarrow{\text{Na(OH) \text{ aqueous solution}}} \\
& \xrightarrow{\text{water, RT}} \\
& \begin{array}{c}
\text{3 (n=4), 4 (n=8), 5 (n=12), 6 (n=16)}
\end{array}
\end{align*} \]

Scheme 2.2: Neutralisation scheme with sodium hydroxide to yield 3, 4, 5, and 6

The carboxylic groups were neutralised using various stoichiometric ratios aqueous solution of sodium hydroxide at a 10g/L concentration. The $\text{H}_2\text{O}_n\text{-COOH}$ dendrimer (1g) was first dissolved in 20 mL Milli-Q water for 30 minutes. To this solution, stoichiometric amounts of
aqueous sodium hydroxide was added so that 4, 8, 12 and 16 of the carboxylic groups were converted to a carboxylate with a sodium counter-ion (referred here as $H_{20}^\text{COO} - 0.25\text{Na}$, $H_{20}^\text{COO} - 0.50\text{Na}$, $H_{20}^\text{COO} - 0.75\text{Na}$ and $H_{20}^\text{COO} - \text{Na}$, respectively). The final solution was evaporated *in vacuo* at 60 degrees for 4h. The final product obtained was found to increase in opacity with increasing degree of neutralisation (Figure 2.4).

![Figure 2.4: Neutralised $H_{20}^\text{COOH}$ products (increasing degree of neutralisation, compounds 3, 4, 5, 6 from left to right).](image)

**2.2.3. Zinc neutralisation**

The carboxylic groups of $H_{20}^\text{COOH}$ were converted into carboxylate with a Zinc counter-ion using various stoichiometric ratios freshly prepared $\text{Zn(OH)}_2$ in aqueous conditions.

**2.2.3.1. Preparation of zinc hydroxide $\text{Zn(OH)}_2$**

Fresh Zinc hydroxide $\text{Zn(OH)}_2$ (Figure 2.5) was prepared using the following procedure: 5g (35 mmol) of zinc chloride was first dissolved in 20mL of Milli-Q water for 5 minutes, then 2.9g (70 mmol) of sodium hydroxide was added to the aqueous solution. The final solution was left to stir for 30 minutes. It was important to make sure that the zinc chloride to sodium hydroxide was in 1 to 2 ratio as otherwise a colourless solution of zincate ion $\text{Zn(OH)}_2^{2^-}$ [7] could have been formed instead of zinc hydroxide. The obtained white precipitate of $\text{Zn(OH)}_2$ was filtered and washed 5 times with Milli-Q water to remove all traces of by-products. The yield of this reaction was found to be around 90%.
2.2.3.2. Neutralisation

As the zinc hydroxide Zn(OH)$_2$ is not soluble into water, the neutralisation of the carboxylic groups of the H$_{20}$-COOH was carried out using a solid-liquid diffusion process (Figure 2.6) similar to the flotation method [8-10] used in industry to separate zinc and its oxides using fatty acids [11].

The neutralisation was carried out as follow: 1g of carboxylic dendrimer (0.58 mmol) was dissolved in 20mL of Milli-Q water and a stoichiometric amount (2 to 1 ratio) of solid Zn(OH)$_2$ was added to solution so that 4, 8, 12 and 16 of the carboxylic groups were converted to a carboxylate with a Zinc counter-ion (Scheme 2.3). The solution was stirred thoroughly for 24h till all the Zn(OH)$_2$ disappeared. The formation a white paste was visually observed as the neutralisation occurred.
2.2.4. Amidation of the $\text{H}_2\text{O}-\text{COOH}$

A recent paper published by Cordier et al [12] disclosed a very efficient way to produce a self-healing material [13] by amidation of di and tri-carboxylic fatty acids using N-aminoethyl-2-imidazolidone (AEIO). This method was adopted in this work to look at the potential self-healing efficiency of the functionalised dendrimer.

2.2.4.1. Synthesis of 1-(2-aminoethyl)-2-imidazolidone (AEIO)

The method we used to synthesise AEIO was similar to what has been reported in [14]. In this work, 1.5g (14.54 mmol) of diethylenetriamine (DETA) and 1.5 mL of Milli-Q water were introduced into a 50 mL two-neck round bottom flask blanketed with nitrogen connected to a water condenser. This mixture was stirred for 10 min and 0.45g (7.49 mmol) of urea was added. The solution was left under nitrogen atmosphere and permanent agitation for approximately 10h after which the condenser was removed. The solution was reduced by evaporation of the water and DETA. The remaining DETA was removed by simple distillation under vacuum at 75°C. Fractional distillation was used to isolate the main product AEIO which was retrieved at a top of the column temperature of 105°C [14] (Scheme 2.4). The obtained...
A colourless solution was washed five times with chloroform (20 mL) in order to remove any by-products. The final yield was around 70%.

Scheme 2.4: Scheme AEIO synthesis

NMR: \( ^1H \) NMR (270 MHz, CDCl$_3$); \( \delta \) (ppm) = 1.66 (br s, 2H, NH$_2$), 2.68 (t, 2H, -CH$_2$-NH$_2$, \( J = 6.2 \) Hz), 3.09 (t, 2H, -CH$_2$-CH$_2$-NH$_2$, \( J = 6.2 \) Hz), 3.31 (s, 4H, C$_2$H$_2$-C$_2$H$_2$, imidazolidone), 5.73 (br s, 1H, NH imidazolidone); \( ^13C \) NMR (100 MHz, CDCl$_3$); \( \delta \) (ppm) = 38.09 (C2, C$_2$H$_2$NH imidazolidone), 40.08 (C5, C$_2$-NH$_2$), 45.49 (C3, C$_2$-N imidazolidone), 46.94 (C4, N-C$_2$H$_2$-CH$_2$-NH$_2$), 163.5 (C1, C=O imidazolidone).

FTIR (ATR-germanium): \( \nu \) (cm$^{-1}$) = 3650-3200 (st, N-H), 3000-2800 (st, CH$_2$), 1670 (st, C=O imidazolidone), 1500-1450 (b, N-H), 1280 (st, C-N).

2.2.4.2. Amidation synthesis

The amidation of H$_2$O-COOH was achieved as follows: 1g (0.30 mmol) of H$_2$O-COOH was dissolved in 20 mL of Milli-Q water and 1g of EDC and 0.7g (5.42 mmol) of AEIO were added to this solution. The reaction was stirred thoroughly for 16h at room temperature (Scheme 2.5). A translucent and highly viscous material was obtained after evaporation of the water under vacuum at 80 degrees. The viscous paste was washed 5 times with chloroform in order to remove the excess of AEIO and potential by-products.

Scheme 2.5: Amidation of H$_2$O-COOH scheme.
NMR: $^1$H NMR (270 MHz, D$_2$O); δ (ppm) = 1.18-1.32 (m, CH$_3$), 2.52 (s, O-CH$_2$-CH$_2$-C=O-NH), 3.02-3.09 (m, O-CH$_2$-CH$_2$-C=O-NH), 3.18-3.22 (t, NH-CH$_2$-CH$_2$-N, $J$ = 6.9 Hz), 3.22-3.27 (m, NH-CH$_2$-CH$_2$-N), 3.28-3.35 (m, N-CH$_2$-CH$_2$-NH imidazolidone), 3.40-3.47 (m, N-CH$_2$-CH$_2$-NH imidazolidone), 3.58-3.74 (m, CH$_2$-O-CH$_2$), 4.18-4.31 (m, CH$_2$-O-R);

$^{13}$C NMR (100 MHz, D$_2$O); δ (ppm) = 16.79 (C7, CH$_3$), 37.69 (C18, NH-CH$_2$-CH$_2$-N), 38.09 (C21, N-CH$_2$-CH$_2$-NH imidazolidone), 38.91 (C6, quaternary), 39.35 (C1, quaternary), 41.85 (C19, NH-CH$_2$-CH$_2$-N), 45.12 (C20, N-CH$_2$-CH$_2$-NH imidazolidone), 55.13 (C16, O-CH$_2$-CH$_2$-C=O-NH), 64.02 (C12, O-CH$_2$-CH$_2$-C=O-NH), 64.63 (C8, C-CH$_2$-O-C=O), 65.94 (C4, O-CH$_2$-CH$_2$-O-C=O), 69.64 (C3, O-CH$_2$-CH$_2$-O-C=O), 70.63 (C2, C-CH$_2$-O-CH$_2$), 160.49 (C17, CH$_2$-C=O-NH), 165.15 (C22, N-C=O-NH imidazolidone), 174.10 (C15, O-C=O-CH$_2$), 175.02 (C5, O-C=O-C-);

FTIR (ATR-germanium): ν (cm$^{-1}$) = 3600-3200 (st, N-H), 3000-2800 (st, CH$_2$), 1730 (st, C=O ester), 1680 (st, C=O imidazolidone), 1624 (st, C=O amide), 1500-1450 (b, N-H), 1280 (st, C-N), 1040 (st, C-O ether), 750 (out-of-plane, N-H).
2.3. Characterisation

2.3.1. Fourier Transformation Infra-Red spectroscopy (FTIR)

Infrared data were collected on a Bruker Vertex 70 FTIR equipped with an ATR unit. The spectra were obtained in attenuated total reflectance mode (ATR). 64 scans at 4 cm\(^{-1}\) resolution were collected for each sample between 600 cm\(^{-1}\) and 4000 cm\(^{-1}\). The data was analysed using OPUS 7.2.

2.3.2. Nuclear Magnetic Resonance spectroscopy (NMR)

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance 270 (at 270 MHz and 100 MHz respectively). All chemical shifts (δ) are reported in ppm downfield of TMS. All spectra were recorded in a 100% deuterated solvent (CDCl\(_3\), D\(_2\)O, CD\(_3\)COCD\(_3\)) at 298 K. The NMR solutions were prepared at a fixed concentration of 5 mg/mL to avoid concentration shifts in the spectra. NMR prediction spectra were achieved with the software Delta 5.2.

\(^1\)H NMR spectra were acquired after 64 scans with a spectral window of 15 ppm, an acquisition time of 4 sec and a relaxation time of 0.1 sec. \(^{13}\)C NMR spectra were acquired after an average of 50000 scans with a spectral window of 250 ppm, an acquisition time of 1 sec and a relaxation time of 0.1 sec.

2D spectra were collected on a Bruker Avance 500 MHz spectrometer. All spectra were collected at room temperature using the residual proton resonance of the deuterated solvent as the internal standard. Proton signals reported as chemical shift (ppm) [integral, multiplicity (s = singlet, br s =broad singlet, d = doublet, dd = doublet of doublets, t = triplet, and m = multiplet)] assignment.
2.3.3. **X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) measurements were performed. Survey spectra were acquired for binding energies of 0 to 1400 eV, using pass energy of 160 eV. Chemical information indicating changes in the surface chemistry was elucidated by curve fitting the carbon 1s (C1s). The spectra were fitted with a Lorentzian-Gaussian mix Voigt profile (SGL) function, using a nonlinear least squares curve fitting program (CasaXPS). The analysis areas for all the samples were 500 μm × 500 μm.

2.3.4. **Differential Scanning Calorimeter (DSC)**

Thermal analyses were performed with a TA Instruments dynamic mechanical thermal analyser (TA DMA Q200 model). Samples of 5-10 mg were embedded in sealed aluminium pans. Conventional and modulated DSC were used depending on the type of sample tested.

2.3.4.1. Conventional DSC

All samples were testing using the same Heat-Cool-Heat cycle (Figure 2.7). The samples were first heated to 100°C at a heating rate of 10°C/min. The samples were held at 100°C for 5 min to erase any previous thermal history. The samples were then cooled down to room temperature at a constant rate of 5 °C/min and heated again to 80-100°C at a heating rate of 10°C/min. The glass transition ($T_g$) was defined as the temperature at half the height of the shift in specific heat ($C_p$).
2.3.4.2. Modulated DSC (MDSC)

Modulated DSC (MDSC) was used in this work to separate overlapping state behaviours into the samples which are impossible to detect with the conventional DSC. The heat cycle for the MDSC is described in Figure 2.8.
2.3.5. **Dynamic Light Scattering (DLS)**

DLS measurements were collected on a Zetasizer Nano ZS light scattering instrument (Malvern Instruments, UK), equipped with a 4mW He-Ne laser (emission 633nm). The Zetasizer instrument employs a non-invasive backscatter (NIBS) optics with a detection angle of 173°. The z-average diameter is measured by the instrument using cumulative analysis thus the size particle measurements reported in this paper are the z-average diameters. Samples for analysis were prepared in Milli-Q water at a concentration of 1μM. All samples were sonicated for 15 min prior to each measurement. All measurements were carried out at 25°C in a glass cell (10 mm path length).

2.3.6. **Scanning Electron Microscopy (SEM)**

Morphology of dendrimers was analysed using a Supra 55V scanning electron microscope (SEM). Samples were casted on silicon wafer after deposition of the aqueous solution and then dried under vacuum overnight at 60 degrees. The samples were vacuum coated with carbon using a Balzers sputter coater. All images were taken using an accelerating voltage of 5-10 keV with a magnification between 200 times and 2000 times.

2.3.7. **Optical Microscopy**

Optical microscopy was used for the assessment of self-healing capabilities of the different compounds. All samples were casted onto glass slides which were previously cleaned with acetone and then ethanol. Five drops of the different solutions of dendrimers dissolved in water were deposited onto the glass slides and let to settle for 2h. The slides were then introduced into a vacuum oven overnight to evaporate the solvent. The crack was initiated directly onto the sample deposited onto the glass slide using a sharp razor blade. The ability of the material to self-heal was assessed by visual closure of the crack at room temperature or after various heat treatments. Optical micrographs were taken using an Olympus DP70
digital camera at 5 and 10 times total magnification coupled with an Olympus BX51M optical microscope and a heating stage.

2.3.8. Self-healing capability

Depending on the class of material studied, a number of testing approaches have been adopted to test their self-healing characteristics. So far however, no standardisation of self-healing test capability has been adopted but a European programme (SHeMat [15]) is working on the development of such procedure.

The assessment of self-healing capabilities in materials depends not only of the type of material but also on the type of healing process itself [16].

2.3.8.1. Tapered Double Cantilever Beam

The evaluation of the stress–strain response under both quasi-static and high loading rate conditions in polymers is fundamental to understand the deformation history of the material. For quasi-static fracture conditions, healing efficiency is defined in terms of the recovery of fracture toughness. Healing evaluation starts with a virgin fracture test of an undamaged tapered double cantilever beam (TDCB, Figure 2.19). Prior to testing, a pre-crack is created with a razor blade into the centre groove of the specimen. The damage is introduced to sharpen the crack-tip, while loading is increased until the crack propagates along the centreline of the sample until failure. The crack is then closed and allowed to heal at room temperature or with the use of external heat. After healing, the sample is loaded again until failure [17].
Static fracture tests evaluate the changes in the crack growth and the absolute fatigue life of the healed material [18]. The fatigue response of the self-healing material is dependent of a wide number of factors, such as stress intensity, healing periods, among others. With this assessment method, it is possible to evaluate the recovery after the induced damage caused by cyclic loading [19]. The healing efficiency $\lambda$, can be determined by the correlation between the fatigue life-extension (Equation 1).

$$\lambda = \frac{N_{\text{healed}} - N_{\text{control}}}{N_{\text{control}}}$$

Where $N_{\text{healed}}$ stands for the total number of cycles until the failure of the healed sample and $N_{\text{control}}$ the total number of cycles until the failure of a non-healed sample.

For elastomeric material, the fracture toughness protocol with the TDCB is generally not the most suitable model to evaluate the healing efficiency. The TDCB fracture toughness protocol is generally utilised to test rigid samples, in most case epoxy based systems.
2.3.8.2. Tear strength recovery

In the case of elastomeric material, the self-healing is typically assessed using a tear strength recovery test. For this purpose, some authors [20] have developed a specific rectangular specimen (Figure 2.10).

![Figure 2.10: Schematic representation of a tear specimen during a test](image)

Healing efficiency \( \eta \), can be defined as the recovery of the tear strength of the healed sample \( (T_{\text{healed}}) \) compared to the non-damaged one \( (T_{\text{virgin}}) \), according to Equation 2.

\[
\eta = \frac{T_{\text{healed}}}{T_{\text{virgin}}}
\]

2.3.8.3. Visual

TDCB or tear recovery cannot be always be used to test the self-healing capability of ultra-soft samples like hydrogels for example. In that case, visual recovery from optical images from a micro-crack using a razor blade is the most common mode of assessment of self-healing. The self-healing is considered fully achieved when the initial razor cut can’t be observed anymore.
2.4. References


Chapter Three – Sodium based ionic dendrimer
3.1. Introduction

In this chapter, the functionalisation of a hydroxyl terminated dendrimer (H\textsubscript{20}) with succinic anhydride to yield a carboxylic acid terminated dendrimer (H\textsubscript{20}-COOH) will be described. The successful functionalisation of H\textsubscript{20} into H\textsubscript{20}-COOH was investigated using a range of techniques such as Fourier Transform Infra-Red (FTIR), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC) and X-Ray Photoelectron Spectroscopy (XPS). A range of sodium based ionic dendrimers were produced by stoichiometric neutralisation of the carboxylic acid groups of the dendrimer with sodium hydroxide (NaOH) yielding carboxylate terminated dendrimer with sodium counter-ions. The chemical properties including spectroscopic data confirming formation of the ionomers will be presented. Finally, the self-healing properties of films casted from the sodium based ionic dendrimers will be analysed and interpreted.
3.2. Functionalisation of the starting material

Boltorn $H_{20}$

The esterification of the terminal hydroxyl group of the starting dendrimer $H_{20}$ (Figure 1) to yield carboxylic acid terminated dendrimer $H_{20}$-COOH described in the next section was first carried out. This material will then be utilised for the preparation of various ionomers by converting the carboxylic acid groups into the corresponding carboxylate salts. The chemical structure of the starting material Boltorn $H_{20}$ which we used in this project is displayed in Figure 3.1. It is a second generation dendrimer containing a polyester core and terminated with 16 hydroxyl groups. The structure of this commercial dendrimer has been previously studied [1 – 7].

Figure 3.1: Starting material $H_{20}$ on the left and its representation on the right
3.2.1. Synthesis of $\text{H}_2\text{O}-\text{COOH}$

In order to functionalise $\text{H}_2\text{O}$, a Steglich esterification was conducted between the starting hydroxyl terminated dendrimer and succinic anhydride using TEA/DMAP as base and coupling agent as depicted in Scheme 2.1.

The esterification proceeds via the ring opening of the succinic anhydride and via an esterification reaction (Scheme 3.1). The mechanism was first reported in 1978 by W. Steglich [8]. DMAP and the succinic anhydride react to form an ion pair of carboxylate and the acylpyridinium ion. In the second step the alcohol attacks the carbonyl group of the acylpyridinium ion to form an ester [8 - 10]. In this esterification, the DMAP acts as an acyl transfer reagent and the triethylamine (TEA) acts as a base to remove the proton from the alcohol while the alcohol acts as a nucleophile and forms a covalent bond with the acyl group. The characterisation of the esterification product: the carboxylic dendrimer $\text{H}_2\text{O}-\text{COOH}$, is described in the following paragraphs.

![Scheme 3.1: Esterification mechanism [9 - 10]](image)

3.2.2. Purification of $\text{H}_2\text{O}-\text{COOH}$

The purification of $\text{H}_2\text{O}-\text{COOH}$ was achieved following several steps. First of all, as the product $\text{H}_2\text{O}-\text{COOH}$ obtained was not soluble into THF as opposed to the other reaction materials. The
reaction product was therefore washed 3 times with 20mL of THF in order to remove the excess of succinic anhydride, TEA and DMAP. Ethyl acetate (3 x 20mL) was used to eliminate the remaining traces of products. Following that, the product was decanted and analysed by $^1$H NMR in CD$_3$COCD$_3$ (Figure 3.2). It was found that traces of TEA were present and visible (quadruplet at 3.2 ppm and triplet at 1.3 ppm). Furthermore, no traces of succinic anhydride or DMAP were detected.

Purification by column separation was employed as triethylamine is very stationary on silica [11]. The product was dissolved in a 9:1 mixture ethyl acetate-methanol. The method was effective as only one run through the column was necessary to remove the traces of TEA. However, the yield achieved after the separation was merely 50%. Therefore another purification was investigated in order to improve the yield. Dialysis of H$_{20}$-COOH into Milli-Q water was carried out (Figure 3.3) using large cassettes (Thermo Fisher, G2 2k) with a cut off molecular weight of 2000 g.mol$^{-1}$. The carboxylic acid terminated dendrimer H$_{20}$-COOH has a theoretical M$_W$ of 3305 g.mol$^{-1}$ and therefore TEA (M$_W$ = 101.2 g.mol$^{-1}$) freely diffused across the membrane.
Complete dialysis took around 2 weeks but this technique was found to be much easier. The quality of the dialysed compound was found to be similar to that of a column separated compound.

![NMR spectrum](image)

**Figure 3.3: $^1$H NMR of H$_{20}$-COOH after dialysis purification into Milli-Q water (spectrum obtained into CD$_3$COCD$_3$)**

The residual multiplets peaks of TEA at 3.25 ppm and 1.26 ppm disappeared after dialysis (Figure 4, showing the $^1$H NMR of H$_{20}$-COOH after dialysis purification). The purification method allows an easy way to obtain a pure product with a better yield than by using column chromatography (~85%).

### 3.2.3. Characterisation of the starting material H$_{20}$ and reaction product H$_{20}$-COOH

#### 3.2.3.1. Nuclear Magnetic Resonance (NMR)

**3.2.3.1.1. Introduction**

Nuclear Magnetic Resonance (NMR) is a useful tool for the characterisation of organic and inorganic compounds both in the solution and solid state. The technique takes advantage of
the ½ integral spin state of nuclei and the most commonly used isotopes are \(^1\)H, \(^{15}\)N, \(^{13}\)C, \(^{19}\)F, \(^{29}\)Si and \(^{31}\)P [12]. Amongst the many experiments possible, the most commonly used for the purpose of molecule characterisation are basic one-dimensional (1D) proton (\(^1\)H) and carbon (\(^{13}\)C) experiments. The information that can be extracted from those proton and carbon spectra such as chemical shifts can give detailed knowledge of either proton or carbon environment and connectivity.

The application of NMR to polymers can be limited as signal strength is highly dependent on the ratios between the atoms of a particular molecule. Size is therefore a great limiting factor for polymer NMR [13].

Despite minor drawbacks, NMR can still be applied to investigate the chemical structure of a polymer and elucidate proton and carbon assignments.

### 3.2.3.1.2. \(^1\)H NMR characterisation

The success of the esterification reaction was supported by the NMR data. Although due to symmetry and the large molecular weight of the molecule, the exact bond of attachment cannot be visualised. The overall shifts and difference of peak integrations indicate attachment has occurred (Table 3.1).

**Table 3.1: Theoretical (I\(_{th}\)) and experimental (I\(_{exp}\)) proton integration of H\(_2\)O and H\(_2\)O-COOH in CD\(_3\)COCD\(_3\)**

<table>
<thead>
<tr>
<th>Position</th>
<th>Functional groups</th>
<th>(\delta) (ppm)</th>
<th>(I_{th})</th>
<th>(I_{exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2O)</td>
<td>7 + 10 R – CH(_3)</td>
<td>1.01 – 1.37</td>
<td>36</td>
<td>36.00</td>
</tr>
<tr>
<td></td>
<td>2 + 3 + 11 R – CH(_2) – R’ + R – CH(_2)OH</td>
<td>3.39 – 3.81</td>
<td>64</td>
<td>63.57</td>
</tr>
<tr>
<td></td>
<td>4 + 8 R – CH(_2) – OR’</td>
<td>3.98 – 4.40</td>
<td>24</td>
<td>23.92</td>
</tr>
<tr>
<td>(H_2O)-COOH</td>
<td>7 R – CH(_3)</td>
<td>1.18 – 1.33</td>
<td>36</td>
<td>36.00</td>
</tr>
<tr>
<td></td>
<td>12 + 13 O – CH(_2) – CH(_2) - COOH</td>
<td>2.52 – 2.58</td>
<td>64</td>
<td>80.36</td>
</tr>
<tr>
<td></td>
<td>2 + 3 R – CH(_2) – R’</td>
<td>3.42 – 3.76</td>
<td>16</td>
<td>16.53</td>
</tr>
<tr>
<td></td>
<td>4 + 8 R – CH(_2) – OR’</td>
<td>4.14 – 4.39</td>
<td>56</td>
<td>55.33</td>
</tr>
</tbody>
</table>

Table 3.1 presents the different integrations related to the \(^1\)H NMR spectra of \(H_2O\) (Appendix A) and \(H_2O\)-COOH (Figure 3.4). The table details the theoretical and experimental integration
for each functional groups present in both H₂O and H₂O-COOH. All proton integrations were normalised to the methyl groups (R-CH₃) which is the only constant moiety after esterification (36 protons).

The appearance of two singlet peaks of the CH₂-CH₂ methylene groups present in the succinic acid at around 2.53 ppm [6] is an indication that the succinic acid is present. The attachment of the succinic anhydride can be most likely indicated by the change of integration of methylene groups characteristic of alcohol and ester moieties. The integration of the protons relative to the characteristic peaks of the -CH₂ (methylene of the core and alcohol) and ester groups (R − CH₂ − OR') found in H₂O at 3.61 ppm and 4.23 ppm, respectively display an opposite trend. The multiplet peak between 3.42 and 3.76 ppm integrated to 64 protons in the starting material H₂O whilst in H₂O-COOH an integration of 16 protons was found. On the other hand, integration of the ester R − CH₂ − OR' multiplet between 4.14 and 4.39 ppm increased from 24 to 56 protons after attachment of the succinic acid. The integrations for each characteristic groups in addition to the presence of the methylene groups at 2.53 ppm is a good indication that the attachment of carboxylic groups at the original alcohol functionality was most probably successful as reported elsewhere [14]. Note that the dendrimer being symmetrical, only one branch is represented in the following proton and carbon NMR. The quaternary carbon in position 1 is representative of the molecule core.

Figure 3.4: ¹H NMR of H₂O-COOH in CD₃COCD₃ (*)

![Figure 3.4: ¹H NMR of H₂O-COOH in CD₃COCD₃ (*)](image-url)
In order to overcome solubility issues between compounds, solubility tests in various common solvents were carried out on the reaction product H$_2$O-COOH. The aim was to determine if there were any interaction in between the solvent and the dendrimer. Chemical shifts for the molecule in 2 deuterated solvents are represented in Table 3.2.

Table 3.2: $^1$H NMR chemical shifts and multiplicity of H$_2$O-COOH peaks in various solvents

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Acetone – d$_6$</th>
<th>D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ (ppm)</td>
<td>multiplicity</td>
</tr>
<tr>
<td>R – CH$_3$</td>
<td>1.18 – 1.33</td>
<td>m</td>
</tr>
<tr>
<td>O – CH$_2$ – CH$_2$ - COOH</td>
<td>2.52 – 2.58</td>
<td>2s</td>
</tr>
<tr>
<td>R – CH$_2$ – R’ + R – CH$_2$OH</td>
<td>3.42 – 3.76</td>
<td>m</td>
</tr>
<tr>
<td>R – CH$_2$ – OR’</td>
<td>4.14 – 4.39</td>
<td>m</td>
</tr>
</tbody>
</table>

It can be seen that there is a shift of the different peaks depending on the solvent used to dissolve the H$_2$O-COOH. Those shifts are coherent with the literature [15]. It is interesting to note that methylene peak characteristic of the addition of succinic anhydride become a multiplet in deuterated water. This change of conformation can be explained by the water carboxylic acid hydrogen bonding [16].

3.2.3.1.3. $^{13}$C NMR characterisation

The quaternary carbon peaks of H$_2$O are situated in the 50 ppm region. Two peaks are distinct: the first one at 48.7 ppm is representative of the carbon at the core of the dendrimer (position 1), the second one at 50.4 ppm belongs to the quaternary carbon at the start of new generations (position 6). The region between 60 and 75 ppm is characteristic of the carbons of CH$_2$ functionalities. In the starting material, the different carbons of the alkyls can be designated as follow: at 65.1 ppm, the alkyl close to the ester groups (positions 8 and 4) and at 71.1 ppm the carbon peak of the ether core (positions 2 and 3). Finally, the carbon peak at 173.4 ppm is characteristic of C=O of the ester groups (positions 5 and 9) of the starting material [14, 17]. The $^{13}$C NMR spectrum of H$_2$O-COOH (Figure 3.5) shows some differences in comparison with the one from the starting material (Appendix B).
To begin with, the carbonyl region between 180 and 160 ppm shows a distinct carbon peak at 173.3 ppm characteristic of the carbon of the carboxylic acid (position 14) of the grafted succinic acid portion. Some differences in the alkyl region (80 to 60 ppm) can be observed as well. For example, the characteristic carbon peaks (positions 2 and 3) of the ether groups of the molecule core are still present around 71.1 ppm, but between 62 and 65 ppm, only peaks of the alkyl carbon (positions 4 and 8) related to the ester groups at 66.3 ppm remain as the alkyl carbon related to the alcohol (position 10) disappeared at 64.6 ppm because of the attachment of the succinic anhydride. The quaternary region is showing some changes as well and notably at 46.5 ppm. The quaternary carbon (position 6) displays a shift of 4 ppm due to the change of environment. Jesberger et al. [18] described the same shift of the quaternary carbon whilst attaching a RAFT agent at the surface of the dendrimer. Finally, the carbon of –CH₃ groups (position 7) remains at 17.2 ppm but this time only one peak is present as all methyl groups present the same environment after the grafting of the succinic anhydride.
3.2.3.2. Fourier Transform InfraRed spectroscopy (FTIR)

3.2.3.2.1. Introduction

Fourier Transform InfraRed spectroscopy (FTIR) is a powerful technique to determine the presence of specific chemical groups of organic compounds. This technique is based on how a sample absorbs light (IR) at a specific wavelength. Depending on the chemical groups present in the molecule, the energy absorbed emphasize the vibration of the bonds between atoms. The dissipation of energy is based on different types of vibrations (stretching or bending) of the specific bonds in the sample. In the case of polymers, each chemical groups absorb light at a particular wavelength which gives a full finger print of the polymer studied. The term Fourier Transform comes from the mathematical process used to convert the raw data into the actual spectrum [19].

3.2.3.2.2. Results

A number of studies have been published on the characterisation of the starting material \( H_2O \) and its esterified product \( H_2O-COOH \) using FTIR analysis [5-8, 20]. In this work, the FTIR spectra of the starting material \( H_2O \) displays number of characteristic bands which correlated well to what has been previously assigned.

The broad/strong band between 3600 and 3200 cm\(^{-1}\) visible in the \( H_2O \) spectra results from the O-H stretch of the alcohol functionalities (Figure 3.6). The band between 3000 and 2800 cm\(^{-1}\) is characteristic of C-H stretch present in the core of the molecule whilst the strong band at 1735 cm\(^{-1}\) is very characteristic of the ester C=O stretch [5]. Another obvious characteristic band of the \( H_2O \) is present at 1020 cm\(^{-1}\) which stands for the ether C-O-C stretching of the core [5].
The formation of an ester bond between the terminal OH of the starting dendrimer H$_2$O and the carboxyl group of succinic anhydride could be determined. The reaction product (i.e. carboxylic dendrimer H$_{20}$-COOH) displays a number of distinctive bands. In the fingerprint
region of the molecule between 1400 cm\(^{-1}\) to 800 cm\(^{-1}\), the disappearance of the methylene stretch characteristic of the alcohol at 1045 cm\(^{-1}\), strongly indicates that all the alcohol functionalities have been grafted with succinic anhydride. In addition, a strong band appears at 1170 cm\(^{-1}\), which is due to the C-O stretch of carboxylic acid moiety (different from the C-O stretch ester at 1240 cm\(^{-1}\) and C-O stretch alcohol at 1045 cm\(^{-1}\)). In addition, the very broad absorption band in the region between 3600 and 2500 cm\(^{-1}\) has been described as being a combination of the vibration of H-bonded carboxylic OH groups (3600 to 3300 cm\(^{-1}\)), C-H stretch of the alkyl groups (3000 to 2800 cm\(^{-1}\)) and a medium but very broad band due to the stretch of free O-H (3300 to 2500 cm\(^{-1}\)) [19, 20]. Finally, the shoulder visible at 1710 cm\(^{-1}\) is due to the presence of the carbonyl stretch of carboxylic acid groups absorbing at 1710 cm\(^{-1}\) [21].

In summary, it can be suggested from analysis of the FTIR spectra that formation of an ester bond between the terminal OH of the starting dendrimer H\(_2\)O and the carboxyl group of succinic anhydride was most likely successful to an appreciable extent.

3.2.3.3. X-Ray Photoelectron Spectroscopy (XPS)

3.2.3.3.1. Introduction

X-ray Photoelectron Spectroscopy (XPS) is a chemical analysis technique that can be used to analyse the surface chemistry of a material. It is often used in addition to FTIR and NMR to measure the surface elemental composition of the material [22]. XPS provides the relative frequencies of binding energies of electrons detected, measured in electron-volts (eV). The binding energies are used to identify the elements to which the peaks correspond. The binding energies of each element have been reported over the past 60 years and can be consulted in several handbooks [23]. The main detection limit of this technique is the concentration of elements at the surface of the material. Usually, concentration of parts per thousand are easily detected, parts per million can be detected but special conditions need to be changed such as longer collection time [24].
3.2.3.3.2. **XPS Survey spectrum**

The low-resolution wide-scan (survey) spectrum of the H$_2$O and H$_2$O-COOH materials displayed in Figure 3.7 serves as the basis for the determination of the elemental composition of the samples, showing primarily the presence of carbon and oxygen elements.

![Figure 3.7: XPS Survey spectra of H$_2$O (a) and H$_2$O-COOH (b)](image)

A relative increase in height of the oxygen O1s peak (at 530 eV) to that of the carbon 1s (C1s) peak (at 285 eV) after esterification with succinic anhydride was observed in the survey spectrum (Figure 10a and Figure 10b). The overall concentration of oxygen atoms is nearly doubled when comparing H$_2$O with H$_2$O-COOH which is confirmed by the increase of the O/C ratio before and after esterification (from 1.03 for the starting H$_2$O to 1.44 for H$_2$O-COOH). This is very obvious in the XPS survey showing a large increase of the oxygen peak in the H$_2$O-COOH compared to the H$_2$O material.

3.2.3.3.3. **High resolution C1s spectra**

High resolution C1s scans were collected to study in more depth the differences in carbon related functional groups between H$_2$O and H$_2$O-COOH. The high resolution C1s peaks were deconvoluted and curve fitted in order to calculate the relative concentration of each present carbon related functional groups as shown in Figure 3.8 and Figure 3.9. A one-point manual normalisation at 284.8 eV energy scale for the C1s line (C-C and C-H) was performed. Three
sub peaks at 285.0, 286.5 and 289.0 eV were assigned to C-C/H, C-O and O-C=O bonds respectively as reported elsewhere [25, 26].

Figure 3.8: C1s XPS spectrum H₂O

Figure 3.9: C1s XPS spectrum H₂O-COOH
Table 3.3 shows the elemental analysis of the different binding energies of the carbon.

Table 3.3: Relative carbon related functional group percentages measured in H$_2$O and H$_2$O-COOH after C1s peaks deconvolution.

<table>
<thead>
<tr>
<th></th>
<th>285 eV C-C/C-H</th>
<th>286.3 eV C-O-C</th>
<th>289 eV O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>47.1 %</td>
<td>42.0 %</td>
<td>10.9 %</td>
</tr>
<tr>
<td>H$_2$O-COOH</td>
<td>41.7 %</td>
<td>37.2 %</td>
<td>21.1 %</td>
</tr>
</tbody>
</table>

The C1s binding energies at 285 and 286.3 eV corresponding to the C-C/C-H and C-O-C bonds were found to be decreasing after the esterification reaction. This is coherent with an overall decrease of the concentration of carbon bonds in comparison to oxygen bonds after attachment of the succinic anhydride. This decrease co-occurred with an increase (10.9 to 21.1%) in the concentration of the O-C=O peak corresponding to the ester and carboxyl moieties. It can therefore be concluded that the XPS data also supports the NMR and FTIR results presented above.

3.2.3.4. Differential Scanning Calorimetry (DSC)

3.2.3.4.1. Introduction

Differential Scanning Calorimetry (DSC) is a thermodynamical tool used for direct characterisation of the heat energy uptake occurring in a sample upon controlled changes in temperature [27]. The technique is based on the difference of heat energy uptake between a reference pan (empty) and the pan containing the sample under the same atmosphere (air or inert gas such as Nitrogen or Argon). DSC is particularly applied to monitor the changes of phase transitions [28, 29] such as crystallisation, meting and glass transitions.
3.2.3.4.2. **DSC analysis**

The changes in thermal phase transitions of the H$_2$O and H$_2$O-COOH materials were investigated using DSC and their respective endotherms are displayed in Figure 3.10. The curves were shifted vertically for clarity.

![DSC curves for H$_2$O (red) and H$_2$O-COOH (black)](image)

It can be seen that the starting material H$_2$O displays a glass transition temperature at -20.8°C whereas the glass transition temperature of H$_2$O-COOH was found to be approximately -16.6°C. This increase in $T_g$ after attachment of the succinic anhydride can be explained by addition of polar carboxylic groups capable of hydrogen bonding. This is consistent with a study reported by Wooley et al. [30] who showed that the nature of the terminal functional groups in dendritic polyesters affects its glass transition temperature and that an increase in $T_g$ was observed following an increase in chain-end polarities. In this work, the absence of
melting transition in the DSC curves of both H₂O and H₂O-COOH demonstrates an amorphous behaviour as also reported by Malmström and al. [31]. Those results are further supporting the successful formation of H₂O-COOH.

### 3.3. Sodium neutralisation of H₂O-COOH

#### 3.3.1. Sodium neutralisation

The terminal carboxylic groups of the H₂O-COOH material were converted into their corresponding carboxylate moieties in order to yield a range of sodium based ionic dendrimers (i.e. ionomers). To do so, stoichiometric amounts of aqueous sodium hydroxide (NaOH) were added to the H₂O-COOH material as a mean of exchanging 4, 8, 12 and 16 of the protons of the terminal carboxyl groups (Scheme 3.3) with a mono-valent counter ion Na⁺. The effect of the mono-valent counter ion on the properties of the resulting materials, referred to here as H₂O-COO – 0.25 Na (n=4), H₂O-COO – 0.50 Na (n=8), H₂O-COO – 0.75 Na (n=12) and H₂O-COO – Na (n=16), was then studied.

![Scheme 2.2: Neutralisation scheme with sodium hydroxide to yield 3, 4, 5, and 6](image)

It is important to point out at this point of the text that the neutralisation of H₂O-COOH with sodium hydroxide needed to be carried out precisely in order to avoid de-esterification of the
core of the dendrimer. A neutralisation experiment using an excess of sodium hydroxide (1.1 part to 1 part \( \text{H}_2\text{O-COOH} \)) was carried out and showed that basic aqueous environment led to de-esterification of the core and the ester moieties disappeared from the \(^1\text{H} \) NMR (Appendix C).

### 3.3.2. Characterisation

#### 3.3.2.1. FTIR characterisation

FTIR was used to monitor the evolution of the carboxylic/carboxylate peak as a function of the neutralisation reaction. Figure 3.11 shows the evolution of these peaks in the carbonyl region between 1800 cm\(^{-1} \) and 1500 cm\(^{-1} \).

![Figure 3.11: FTIR (ATR mode) representing the carbonyl absorption of \( \text{H}_2\text{O-COOH} \) and Na ionomers](image)

Figure 3.11: FTIR (ATR mode) representing the carbonyl absorption of \( \text{H}_2\text{O-COOH} \) and Na ionomers
The FTIR spectrum shows that the band characteristic to carboxylate function at 1555 cm\(^{-1}\) keeps increasing in intensity with increasing degree of neutralisation. On the other hand, the carboxylic band at 1735 cm\(^{-1}\) decreases (data normalised at 1040 cm\(^{-1}\) corresponding to the stretching vibration of the ether C-O-C bond). However, because this band also overlaps with the ester band, it never completely disappeared even after complete neutralisation of the carboxylic groups (n=16) as the core poly-ester function of the dendrimer is still present. The single and sharp band of the carboxylate indicates a mono coordination of the dendrimer with the sodium ion [32] (Figure 3.12). The gradual increase in the intensity of the carboxylate band at 1535 cm\(^{-1}\) indicates that the neutralisation is quite controlled. It can also be seen that the shoulder at 1690 cm\(^{-1}\), typical of the free OH bonding of the carboxylic function, is only present in the H\(_2\)O-COOH; however, as soon as the sodium salt is introduced (n>4), the shoulder disappears. This can be explained by the breakage of the hydrogen bonding of the free OH of the carboxylic function which is in our case due to the ionic bonding with the sodium counter-ion.

**Figure 3.12: FTIR peak assignment following various types of interactions in carboxylic and mono-coordinated carboxylate groups (adapted from [32])**
3.3.2.2. $^1$H NMR characterisation

The effect of neutralisation was also visible on the $^1$H NMR of the dendrimers in the 2.35-2.50 ppm region (CH$_2$ region associated with the grafting of succinic anhydride) in Figure 3.13.

![Figure 3.13: $^1$H NMR of sodium based ionic dendrimers in D$_2$O](image)

A gradual shift of up to 0.13 ppm of the proton at the position 13 could be measured as a result of a stoichiometric neutralisation of the carboxylic groups with a mono-valent counter-ion (Na$^+$). The same phenomenon has already been reported by Kriz et al. [33]. They observed an upfield shift of CH$_2$ protons close to the carboxylic groups after neutralisation of PMMA-PAAc with NaOH. This again can be attributed to the changes in the electronic environment of these protons.
3.3.2.3. XPS characterisation

The concentration of the carbon related functional groups after neutralisation was studied from the high resolution spectra C1s of the materials. The C1s peak was deconvoluted and the under each binding energies has been tabulated (Table 3.4). An illustrative example of deconvolution for the $\text{H}_2\text{O}-\text{COO}^-\cdot0.5\text{Na}$ and $\text{H}_2\text{O}-\text{COO}^-\cdot\text{Na}$ C1s spectra are shown respectively in Figure 3.14 and Figure 3.15. C1s spectra for $\text{H}_2\text{O}-\text{COO}^-\cdot0.25\text{Na}$ and $\text{H}_2\text{O}-\text{COO}^-\cdot0.75\text{Na}$ are presented in Appendix D.

Table 3.4: Relative carbon related functional group percentages measured in the various materials after C1s peaks deconvolution

<table>
<thead>
<tr>
<th></th>
<th>285 eV C-C and C-H</th>
<th>286.3 eV C-O-C</th>
<th>288 eV O-C=O</th>
<th>289 eV HO-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}-\text{COOH}$</td>
<td>41.7%</td>
<td>37.2%</td>
<td>X</td>
<td>21.1%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}-\text{COO}^-\cdot0.25\text{Na}$</td>
<td>39.9%</td>
<td>39.1%</td>
<td>0.6%</td>
<td>20.4%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}-\text{COO}^-\cdot0.50\text{Na}$</td>
<td>38.3%</td>
<td>41.2%</td>
<td>0.8%</td>
<td>19.7%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}-\text{COO}^-\cdot0.75\text{Na}$</td>
<td>39.5%</td>
<td>39.1%</td>
<td>2.7%</td>
<td>18.7%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}-\text{COO}^-\cdot\text{Na}$</td>
<td>43.3%</td>
<td>37.0%</td>
<td>5.7%</td>
<td>14.0%</td>
</tr>
</tbody>
</table>

It can be seen that the first two binding energies of 285 eV (C-C/C-H) and 286.3 eV (C-O-C) are relatively unchanged in respect to the increase of the degree of neutralisation. This result is expected as this group is unaffected by neutralisation.
Chapter Three – Sodium based ionic dendrimer

Figure 3.14: C1s XPS of H$_2$O–COO – 0.5Na

Figure 3.15: C1s XPS of H$_2$O–COO – Na
In Figure 3.14 and 3.15, it can be seen that an additional peak at 288.2 eV appeared. This peak has been previously assigned to the carboxylate functionality (−O-C=O) [34, 35]. Integration of the −O-C=O peak indicates an increase from 0.6% to 5.7% of the carboxylate groups whilst the O-C=O (ester and acid) peak area decreased from 20.4% to 14%, respectively (Table 3.4). This results correlates well with the FTIR data showing an increase in carboxylate moieties upon neutralisation.

3.3.2.4. DSC characterisation

The changes in thermal transitions after neutralisation of the carboxylic functionalities in H₂O-COOH have been investigated and Table 3.5 below shows the glass transitions of the various ionomers.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>T₉₁ (°C)</th>
<th>T₉₂ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O-COOH</td>
<td>-16.6</td>
<td>x</td>
</tr>
<tr>
<td>H₂O-COO – 0.25 Na</td>
<td>-15.2</td>
<td>22.1</td>
</tr>
<tr>
<td>H₂O-COO – 0.50 Na</td>
<td>-14.7</td>
<td>31.9</td>
</tr>
<tr>
<td>H₂O-COO – 0.75 Na</td>
<td>-15.7</td>
<td>35.3</td>
</tr>
<tr>
<td>H₂O-COO – Na</td>
<td>-14.5</td>
<td>43.9</td>
</tr>
</tbody>
</table>

The carboxylic dendrimer H₂O-COOH only displays a single T₉₁ corresponding to the transition in the non-ionic amorphous phase. However it is important to highlight that all the ionic counterparts displayed two separate T₉ (T₉₁ and T₉₂). The presence of a second T₉₂ implies the presence of a distinct phase separated ionic domain [36] which must be of restricted mobility large enough to exhibit its own T₉ [36, 37]. Our results are also consistent with Register et al. [38, 39] who reported the multiple glass transitions in semi-crystalline ethylene/methacrylic acid ionomers (Figure 3.16) reinforced by metal soaps (Magnesium acetate for example).
In another study, Zhu et al. [40] studied the physical hindrance between soft and hard segments of shape memory polyurethane (SMPU) ionomers. The increase of the degree of neutralisation of those ionomers induced an increase of the $T_g$ of the hard segments. Boas et al. [41, 42] demonstrated that the increase/decrease of pH, presence of hydrogen bonding was having an effect on the conformational changes of a PAMAM dendrimer. He demonstrated that a PAMAM dendrimer terminated with protonated amine at pH>9 was presenting a high degree of back-folding (Figure 3.17) due to the repulsion in between the inner and outer functionalities [41]. The back-folding of the chains or clustering [43] was found to be responsible for an increase of the glass transition temperature of the PAMAM dendrimer.

**Figure 3.16: Morphological changes that EMAA ionomers undergo upon heating [39]**

**Figure 3.17: Difference of morphology of a dendrimer (left) and a dendrimer subjected to back-folding (right) [41]**
Chapter Three – Sodium based ionic dendrimer

In light of the published literature, it is suggested that the increase in \( T_{g2} \) observed in our work upon neutralisation of the carboxylic moieties could be explained by the back-folding of the chains and/or the ionic clusters. The gradual increase in \( T_g \) with neutralisation also suggests that the ionic domains are relatively uniformly dispersed through the amorphous non-ionic domains as reported by Otocka et al. [44].

3.3.2.5. Size evolution study

The morphology and size of the carboxylic dendrimer \( H_{2n-}-COOH \) and its corresponding sodium ionomers were investigated. The aim of this study was to determine if it was possible to correlate the size and shape of the produced dendrimers with the degree of neutralisation. Two techniques were used: Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM). The former method allowed to study the changes in sizes of the various samples in their dissolved state (aqueous environment), whereas the latter method allowed us to study the morphology of the dendrimers in their dry solid state after evaporation of the water solvent.

3.3.2.5.1. Size evaluation by DLS

DLS samples were prepared in aqueous solution at a concentration of 0.5mg/mL. The samples were first sonicated for 15 min and filtered using a 0.2\( \mu \)m filter prior to measurement. The evolution of the hydrodynamic radius as a function of the neutralisation is displayed in Figure 3.18, the results are tabulated in Table 3.6.
Figure 3.17: DLS size distribution of $\text{H}_2\text{O-COOH}$ (a), $\text{H}_2\text{O-}0.25\text{Na}$ (b), $\text{H}_2\text{O-}0.50\text{Na}$ (c), $\text{H}_2\text{O-}0.75\text{Na}$ (d) and $\text{H}_2\text{O-}\text{Na}$ (e)

Table 3.6: Hydrodynamic diameters (nm) of $\text{H}_2\text{O-COOH}$ and ionomers

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O-COOH}$</th>
<th>$\text{H}_2\text{O-}0.25\text{Na}$</th>
<th>$\text{H}_2\text{O-}0.50\text{Na}$</th>
<th>$\text{H}_2\text{O-}0.75\text{Na}$</th>
<th>$\text{H}_2\text{O-}\text{Na}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (nm)</td>
<td>122.4</td>
<td>233.8</td>
<td>342.0</td>
<td>458.7</td>
<td>518.4</td>
</tr>
</tbody>
</table>

The hydrodynamic diameters of all samples were observed to increase with the increase of the degree of neutralisation.
3.3.2.5.2. Morphology evaluation by SEM

The morphology of $\text{H}_2\text{O}-\text{COOH}$ and its corresponding sodium ionomers was examined by Scanning Electron Microscopy (SEM) after deposition of the samples used for DLS onto a silicon wafer and drying (Figure 3.19 and 3.20).

![Figure 3.18: SEM images of $\text{H}_2\text{O}-\text{COOH}$](image)

The presence of 2D tree like structures could be observed on all sample. This type of morphology derives from the 2D self-assembly resulting from the hydrogen bonding of the free OH of carboxylic groups or electrostatic inter-molecular interactions between the $\text{Na}^+$ counter-ion and the carboxylate or a combination of both. This is consistent with other reported works [45, 46].
3.4. Self-healing behaviour

Self-healing tests were carried out by initiating a thin crack using a razor blade on samples deposited on a glass slide. The self-healing potential of these materials was investigated. The films were left at room temperature for up to 24 h under a microscope, hoping for crack closure to occur. None of the sample was found to be effective at self-healing. Attempts were also made at initiating self-healing by thermal stimuli, dynamically (by bringing the sample to 100 degrees using a 10°C/min ramp) or isothermally (30 min at 100°C). Unfortunately none of the sample was found to be display self-healing behaviour. Figure 3.21 illustrates the H$_2$O, H$_2$O-COOH and H$_2$O-COO – 0.50 Na samples containing a micro-crack and after thermal treatment.

![Figure 3.20: H$_2$O, H$_2$O-COOH and H$_2$O-COO – 0.50 Na samples (top to bottom, respectively) just after crack opening (left) and after heat treatment (30 min at 100°C) (right)](image)
In this work, the self-healing ability of the sodium based ionic dendrimers was anticipated. The self-healing behaviour of a sodium based ionic polymer such as EMAA has been previously reported by Varley et al. [47] and Binder et al. [48]. The self-healing mechanism were attributed to ion hopping between the counter-ion Na\(^+\) and the carboxyl groups present in the backbone of the polymer. In our study, the sodium based ionic dendrimers were found to exhibit some degree of back-folding (Refer to section 3.2.4). This mobility of the chains was found to be reduced with the increasing amount of neutralisation, coinciding with an increase in T\(_g\). It can be hypothesised that the reduction of the chain mobility coupled with back-folding of the dendrimer chains inhibited the ion hopping responsible for the self-healing ability.

### 3.5. Conclusions

This work has demonstrated that the neutralisation of a carboxylic acid terminated dendrimer H\(_2\)O-COOH can be controlled using sodium hydroxide to yield a carboxylate groups linked to a mono-valent sodium counter-ion. A range of spectroscopic characterisation techniques such as FTIR, NMR, and XPS confirmed the formation of the sodium based ionic dendrimers. The DSC thermal properties of these materials revealed the presence of both amorphous and ionic domains. The ionic domain were found to be large enough to display their own glass transition temperature. In the bulk, these sodium based ionic dendrimers displayed 2D tree like structures resulting from the hydrogen bonding of the free OH of carboxylic groups and/or electrostatic inter-molecular interactions between the Na\(^+\) counter-ion and the carboxylate as shown by SEM analysis images. These electrostatic interactions were found to be at the origin of a reduction of the chain mobility coupled with some back-folding of the dendrimer, inhibiting ion hopping. The lack of self-healing ability displayed by the sodium based ionic dendrimers was attributed to the hindering of the ion hopping process.
Chapter Three – Sodium based ionic dendrimer

3.6. References

Chapter Three – Sodium based ionic dendrimer


Chapter Four – Zinc-based metallosupramolecular dendrimer
4.1. Introduction

In this chapter, the neutralisation of the carboxylic acid terminated dendrimer (H₂₀-COOH) to yield a range of zinc-based metallosupramolecular dendrimers will be presented. Both the nature of the carboxylate interactions with the divalent zinc (Zn²⁺) counter-ions and the nature of inter and intra-molecular interactions generated from the various states of coordination of the Zn²⁺ will be discussed. The thermal analysis trends (DSC) will be to some extent correlated to the nature of these interactions. Finally, the self-healing capabilities will be assessed on the neat ionic dendrimers as well as in a blend with poly(lactic acid) thermoplastic (PLA).
4.2. Zinc neutralisation of H$_2$O-COOH

The properties of the carboxylate terminated metallosupramolecular dendrimers based on Zn$^{2+}$ counter-ion will be described.

4.2.1. Neutralisation scheme

As previously studied in Chapter Three, four levels of neutralisation of H$_2$O-COOH using zinc hydroxide Zn(OH)$_2$ were achieved as per Scheme 4.1.

![Scheme 2.3.: Neutralisation scheme with Zinc Hydroxyde to yield 7, 8, 9 and 10. An idealised metallosupramolecular dendrimer sharing a zinc ion is shown on the right hand side.](image)

However, because Zn(OH)$_2$ is not soluble in water, the neutralisation was carried out via a solid-liquid diffusion process similar to the flotation method [1-3] used in industry to separate zinc and its oxides from minerals using fatty acids in solution [4]. Stoichiometric amounts of freshly prepared solid Zn(OH)$_2$ were added to a beaker containing an aqueous solution of H$_2$O-COOH. The amount of Zn(OH)$_2$ varied so that 4, 8, 12 and 16 of the protons of the terminal carboxyl groups could be exchanged with a bivalent counter-ion Zn$^{2+}$. All neutralisations were achieved following the same protocol only using different quantities of Zn(OH)$_2$. The resulting materials are referred to here as H$_2$O-COO – 0.25 Zn (n=4), H$_2$O-COO – 0.50 Zn (n=8), H$_2$O-COO – 0.75 Zn (n=12) and H$_2$O-COO – Zn (n=16).
An example of protocol used for the exchange of 4 of the proton of H$_2$O-COOH to yield H$_2$O-COO-0.25Zn is as follow: 0.5g (0.15 mmol) of H$_2$O-COOH was dissolved in 25 mL Milli-Q water for 30 min. After total dissolution of the dendrimer, 29.5 mg (0.30 mmol) of freshly prepared Zn(OH)$_2$ powder was added to the solution and left under high agitation (1300 rpm) till complete disappearance of the Zn(OH)$_2$. In solution the product forms a thick paste which can be isolated after evaporation of the water (Figure 4.1).

![Image of zinc-based metallosupramolecular dendrimer sample](image)

**Figure 4.1: Example of a zinc-based metallosupramolecular dendrimer sample (H$_2$O-COO-0.75Zn shown here)**

In solution the paste already displayed strong intra-molecular attraction. Indeed, after ultrasonication of the solution for a minute, the paste was found to break down into a suspension of small pasty globules; however shortly after the globules were observed to re-aggregate very rapidly.

### 4.2.2. XPS measurement

The low-resolution wide-scan (survey) spectrum of the neutralised samples showed the appearance of several peaks around 1000 eV characteristic of zinc ions in the samples [5].
4.2.2.1. High resolution C1s

Similarly to what has been seen in Chapter Three section 3.3.2.3, it can be seen that a sub peak at 288.0 eV corresponding to carboxylate groups \(^{-}\text{O-C}=\text{O}\) [6] appeared and evolved as a function of the degree of neutralisation (Figures 4.2 and 4.3). The C1s spectra of \(\text{H}_2\text{O-COO} – 0.75\text{Zn}\) and \(\text{H}_2\text{O-COO} – \text{Zn}\) are displayed in Appendix E.

![Figure 4.2: C1s XPS of H2O-COO – 0.25Zn](image)
The C1s spectra were curve fitted to calculate the relative concentration of carbon related functional groups present in the various neutralised samples (Table 4.1).

Table 4.1: Relative carbon related functional group percentages measured in the various materials after C1s peaks deconvolution

<table>
<thead>
<tr>
<th></th>
<th>285 eV C-C and C-H</th>
<th>286.3 eV C-O-C (ether)</th>
<th>288 eV O-C=O</th>
<th>289 eV O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}_2\text{-COOH}$</td>
<td>41.7%</td>
<td>37.2%</td>
<td>X</td>
<td>21.1%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2\text{-COO} - 0.25\text{Zn}$</td>
<td>42.8%</td>
<td>36.9%</td>
<td>1.2%</td>
<td>19.2%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2\text{-COO} - 0.50\text{Zn}$</td>
<td>41.9%</td>
<td>37.7%</td>
<td>2.3%</td>
<td>18.1%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2\text{-COO} - 0.75\text{Zn}$</td>
<td>42.4%</td>
<td>36.7%</td>
<td>3.2%</td>
<td>17.7%</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2\text{-COO} - \text{Zn}$</td>
<td>41.1%</td>
<td>37.1%</td>
<td>4.9%</td>
<td>16.9%</td>
</tr>
</tbody>
</table>
Similarly to what has been seen in the previous Chapter, an increase of carboxylate groups’ concentration co-occurring with a decrease of carboxylic/ester groups concentration was measured. This result correlates well with the FTIR results which will be presented below in section 4.2.4.

4.2.2.2. High resolution Zn2p

Because the Zn$^{2+}$ displayed various forms of coordination, a number of Zn2p high resolution scans (Figure 4.4) were gathered on the various neutralised samples to determine if the changes electronic environment of the zinc ions could be detected upon neutralisation.

![Zn2p spectra](image)

Figure 4.4 shows the Zn2p spectra of the H$_{2}O$-COO – 0.50Zn sample where 2 peaks are visible at 1044.65 eV and at 1021.45 eV corresponding to the two split spin-orbit components [7] of Zinc ions. The first peak at 1044.65 eV is related to Zn2p$_{1/2}$ whilst the second one at 1021.45 eV relates to Zn2p$_{3/2}$ [8]. The measured difference of energy between those 2 peaks of 23.20
eV is consistent with the literature [9]. Unfortunately, no information could be used to further improve our understanding of the changes in coordination as all spectra were similar in intensity and position. It has been reported that high-resolution Zn2p spectra is not always sufficient to determine the chemical state of zinc ion [10].

4.2.3. In-situ NMR measurement

In-situ NMR diffusion was employed to monitor the changes in chemical shifts of the carboxylic acid terminated dendrimer H20-COOH upon neutralisation. H20-COOH was dissolved into D2O (5mg/mL) and introduced into a NMR tube. Zn(OH)2 was introduced into the NMR tube (1 to 4 Zn(OH)2 to dendrimer ratio) in order to neutralise half of the carboxylic acid terminal groups. As no agitation was possible inside the NMR tube, a slow liquid-solid diffusion of the Zn(OH)2 in solution was observed over the course of 7 days. Similarly to what has been observed in the previous Chapter Three section 3.2.3, the effect of neutralisation was visible in the 2.35-2.50 ppm region where the methylene CH2 protons (positions 12 and 13) close to the carboxylic groups can be detected. Figure 4.5 displays the evolution of the peaks between 2.40 and 2.70 ppm as a function of the time.

![Figure 4.5: Evolution of the methylene peaks (position 12 and 13) resulting from the diffusion of Zn(OH)2 in a D2O/H20-COOH solution as a function of time.](image)
The broad peak between 2.56 and 2.64 ppm was found to split-up into two separate peaks with the ongoing diffusion. The changes in the electronic environment of the methylene groups (position 13) next to the carboxylic induced a shifting upfield with the diffusion (Figure 4.6). On the other hand, the methylene groups (position 12), attached to the backbone of the dendrimer were not found to display any significant shift after up to 192h of diffusion.

![Figure 4.6: Evolution of the upfield shift of the methylene moieties in position 13 over time](image)

The diffusion of Zn(OH)$_2$ resulting in the neutralisation of the terminal carboxylic groups displayed two stages. In the first stage (0<time< 38h), the peak associated with the methylene was found to shift rapidly from 0 to 0.70 ppm. During the second stage (38h<time<192h) the shift evolved more moderately from 0.70 ppm to 0.95 ppm. Obviously, the specific change of diffusion rate in a NMR tube is limited but on the other hand it is very useful in capturing the ionic exchange between the Zn$^{2+}$ cations and carboxylic groups of H$_2$O-COOH.

In order to confirm the upfield shift observed in the $^1$H NMR spectra, 2D NMR experiments were carried out onto the sample after 192h. Of particular interest is the carbonyl region between 150 and 190 ppm to look at the differences before and after diffusion of Zn(OH)$_2$. 

105
Figure 4.7 presents the HSQC spectra of $\text{H}_2\text{O}-\text{COOH}$ and $\text{H}_2\text{O}-\text{COO} - 0.50 \text{ Zn}$ in the carbonyl region (between 190 and 150 ppm).

![Graph showing HSQC spectra of $\text{H}_2\text{O}-\text{COOH}$ and $\text{H}_2\text{O}-\text{COO} - 0.50 \text{ Zn}$ in D$_2$O after 192h of diffusion]

**Figure 4.7:** HMBC spectra of $\text{H}_2\text{O}-\text{COOH}$ and $\text{H}_2\text{O}-\text{COO} - 0.50 \text{ Zn}$ in D$_2$O after 192h of diffusion

The evolution of the carbonyl peak of $\text{H}_2\text{O}-\text{COOH}$ through the diffusion process in D$_2$O can be clearly identified in the figure above. As for $^1\text{H}$ NMR, the carbonyl peak is splitting into two peaks at 175 ppm and at 181 ppm. This is due to the association of Zn$^{2+}$ with carboxylate groups of $\text{H}_2\text{O}-\text{COOH}$. The new peak at 181 ppm has been confirmed as a carbonyl peak with a DEPT experiment (Appendix F) as it appears to be a quaternary carbon. These NMR experiments can confirm the success of the solid/liquid diffusion process in water.

### 4.2.4. FTIR characterisation

The FTIR spectra of the on the various zinc-based metallosupramolecular networks formed after neutralisation are shown in Figure 4.8. The spectra have been resumed to the carbonyl absorbing region between 1800 cm$^{-1}$ and 1500 cm$^{-1}$. 
The FTIR spectrum shows that the band characteristic to carboxylate group at 1580 cm$^{-1}$ is increasing in intensity with increasing degree of neutralisation whilst the carboxylic band at 1735 cm$^{-1}$ decreases (data normalised at 1040 cm$^{-1}$ corresponding to the stretching vibration of the ether C-O-C bond). In comparison to the sodium based ionic dendrimers where a sharp band representative of the carboxylate groups absorbed at 1535 cm$^{-1}$ [11], a broad and less intense band appeared between 1500 cm$^{-1}$ and 1675 cm$^{-1}$ [12] in Figure 4.6. The broadening, arising from the association between zinc ion and carboxylate groups has already been reported [13-18] and has been attributed to the coordination state of the cation Zn$^{2+}$ with several carboxylate groups, namely Carboxylate/Zn$^{2+}$ (T) and Carboxylate/Zn$^{2+}$ (H).

Kim et al. [19] proposed a molecular model based on a carboxylated Nitrile Butadiene Rubber (NBR) compounds ionically cross-linked with zinc ions. Figure 4.9 presents a schematic representation adapted from Kim et al. [19] showing the potential molecular arrangement.
surrounding two $\text{Zn}^{2+}$ ions in either tetra (T) or hexa (H) state of coordination with the carboxylate groups of the H$_2\text{O}$-COOH dendrimer.

Figure 4.9: Potential zinc coordination molecular arrangements in the neutralised H$_2\text{O}$-COOH dendrimer adapted from [19]

In order to understand the changes in the coordination state of the zinc cations upon neutralisation with Zn(OH)$_2$, the area of the bands corresponding to the carboxylate/Zn$^{2+}$ (H) and Carboxylate/Zn$^{2+}$ (T) associations were quantified using deconvolution of the carbonyl absorption band between 1675 cm$^{-1}$ and 1500 cm$^{-1}$. Figure 4.10 shows an example of a deconvoluted spectrum for the H$_2\text{O}$-COO - 0.75Zn sample. Other neutralisation figures can be found in Appendix G.
Figure 4.10: Example of deconvolution in the carboxylate region (H$_{20}$-COO - 0.75Zn is presented here)

The ratios between the absorption bands’ areas at 1615 cm$^{-1}$ and 1571 cm$^{-1}$ were calculated [20, 21] and the quantitative analysis results showing the relative percentage association in the samples as a function of the neutralisation are displayed in Table 4.2.

Table 4.2: Quantitative analysis of the tetra and hexa ratios present in the various materials from peak deconvolution.

<table>
<thead>
<tr>
<th>Association</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_{20}$-COO - 0.25Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (T)</td>
<td>1608</td>
<td>72.9</td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (H)</td>
<td>1566</td>
<td>27.1</td>
</tr>
<tr>
<td>H$_{20}$-COO - 0.50Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (T)</td>
<td>1619</td>
<td>57.3</td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (H)</td>
<td>1570</td>
<td>42.7</td>
</tr>
<tr>
<td>H$_{20}$-COO - 0.75Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (T)</td>
<td>1615</td>
<td>49.8</td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (H)</td>
<td>1571</td>
<td>50.2</td>
</tr>
<tr>
<td>H$_{20}$-COO - Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (T)</td>
<td>1618</td>
<td>45.8</td>
</tr>
<tr>
<td>Carboxylate/Zn$^{2+}$ (H)</td>
<td>1570</td>
<td>54.2</td>
</tr>
</tbody>
</table>
The band wavenumber measured for each type of association was found to be relatively unchanged with the increase of the degree of neutralisation and were conformed to the literature examples [20, 21]. Looking closely at the trends it can be observed that the relative percentage of tetra-coordination decreases with increasing degree of neutralisation (from 73% to 46%) whilst the relative percentage of hexa-coordination increases from 27% to 54%. Our results are consistent with Coleman [20] and Gao [22] who also measured an increase of hexa-coordinated zinc present in ethylene methacrylic acid copolymer (EMAA) ionomer systems as a function of the zinc neutralisation of the carboxylic acid groups.

### 4.2.5. DSC measurement

The changes in thermal transitions after neutralisation with Zn(OH)$_2$ were investigated. Table 4.3 below shows the glass transitions of the various zinc-based metallosupramolecular dendrimers.

**Table 4.3: Glass transition temperatures for H$_2$O-COOH and its metallosupramolecular dendrimers with zinc counter-ions.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_{g1}$</th>
<th>$T_{g2}$</th>
<th>$T_{g3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O-COOH</td>
<td>-16.62</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>H$_2$O-COO – 0.25Zn</td>
<td>-15.19</td>
<td>19.79</td>
<td>47.45</td>
</tr>
<tr>
<td>H$_2$O-COO – 0.50Zn</td>
<td>-12.52</td>
<td>18.22</td>
<td>42.06</td>
</tr>
<tr>
<td>H$_2$O-COO – 0.75Zn</td>
<td>-8.65</td>
<td>17.67</td>
<td>36.66</td>
</tr>
<tr>
<td>H$_2$O-COO – Zn</td>
<td>-11.1</td>
<td>16.98</td>
<td>31.47</td>
</tr>
</tbody>
</table>

The DSC experiments reveal the presence of three distinct glass transition temperatures in the zinc-based metallosupramolecular dendrimers ($T_{g1}$, $T_{g2}$ and $T_{g3}$) in contrast to the starting carboxylic acid dendrimer H$_2$O-COOH which only displayed a single glass transition ($T_{g1}$). It has already been mentioned in the previous Chapter Three that $T_{g1}$ relates to the non-ionic
domains (i.e. amorphous phase). Here \( T_{g1} \) was found to be unchanged between the starting material H\(_{20}\)-COOH and the H\(_{20}\)-COO-0.25Zn. At higher degrees of neutralisation however \( T_{g1} \) increased from \( \sim -16^\circ\text{C} \) to \( \sim -11^\circ\text{C} \). This change can be explained from the presence of a small amounts of ionic clusters in the amorphous phase which act as multifunctional electrostatic cross-linkers as previously reported by Eisenberg et al. [23]. Castagna et al. [24, 25] also demonstrated that small fractions of kinetically or sterically trapped zinc ionic species in a sulfonated polystyrene amorphous phase led to an increase in \( T_{g} \).

In regards to \( T_{g2} \) and \( T_{g3} \) which only appear in the ionomers, it is suggested that they correspond to the various ionic domains in the sample in a similar way to what has been previously discussed in the previous Chapter with sodium counter-ions (H\(_{20}\)-COO – Na series). This was verified using a Modulated DSC mode by looking at the effect of thermal cycling using a heating, cooling and re-heating (Chapter Two section 2.3.4). Figure 4.11 shows the first and second MDSC heat curves for the H\(_{20}\)-COO – 0.25Zn sample.

![Figure 4.11: MDSC Reversible Heat Flow curve for the first and second Heat cycle of H\(_{20}\)-COO – 0.25Zn](image)
Chapter Four – Zinc-based metallosupramolecular dendrimer

The non-ionic domain is unaffected by the heat-cool-heat cycle and remains stable (~-16°C). One the other hand, the ionic domains relative to both $T_{g2}$ and $T_{g3}$ disappeared after the second heat cycle. The same behaviour was observed with all zinc-based metallosupramolecular dendrimer samples but only the $H_2O\text{-COO} - 0.25Zn$ sample is shown here for brevity. The disappearance of glass transition of the ionic domains can be explained by the melting of ionic species which has been previously referred to in the particular case of ionomers as thermal hysteresis [26]. This phenomenon is attributed to order – disorder transition in the ionic clusters and it is described below in Figure 4.12.

It can be noted in Table 4.3 that the glass transitions of the ionic domains (i.e. $T_{g2}$ and $T_{g3}$) are much higher than $T_{g1}$ of the amorphous phase. This can be explained from the presence of localised ionic clusters acting as electrostatic cross-linkers, significantly reducing the steric hindrance of the chains [23].

It can also be seen that $T_{g2}$ decreased slightly from 19.8°C to 17°C upon neutralisation. On the other hand, the decrease displayed by $T_{g3}$ was much more pronounced (47.5°C to 31.5°C).

The appearance of several $Tg$'s in a zinc based EMAA system has been for instance observed by both Tanado et al. [27] and Tachino et al. [28] and has been explained from the differences
of relaxation mechanism in the ionic regions of restricted mobility [23, 29]. In line with what has been proposed by Tanado et al, we can suggest that changes in relaxation mechanism in the ionic regions manifested by $T_{g2}$ and $T_{g3}$ might correspond to the various states of coordination of the zinc in the ionic domains.

Further to that, in the particular case of a second generation poly(ethylene imine) dendrimer, Bazzicalupi et al. [30] showed that mono-, bi-, and tri-nuclear complexes (Zn$^{2+}$ and Cu$^{2+}$), as well as 3:2 metal/ligand species can be formed. It was demonstrated that depending on the nature of the metal cation and the metal/ligand molar ratio, metal ion binding can take place either in the inner core region or on the surface of the dendrimer molecules leading to intra or inter-molecular types of interactions.

This type of phenomena was also reported by Ottaviani et al. who showed the presence of external and internal ionic regions due to the complexation of PAMAM dendrimer bivalent cations such as Mn$^{2+}$ or Cu$^{2+}$ [28-30]. In their paper, it was demonstrated that ligand complexes between terminal carboxylic groups and internal core nitrogens of the dendrimers can be formed.

In relation to our work, it is then clear from the literature that there must exist differences in inter or intra-molecular ionic interactions resulting from the two coordination states of the Zn$^{2+}$ cations. A schematic representation of the possible coordinations arrangements in this work, adapted from the work in [30] is presented in Figure 4.13. The various types of inter and intra-molecular arrangements are highlighted in regions A, B, C, D and E in the Figure 4.13 and will be discussed more precisely in the following section.
Figure 4.13: Schematic representation of the coordination environments suggested for poly(ethylene imine)/metal ions complexes (top) [30] and the possible coordinations arrangements (A, B, C, D and E) in this work (bottom).
Looking at the tetra coordinated zinc ions, it is possible to envisage an intra-molecular type of association where the zinc is shared between two terminal carboxylate groups of the same dendrimer (Figure 4.13, area B). This is not impossible considering that the branches of the dendrimer were found be flexible enough to be able to achieve back-folding because of the ionic associations between the carboxylate moieties and the sodium counter-ion as described in the previous Chapter. In contrast to that, there is the inter-molecular type of association where a zinc is shared between two terminal carboxylate groups of two separate dendrimers (Figure 4.13, area A). The different types of configuration for the tetra-coordinated arrangement are presented in Figure 4.14.

Looking specifically at the hexa coordinated zinc ions, having a zinc ion shared between 3 dendrimers is the most logical configuration (Figure 4.13, area C). However it could be possible to observe a mixture between intra/inter molecular interactions (Figure 4.13, area D) where the counter-ion could be shared between 2 carboxylate of a same dendrimer and a carboxylate from another dendrimer. Finally, the last option would be a same dendrimer being able to share a Zn$^{2+}$ cation in between three carboxylate branches (Figure 4.13, area E). The different arrangements for the hexa-coordinated zinc ions are presented in Figure 4.15.
Changes in the modes of inter/intra molecular interactions would without a doubt also affect the physical hindrance of the ionic domains and thus the glass transition of the systems. Here the decrease in $T_g$ observed as a function of the neutralisation may be linked to both the changes in coordination and nature of the inter/intra-molecular interactions. It is however still unclear at this stage how these effects resulted in a decrease in the $T_g$'s of the ionic domains as the effects cannot be isolated and quantified individually in order to establish a sound correlation.
4.3. Assessment of the self-healing behaviour

4.3.1. Self-healing in bulk and film

Before carrying out the self-healing tests, all samples of zinc-based metallosupramolecular dendrimers were dried at 60 °C under vacuum overnight to eliminate all possible traces of water (reducing the possible effect of swelling). Self-healing tests were achieved by cutting the materials into two halves using a sharp razor (Figure 4.16). The two halves were then put back together applying a slight manual pressure in order to initiate the healing process. This was achieved at room temperature without the use of external stimuli.
Figure 4.16: Self-healing of zinc-based metallosupramolecular dendrimer $\text{H}_2\text{O-COO}^{-0.75\text{Zn}}$

We found that all zinc-based metallosupramolecular dendrimers exhibited self-healing behaviour and the two halves were able to “stick” together. A visual example of the self-healing test in the case of $\text{H}_2\text{O-COO}^{-0.75\text{Zn}}$ is displayed in Figure 4.16. It was observed that the time of contact needed to join both part varied according to the degree of neutralisation (Table 4.4).

### Table 4.4: Time needed for the two halves to be able to “stick” together and be stretched to twice their original length

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O-COO}^{-0.25\text{Zn}}$</th>
<th>$\text{H}_2\text{O-COO}^{-0.50\text{Zn}}$</th>
<th>$\text{H}_2\text{O-COO}^{-0.75\text{Zn}}$</th>
<th>$\text{H}_2\text{O-COO}^{-\text{Zn}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>10</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

The time needed to full recovery was found to be the fastest in the particular case of the $\text{H}_2\text{O-COO}^{-0.75\text{Zn}}$ sample (2 min). The $\text{H}_2\text{O-COO}^{-0.25\text{Zn}}$ sample recovered the slowest, taking approximately 10 min. It is suggested that the changes in healing efficiency are related to the type of coordination (tetra/hexa) and nature of the interactions (inter/intra) present into the sample as reported by Burnworth et al. [31-33]. He demonstrated that a poly(ethylene-co-butylene) polymer cross-linked via metal-ligand coordination complexes (zinc or aluminium were used as a metal) and exposed to UV light were able to exhibit fast self-healing properties depending on the coordination.
In our work, when the amount of zinc present in the sample is at its lowest ($H_{2O}$-COO$–0.25Zn$) the healing process is the slowest possibly because the ion hopping is not facilitated due to the possible lack of surface charges around the periphery of the dendrimer. However, at higher levels of zinc, the healing seems to be quite efficient and it is relatively unchanged at a level of neutralisation exceeding 50%.

In order to better understand the mechanism involved during the self-healing process of the zinc-based metallosupramolecular dendrimers, a FTIR dynamic study during the self-healing process of the $H_{2O}$-COO$–0.50Zn$ sample was carried out on a thin film undergoing repair. This study allowed to spectroscopically track the changes in the states of coordination taken by the zinc ions during the self-healing at the crack interface. In order to produce a thin film, an aqueous solution of $H_{2O}$-COO$–0.50Zn$ was casted onto a Mg alloy substrate (AZ91) and dried overnight in a vacuum oven at 50 degrees. A crack of approximately 10 microns in width by longitudinal cut using a sharp razor across the film. ATR-FTIR spectra were acquired on a Bruker Lumos in video wizard mode, using a 5 * 5 μm aperture, a resolution of 4 cm$^{-1}$ and spectra averaged from 64 scans. 5 separate measurements were achieved with a 1 min interval until full healing of $H_{2O}$-COO$–0.50Zn$ sample. As per section 4.2.4., the FTIR study was focused on the carboxylate region between 1675 cm$^{-1}$ and 1500 cm$^{-1}$ (all spectra were normalised at 1040 cm$^{-1}$ corresponding to the stretching vibration of the C-O-C bond). The optical images of the thin film as well as the corresponding infra-red spectra at various locations of the film are shown in Table below. The red hashed dot in the images represents the 5 * 5 μm spot aperture where the spectra were taken.
Table 4.5: FTIR dynamic study of self-healing process in H$_2$O-COO – 0.50Zn

<table>
<thead>
<tr>
<th>Time</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before the crack</td>
<td>![Before the crack image]</td>
</tr>
<tr>
<td>t = 1 min</td>
<td>![t = 1 min image]</td>
</tr>
</tbody>
</table>
Firstly, it can be pointed out that before crack opening and after complete self-healing (e.g. equilibrium mode), only the two bands relating to the association of the carboxylate with either a tetra-coordinated (T) or hexa-coordinated (H) zinc ions were visible at 1615 cm$^{-1}$ and at 1571 cm$^{-1}$, respectively as previously discussed in section 4.2.4. During the self-healing process (for 1 min < t < 4 min), a third band appeared at 1537 cm$^{-1}$ and this particular stretching band, previously reported by Coleman et al. [20], corresponds to the association of the carboxylate group with tetra-coordinated zinc ions coupled with hydrogen bonding.
between the carboxylate groups and carboxylic groups (Carboxylate/Zn\(^{2+}\)/-COOH) as shown in Figure 4.17.

![Schematic representation of the association of the carboxylate group with tetra-coordinated Zn\(^{2+}\) ions coupled with hydrogen bonding between the carboxylate groups and carboxylic groups absorbing at 1537 cm\(^{-1}\) (top) [20] and a possible arrangement in this work (bottom)](image)

**Figure 4.17:** Schematic representation of the association of the carboxylate group with tetra-coordinated Zn\(^{2+}\) ions coupled with hydrogen bonding between the carboxylate groups and carboxylic groups absorbing at 1537 cm\(^{-1}\) (top) [20] and a possible arrangement in this work (bottom)

Looking specifically at this band (plotted in green in the spectra), it can be seen that its intensity gradually decreased upon the crack closure co-occurring with an increase of the hexa type of coordination. It can also be seen that this band is only detectable at the crack interface and that further away from the interface only the bands corresponding to the association of the carboxylate group with either tetra or hexa-coordinated zinc ions are visible (see t=1 min). After complete healing and equilibrium (t>4 min), it is important to note that this band disappeared altogether. This simple experiment demonstrate that there exists a self-healing mechanism process in the zinc-based metallosupramolecular dendrimers which relies on a
transitional mode of association witnessed by the particular band at 1537 cm\(^{-1}\). The dynamic changes and molecular reorganisation of the molecules at the interface, due to hopping of the zinc ions, can be detected through this specific association / hydrogen bonding band. During this transitional phase of self-repair, the zinc ions must overcome the electrostatic forces with the carboxylate groups because of the formation of hydrogen bonding between the carboxylic and the carboxylate groups, allowing for the zinc ions to transit between molecules and thus resulting in localised repair.

4.3.2. Self-healing in a blend with PLA

Because the zinc-based metallosupramolecular dendrimers were found to display a good self-healing, the next stage of this work involved the blending of an ionic dendrimer (here we chose the H\(_{2}O\)-COO – 0.75Zn) as it possessed the most promising self-healing properties, with polylactide acid, a thermoplastic aliphatic polyester. PLA is a thermoplastic of engineering relevance and has been used in many applications including packaging and biomedical for example.

PLA and H\(_{2}O\)-COO – 0.75Zn sample were mixed (4 wt% of the H\(_{2}O\)-COO – 0.75Zn) in the presence of THF solvent overnight at 60 degrees. The obtained clear solution was subsequently casted on glass slides to produce a thin film. The mixture was analysed by FTIR to detect the presence of the zinc-based metallosupramolecular dendrimer into the PLA matrix (Figure 4.18).
The characteristic bands of both the $\text{H}_2\text{O-COO} - 0.75\text{Zn}$ and PLA were visible in the blend spectra. For instance the carbonyl band at 1700 cm$^{-1}$ of the $\text{H}_2\text{O-COO} - 0.75\text{Zn}$ and at 1750 cm$^{-1}$ of the PLA [34] could be detected. The fingerprint region of the matrix presented mixture of characteristic peaks of the dendrimer (C-H bending at 1400 cm$^{-1}$, C-O stretch of the ester groups at 1180 cm$^{-1}$) and PLA (bending vibrations of CH$_3$ at 1511 and 1434 cm$^{-1}$, C-O-C asymmetrical and symmetrical vibrations at 1200 and 1100 cm$^{-1}$) [35].

Self-healing of the film at room temperature didn’t work and required the use of a dynamic cycle to be observed (room temperature to 100 degrees at 10$^{\circ}\text{C/min}$ and 30 min at 100$^{\circ}\text{C}$). In Figure 4.19, it can be seen that the crack width decreases after the heat treatment to eventually disappear.
This test shows that the self-healing ability of the dendrimer can be translated to a blend with PLA, although it does require some external heat stimuli. It is also suggested that the self-healing process could be improved by increasing the percentage of the ionic dendrimer in the blend.

4.4. Conclusions

In this Chapter, it has been shown that the neutralisation of H$_{20}$-COOH with zinc hydroxide could be controlled and the resulting materials were characterised using FTIR, XPS and NMR. When using a bivalent zinc counter-ion, the physical behaviour of the dendrimer was found to be different (paste like) and displayed notable physical interaction (strong attraction like). The various ionomers were found to contain zinc counter-ions in various states of coordinations (tetra and hexa coordination) associated with the carboxylate groups as shown by FTIR. The ability for the zinc counter-ions to be associated between a number of carboxylate groups in various ways has been proposed based on previous scientific literature, leading to various possible modes of inter or intra molecular interactions. As a result, the glass
transition temperatures of the zinc-based metallosupramolecular dendrimers were found to be dependent on the degree of neutralisation. The self-healing behaviour of all of these zinc-based metallosupramolecular dendrimers was successful in bulk and in thin films. A time-monitoring FTIR experiment was conducted analysing the dynamic changes in the modes of association between zinc counter-ions and carboxylates groups at the crack interface. During repair, we found that a transitional mode of association between the carboxylate and tetra-coordinated zinc ions coupled with hydrogen bonding between carboxylate and carboxylic groups (at 1537 cm\(^{-1}\)) appeared at the crack interface, but disappeared after repair. It is therefore believed that this particular transitional mode of association and interaction must be responsible for the mechanism of self-healing of the zinc-based metallosupramolecular dendrimers. Blending a zinc-based metallosupramolecular dendrimer with poly(lactic acid) matrix was achieved using a very small amount (i.e. 4wt%) of a self-healing metallosupramolecular dendrimer and the resulting material displayed some self-healing abilities after thermal treatment. This opens the possibility of using these zinc-based metallosupramolecular dendrimers as a self-healing agents in combination with other thermoplastics such as PLA.
4.5. References


Chapter Four – Zinc-based metallosupramolecular dendrimer


Chapter Five – Hydrogen bonded
dendritic supramolecular network
5.1. Introduction

In this chapter, the functionalisation via a based mediated amidation reaction of the carboxylic acid terminated dendrimer (H$_{20}$-COOH) with 1-(2-aminoethyl)-2-imidazolidone (AEIO) to yield a supramolecular dendritic network (H$_{20}$-COO – AEIO) will be described. The successful attachment of AEIO was investigated using FTIR as well as 1D and 2D NMR. Additionally, 2D NMR (NOESY) and 2D FTIR were employed to study the presence of hydrogen bonding interactions in the functionalised material H$_{20}$-COO - AEIO. Finally, the self-healing properties of films casted from this supramolecular network will be analysed and interpreted.
5.2. Synthesis of 1-(2-Aminoethyl)-2-imidazolidone (AEIO)

The synthesis of the urea derivative AEIO (Figure 5.1) was first introduced in 1995 by J.-M. Lehn [1].

![Figure 5.1: Imidazolidone ring](image)

Only very recently, the grafting of 1-(2-aminoethyl)-2-imidazolidone (AEIO) onto various carboxylic moieties has recently been showed to yield supramolecular networks capable of self-healing via hydrogen bonding interactions. This project draws on this concept and looked at grafting 1-(2-aminoethyl)-2-imidazolidone (AEIO) onto the carboxylic acid terminated dendrimer (H₂₀-COOH) in order to develop a novel self-healing material.

5.2.1. Synthesis of AEIO

In order to synthesise 1-(2-aminoethyl)-2-imidazolidone (AEIO), a mixture of diethylenetriamine (DETA) and urea (1 to 1 ratio) was dissolved into water and the solution was heated up to 100 °C to initiate the formation of the imidazolidone ring as depicted in Scheme 5.1 [4].
After extraction in chloroform (5 x 20mL), a translucent and slightly viscous liquid in a yield of 70% was obtained. The structure characterisation of the synthesised product will be described in the following paragraphs.

### 5.2.2. FTIR characterisation

The characterisation of AEIO using FTIR has been published elsewhere [5] and we used this reference to assess the success of the reaction. Figure 5.2 shows the FTIR spectra of the reaction product AEIO.
Of particular interest is the formation of the imidazolidone ring between urea and diethylenetriamine which could be determined in the product. For instance, the absorption band C=O of the imidazolidone ring at 1680 cm\(^{-1}\) [5] was present as well as the broad absorption band in the region between 3000 cm\(^{-1}\) and 3650 cm\(^{-1}\) representative of the N-H stretch. The other characteristic bands of amine can be detected between 1500 and 1450 cm\(^{-1}\) for N-H bend and 1280 cm\(^{-1}\) for the C-N stretch. The C-H stretch of the alkyl moieties could be detected between 2800 and 3000 cm\(^{-1}\). From the FTIR spectra, it can be suggested that the formation of the imidazolidone ring and therefore the synthesis of AEIO was most likely successful.

Figure 5.2: FTIR spectra of AEIO
5.2.3. \(^1\text{H} \) NMR characterisation

It is important to first mention here that in order to compare our NMR spectroscopy data to the only literature available [4], the NMR analysis was first performed in CDCl\(_3\) but subsequent analysis were conducted in D\(_2\)O for which all materials (H\(_2\text{O}-\text{COOH}, \) AEIO and H\(_2\text{O}-\text{COO} \) – AEIO the product of amidation between H\(_2\text{O}-\text{COOH} \) and AEIO) were miscible in. H\(_2\text{O}-\text{COOH} \) and AEIO was not found to be miscible in other common solvents such as acetone, THF, ethyl acetate or DMSO.

The success of the cyclisation reaction was more obvious from the NMR data. The \(^1\text{H} \) NMR spectra of AEIO in CDCl\(_3\) (marked in the spectra as *) shown in Figure 5.3 was found to be consistent with the literature [3].

![Figure 5.3: \(^1\text{H} \) NMR of AEIO in CDCl\(_3\) (*)](image)

The characteristic peak of the primary amine was detected at 1.66 ppm (position 8). It can be noticed that this peak is broad and can be explained by the potential hydrogen bonding...
between the protons and oxygen of the imidazolidone ring or between the primary amine and water as reported in [6]. The two triplets at 2.68 ppm (position 7) and 3.09 ppm (position 6) are representative of the alkyl chain protons. The sharp and intense peak resonating at 3.31 ppm belongs to the protons of the imidazolidone ring at positions 4 and 5. The experimental proton peak integrations ($I_{\text{exp}}$) as well as chemical shifts we obtained on our product of AEIO in CDCl$_3$ are presented in Table 5.1 and these are compared with the theoretical integration ($I_{\text{th}}$).

### Table 5.1: Integration of each proton peaks of AEIO in CDCl$_3$

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Position</th>
<th>$\delta$ (ppm)</th>
<th>multiplicity</th>
<th>$I_{\text{th}}$</th>
<th>$I_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2$</td>
<td>8</td>
<td>1.66</td>
<td>s</td>
<td>2.00</td>
<td>2.05</td>
</tr>
<tr>
<td>$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2$</td>
<td>7</td>
<td>2.68</td>
<td>t ($J = 6.2$ Hz)</td>
<td>2.00</td>
<td>2.05</td>
</tr>
<tr>
<td>$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2$</td>
<td>6</td>
<td>3.09</td>
<td>t ($J = 6.2$ Hz)</td>
<td>2.00</td>
<td>1.98</td>
</tr>
<tr>
<td>$\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}$</td>
<td>4 + 5</td>
<td>3.31</td>
<td>m</td>
<td>4.00</td>
<td>4.07</td>
</tr>
<tr>
<td>$\text{CH}_2-\text{NH}-\text{C}=\text{O}$</td>
<td>3</td>
<td>5.73</td>
<td>s</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

All proton integrations were normalised to the secondary amine of the imidazolidone ring (R-NH-R') integrated at 1 proton. It can be seen that the experimental data well the expected theoretical data.

Analysis was also carried out in D$_2$O in which all reaction products (H$_2$O-COOH, AEIO, H$_2$O-COO-AEIO) were miscible in. As previously explained, AEIO molecules are subject to strong intermolecular hydrogen bonding so NMR characterisation in D$_2$O was expected to be significantly different from the one in CDCl$_3$.

In Figure 5.4, no peak characteristic of amine (proton in position 8) or amide (proton in position 3) could be detected because of the deuterium exchange phenomenon [7]. Protons in position 6 and 7 resonating at 3.14 ppm and 2.72 ppm respectively were found to be slightly shifted after a change in solvent. However, the methylene groups of the imidazolidone ring in position 4 and 5 split into two triplets of protons in position 4 and 5 after a change in solvent. This difference of behaviour between both deuterated solvents could be explained
by hydrogen bonding between D₂O and amide moieties which would cause protons in position 4 and 5 to become more non-equivalent and therefore diastereotopic leading to the dissociation of the peaks [8]. As no literature explained the characterisation of AEIO into D₂O, no exact bond of attachment of those two protons could be visualised.

Figure 5.4: ¹H NMR AEIO in D₂O (*)

5.2.4. ¹³C NMR characterisation

Figure 5.5 shows the ¹³C NMR of AEIO in CDCl₃. The characteristic carbon peak at 164.1 ppm corresponding to the carbonyl C=O of the imidazolidone ring (position 2) was detected. The alkyl carbon peaks from the ring were found to resonate at 38.3 ppm (position 4) and 45.5 ppm (position 5) whilst the alkyl carbon peaks of the amine chain were detected at 40.2 ppm (position 7) and 47.8 ppm (position 6).
The $^{13}$C NMR data was found to correlate well with the literature [5] reported in CDCl$_3$.

The $^{13}$C NMR spectra obtained in D$_2$O (Appendix H) was found to be similar from the one performed in CDCl$_3$. Only slight changes in chemical shifts were observed, which are presented in Table 5.2.

Table 5.2: $^1$H NMR shifts of AEIO in CDCl$_3$ and D$_2$O

<table>
<thead>
<tr>
<th>Position</th>
<th>Functional groups</th>
<th>$\delta$ (ppm) in CDCl$_3$</th>
<th>$\delta$ (ppm) in D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>N-C=O-NH</td>
<td>164.1</td>
<td>165.15</td>
</tr>
<tr>
<td>4</td>
<td>N-CH$_2$-CH$_2$-NH</td>
<td>38.3</td>
<td>38.00</td>
</tr>
<tr>
<td>5</td>
<td>N-CH$_2$-CH$_2$-NH</td>
<td>45.5</td>
<td>45.01</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$N-CH$_2$-CH$_2$-N</td>
<td>47.8</td>
<td>45.08</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$N-CH$_2$-CH$_2$-N</td>
<td>40.2</td>
<td>38.12</td>
</tr>
</tbody>
</table>

In order to identify and confirm the exact position of each proton and carbon peaks of the AEIO in D$_2$O, a series of 2D NMR experiments were performed.
5.2.5. 2D NMR

5.2.5.1. Introduction on 2D NMR

Two-dimensional nuclear magnetic resonance spectroscopy (2D NMR) involves a combination of methods used together in order to elucidate a structure as a support to traditional 1D NMR $^1$H and $^{13}$C experiments. 2D NMR was employed in this work to further elucidate the structure of the AEIO molecule and assess the grafting of AEIO onto H$_2$O-COOH (amidation reaction). Heteronuclear Single-Quantum Correlation (HSQC) is a proton detected 2D experiment which correlations between nuclei of two different types (in this work proton and carbon) which are separated by one bond [9]. In this work, HSQC correlations will be resolved between $^1$H (x frequency axis) and $^{13}$C (y frequency axis) experiments. Heteronuclear Multiple-Bond Correlation (HMBC) was also employed. It is important to note that not all long-range coupling will be observed, therefore HMBC experiments need to be supported by other 2D data for comprehensive structure elucidation [10]. The x and y frequency axes are plotted in the same manner as for a HSQC experiment. In order to elucidate the 3D structure and conformation as well as potential hydrogen bonding, a through-space Nuclear Overhauser Effect Spectroscopy (NOESY) NMR experiment was used. NOESY is usually applied to probe proton-proton interactions through space, up to approximately 5 Å.

5.2.5.2. Analysis

The 2D correlations are summarised in Table 5.3.
Chapter Five – Hydrogen bonded dendritic supramolecular network

Table 5.3: Complete structure assignment of AEIO in D$_2$O for HSQC

<table>
<thead>
<tr>
<th>$^{13}$C $\delta$ (ppm)</th>
<th>$^1$H attached (ppm)</th>
<th>$^1$H multiplicity</th>
<th>Molecule assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>165.15</td>
<td>----</td>
<td>----</td>
<td>C=O (C2)</td>
</tr>
<tr>
<td>45.08</td>
<td>3.14</td>
<td>t</td>
<td>C6</td>
</tr>
<tr>
<td>45.01</td>
<td>3.46</td>
<td>t</td>
<td>C5</td>
</tr>
<tr>
<td>38.12</td>
<td>2.72</td>
<td>t</td>
<td>C7</td>
</tr>
<tr>
<td>38.00</td>
<td>3.35</td>
<td>t</td>
<td>C4</td>
</tr>
</tbody>
</table>

The molecular assignment of each carbon of the AEIO molecule in D$_2$O are similar to the assignment in CDCl$_3$. Figure 5.6 and Figure 5.7 displays respectively the 2D HSQC and 2D HMBC NMR spectra which were used to elucidate the structure.

5.2.5.2.1. HSQC

From the HSQC spectrum (Figure 5.6), no correlations were found with the carbon C=O at 165.15 ppm (not shown here), which was expected as this is a quaternary carbon. However, the proton at 3.46 ppm correlated to the carbon in C5 position, the one at 3.35 ppm with the carbon in C4, then the proton at 3.14 ppm with C6 and finally the last proton at 2.72 ppm was found to correlate with the carbon C7. The protons were therefore assigned to the mentioned carbons accordingly to Table 5.3.
5.2.5.2.2. **HMBC**

In the HMBC (Figure 5.7) spectrum, the proton at 3.46 ppm correlated to the C4 position as well as the carbonyl C=O at 165.15 ppm. The proton at 3.35 ppm correlated to both carbons in the C5 and C6 positions as well as to the C=O which resonates at 165.15 ppm. The proton at 3.14 ppm was found to correlate to all carbons except from carbon in the C6 position. Finally, the proton at 2.72 ppm correlated only to both carbons in the C5 and C6 positions.
In summary, the complete structure elucidation of AEIO in D$_2$O was achieved using 2D NMR. The collective FTIR, 1D and 2D NMR data supported the assumption that the formation of the imidazolidone ring between DETA and urea was successful.

### 5.3. Amidation of H$_2$O-COOH with AEIO

The amidation reaction between H$_2$O-COOH and AEIO to create a supramolecular network based on hydrogen bonding interactions is described in this section.
5.3.1. Synthetic route

The amidation reaction conducted between the carboxylic groups of $\text{H}_2\text{O}^+\text{-COOH}$ and the primary amine of the AEIO molecule is displayed below (Scheme 5.2). The reaction product is referred to as $\text{H}_2\text{O}^+\text{-COO} – \text{AEIO}$ here.

1-Ethyl-3-(3-Dimethylaminopropyl)Carbodiimide hydrochloride (EDC or EDAC) was used as the carbodiimide crosslinker due to its practicality, it is water soluble and so are the other reaction products AEIO and $\text{H}_2\text{O}^+\text{-COOH}$ (Scheme 5.3). EDC is typically used as a carboxyl activating agent for the coupling of primary amines to yield amide bonds for practical bio-conjugation of proteins and peptide [11].
During the reaction the carboxylic acid groups react with EDC and from an active \( O \)-acylisourea intermediate that reacts easily by nucleophilic attack from primary amino groups in the reaction mixture. The primary amine then forms an amide bond with the original carboxyl group, and a soluble iso-urea derivative by-product is released [12-13].

### 5.3.2. NMR characterisation

The NMR characterisation of the amidation product \( \text{H}_{20}\text{COO} - \text{AEIO} \) was challenging because of the symmetry of the molecule and the repetitiveness of the units. In order to facilitate the characterisation and elucidation of the structure, the carbon present in the theoretical structure have been numbered from the core (position C1) outwards (Figure 5.8).

![Figure 5.8: Visual representation of one branch of an ideal \( \text{H}_{20}\text{COO} - \text{AEIO} \) molecule](image)

The NMR characterisation will be based on this representation.
5.3.2.1. $^1$H NMR characterisation

The $^1$H NMR spectrum of H$_{20}$-COO – AEIO is presented in Figure 5.9.

![Figure 5.9: $^1$H NMR of H$_{20}$-COO – AEIO in D$_2$O (*)](image)

The spectrum displays the characteristic peaks of the starting material H$_{20}$-COOH. The methylene peak at 4.25 ppm representing the ester moieties (position 4 and 8), the methylene of the molecule core at 3.53 ppm (position C2 and C3) and the methyl groups of H$_{20}$-COOH at 1.24 ppm (position C7) were detected. The strong and intense peak at 2.52 ppm representative of the methylene groups close to the carboxylic acid group in position C16 (Chapter Three section 2.3.1) was found to disappear. The absence of this peak is an indication that its electronic environment has significantly changed and that the grafting of AEIO onto the carboxylic group next to it (position C17) has most likely occurred. On the other hand the adjacent protons in position C12 were found to resonate at 2.54 ppm which is similar to what can be detected in the starting material H$_{20}$-COOH.
Of interest also is the region between 3.0 and 3.6 ppm which revealed an accumulation of several multiplets corresponding several protons found in the AEIO molecule. For instance the peaks at 3.51 ppm and 3.38 ppm have been attributed to methylene groups in the imidazolidone ring respectively in position C20 and position C21. The additional multiplets at 3.32, 3.27, 3.19 and 3.13 ppm could be attributed to the methylene groups in positions 16, 18 or 19 of H$_2$O-COO – AEIO compound.

5.3.2.2. $^{13}$C NMR characterisation

The $^{13}$C NMR spectra of the H$_2$O-COO - AEIO revealed a number of additional peaks compared to the spectrum of H$_2$O-COOH and AEIO alone (Figure 5.10).

The carbonyl region between 180 and 160 ppm compared to the one measured for H$_2$O-COOH. In addition, the peak at 164.75 ppm, representative of the carbonyl of the imidazolidone ring
(position C22) was also detected. Other peaks characteristic to AEIO molecule are visible in the region between 60 and 30 ppm, for instance at 45.12 ppm and 38.09 ppm which are characteristic of the methylene groups of the imidazolidone ring (C20 and C21 position respectively).

The disappearance of the characteristic peak of the carboxylic group at 172 ppm co-occurring with the appearance of a peak at 160.49 ppm, which has not been attributed to any previous carbons could be representative of the amide bond (position C17) after attachment of the AEIO molecule onto the carboxylic group. This assumption will be further investigated in the 2D NMR section below.

In summary, using $^1$H and $^{13}$C NMR, it was possible to observe in the spectra of H$_2$O-COO - AEIO the presence of characteristic peaks relating to both starting materials H$_2$O-COOH and AEIO. Further to that, the disappearance of some characteristic peaks (found in H$_2$O-COOH) co-occurring with the appearance of unattributed peaks provided a mild indication that the attachment of AEIO was most likely successful. As the exact bond of attachment cannot be determined using 1D NMR alone, further analysis using 2D NMR was carried out.

HSQC and HMBC were used to determine the exact bond of attachment of H$_2$O-COO – AEIO. In order to facilitate the understanding of the NMR data, only certain regions of interest will be displayed.

5.3.2.3. HSQC

Figure 5.11 displays the HSQC spectrum of H$_2$O-COO – AEIO in the $^1$H region between 3.0 ppm and 3.5 ppm and $^{13}$C region between 30 to 60 ppm (y axis, $^{13}$C data) where the peaks of interest were found to resonate.
The characteristic proton peaks of the imidazolidone ring at 3.51 ppm (position C20) and at 3.38 ppm (position 21) are directly correlated to carbons at 45.19 ppm and 38.09 ppm respectively. These correlations are coherent with the AEIO molecule identification described in the previous sections. The four other protons signals could be correlated to their direct carbons in the same region. The correlations are summarised in Table 5.4.

**Figure 5.11: 2D HSQC spectrum of H$_{20}$-COO – AEIO region of interest.**

**Table 5.4: 2D HSQC correlations $^1$H with $^{13}$C signals of H$_{20}$-COO - AEIO.**

<table>
<thead>
<tr>
<th>$^1$H δ (ppm)</th>
<th>$^1$H multiplicity</th>
<th>$^{13}$C δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.51</td>
<td>m</td>
<td>45.19</td>
</tr>
<tr>
<td>3.38</td>
<td>m</td>
<td>38.09</td>
</tr>
<tr>
<td>3.32</td>
<td>t</td>
<td>41.85</td>
</tr>
<tr>
<td>3.27</td>
<td>t</td>
<td>37.69</td>
</tr>
<tr>
<td>3.19</td>
<td>m</td>
<td>36.49</td>
</tr>
<tr>
<td>3.13</td>
<td>m</td>
<td>55.13</td>
</tr>
</tbody>
</table>
Further correlations between characteristic protons and carbons were studied using HMBC in order to identify the nature of each characteristic bonds.

5.3.2.4. HMBC

The first region of interest is the carbonyl region of $\text{H}_2\text{O}^-\text{COO}^-\text{AEIO}$. Figure 5.12 presents the correlations of the previously unassigned protons (between 3.55 and 2.00 ppm) and the carbon peaks in the C=O region (between 180 and 150 ppm).

The first correlation of interest is between the broad singlet at 2.52 ppm (position C12) and the carbon at 160.49 ppm. In addition to that correlation, the multiplets at 3.08 ppm and 3.19 ppm are correlated to the same carbonyl. From the structure (Figure 5.8), this peak at 160.49 ppm can be assigned to the carbonyl of the amide group (position C17). The absence of correlations with the proton peaks characteristic of the imidazolidone ring (i.e. 3.51 ppm (position C20) and 3.38 ppm (position C21)) and this carbon peak seems to emphasize this observation. The other interesting correlation is between the multiplet at 3.08 ppm is correlated with the carbonyl in position C15 representative of the ester moieties of $\text{H}_2\text{O}^-\text{COOH}$. 
These two correlations indicate that the multiplet at 3.08 ppm is most likely representative of the methylene moieties attached to the amide in position C16. If we have a closer look at the correlations with the carbonyl at 165.15 ppm (representative of the C=O of the imidazolidone ring), three protons peaks are correlated: the multiplet at 3.51 ppm (position C20), the multiplet at 3.38 ppm (position C21) and a third multiplet at 3.32 ppm. The last multiplet is only correlated to this carbon in that region which means it most likely corresponds to the methylene protons in position C19.

Figure 5.13 displays the second region of interest between 80 and 30 ppm.

![Figure 5.13: 2D HMBC of H₂O-COO – AEIO in the carbonyl region between 80 and 30 ppm](image)

The protons resonating at 2.52 ppm is correlated to the carbon at 55.13 ppm, which could be attributed to the carbon in position C16. The multiplet at 3.32 ppm is correlating with carbon position C21 and position C20 which confirms that this peak is representative of the methylene groups in position C19. The correlations of the multiplet at 3.08 ppm with the carbon in position C18 (37.69 ppm) and position C12 (64.89 ppm) can be explained by assigning this peak to the methylene protons in position C16. The carbons in position C19 (41.85 ppm) and
position C20 (55.13 ppm) are correlating to the multiplet at 3.27 ppm which can be assigned to the methylene protons attached to C18.

The 2D correlations which lead to structure elucidation are summarised in tables 5.5 and 5.6.

Table 5.5: HMBC correlations for H$_2$O-COO – AEIO in D$_2$O

<table>
<thead>
<tr>
<th>$^1$H δ (ppm)</th>
<th>$^{13}$C δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.51</td>
<td>37.69</td>
</tr>
<tr>
<td></td>
<td>38.09</td>
</tr>
<tr>
<td></td>
<td>41.85</td>
</tr>
<tr>
<td></td>
<td>165.15</td>
</tr>
<tr>
<td>3.38</td>
<td>37.69</td>
</tr>
<tr>
<td></td>
<td>41.85</td>
</tr>
<tr>
<td></td>
<td>45.12</td>
</tr>
<tr>
<td></td>
<td>165.15</td>
</tr>
<tr>
<td>3.32</td>
<td>37.69</td>
</tr>
<tr>
<td></td>
<td>38.09</td>
</tr>
<tr>
<td></td>
<td>45.12</td>
</tr>
<tr>
<td></td>
<td>165.15</td>
</tr>
<tr>
<td>3.27</td>
<td>41.85</td>
</tr>
<tr>
<td></td>
<td>55.13</td>
</tr>
<tr>
<td></td>
<td>160.49</td>
</tr>
<tr>
<td>3.08</td>
<td>37.69</td>
</tr>
<tr>
<td></td>
<td>64.89</td>
</tr>
<tr>
<td></td>
<td>160.49</td>
</tr>
<tr>
<td></td>
<td>174.10</td>
</tr>
</tbody>
</table>

The multiplet at 3.19 ppm doesn’t seem to be correlated to many of the carbon of H$_2$O-COO - AEIO and therefore is more likely an excess of AEIO starting material which couldn’t be removed from the final compound. The presence of unreacted AEIO into the final product
could also explain the additional protons and carbons peaks into the different 1D and 2D NMR spectra (Figures 5.9 and 5.10).

Table 5.6: Complete structure assignment of $\text{H}_2\text{O-COO - AEIO}$ in $\text{D}_2\text{O}$

<table>
<thead>
<tr>
<th>$^{13}\text{C} \delta$ (ppm)</th>
<th>$^1\text{H}$ attached (ppm)</th>
<th>$^1\text{H}$ multiplicity</th>
<th>Molecule assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.02</td>
<td>-----</td>
<td>-----</td>
<td>$\text{C}=\text{O}$ (C5)</td>
</tr>
<tr>
<td>174.10</td>
<td>-----</td>
<td>-----</td>
<td>$\text{C}=\text{O}$ (C15)</td>
</tr>
<tr>
<td>165.15</td>
<td>-----</td>
<td>-----</td>
<td>$\text{C}=\text{O}$ (C22)</td>
</tr>
<tr>
<td>160.49</td>
<td>-----</td>
<td>-----</td>
<td>$\text{C}=\text{O}$ (C17)</td>
</tr>
<tr>
<td>70.63</td>
<td>3.58-3.74</td>
<td>m</td>
<td>C2</td>
</tr>
<tr>
<td>69.64</td>
<td>3.58-3.74</td>
<td>m</td>
<td>C3</td>
</tr>
<tr>
<td>65.94</td>
<td>4.18-4.31</td>
<td>m</td>
<td>C4</td>
</tr>
<tr>
<td>64.63</td>
<td>4.18-4.31</td>
<td>m</td>
<td>C8</td>
</tr>
<tr>
<td>64.02</td>
<td>4.18-4.31</td>
<td>m</td>
<td>C12</td>
</tr>
<tr>
<td>55.13</td>
<td>3.13</td>
<td>m</td>
<td>C16</td>
</tr>
<tr>
<td>45.12</td>
<td>3.51</td>
<td>m</td>
<td>C20</td>
</tr>
<tr>
<td>41.85</td>
<td>3.35</td>
<td>t</td>
<td>C19</td>
</tr>
<tr>
<td>39.38</td>
<td>-----</td>
<td>-----</td>
<td>C1</td>
</tr>
<tr>
<td>38.91</td>
<td>-----</td>
<td>-----</td>
<td>C6</td>
</tr>
<tr>
<td>38.09</td>
<td>3.38</td>
<td>m</td>
<td>C21</td>
</tr>
<tr>
<td>37.69</td>
<td>3.27</td>
<td>t</td>
<td>C18</td>
</tr>
<tr>
<td>16.79</td>
<td>1.18-1.32</td>
<td>m</td>
<td>C7</td>
</tr>
</tbody>
</table>
The use of NOESY experiments to determine the presence of hydrogen-bonding has been explored, however, as the hydrogen bonded to nitrogen were not detected in any of the 1D or 2D spectra it was not possible to detect any correlations due to hydrogen bonding. The only correlations displayed in the NOESY spectrum were between methyl protons in position C7 and the methylene protons in position C8.

### 5.3.3. FTIR characterisation

A number of studies have been published on the characterisation of the amide bonds most particularly in the area of proteins [14-18]. In this work, the FTIR spectra of the product of amidation H$_2$O–COO – AEIO is presented in Figure 5.14.

![Figure 5.14: Characteristics region of the H$_2$O–COO – AEIO FTIR spectrum](image-url)
The formation of an amide bond between the carboxylic groups of $\text{H}_2\text{O-COOH}$ and the primary amine of the AEIO molecule could be determined. The $\text{H}_2\text{O-COO - AEIO}$ displays a number of distinctive bands which correlated well to amide moieties.

The broad and strong band between 3675 and 3025 cm$^{-1}$ visible in the $\text{H}_2\text{O-COO - AEIO}$ spectra results from the N-H stretch of the amide functionalities. In comparison with the FTIR spectrum of AEIO, there is a shift of the strong peak from 3310 cm$^{-1}$ for AEIO to 3270 cm$^{-1}$ for $\text{H}_2\text{O-COO – AEIO}$; it can be explained by the change from a primary amine N-H stretch to secondary amide for $\text{H}_2\text{O-COO – AEIO}$ after amidation. An amide characteristic band at 3107 cm$^{-1}$ is due to the overtone of the in-plane N-H bending band [19]. This is characteristic of molecules containing amide groups; two bands in this region arise from Fermi resonance between the N-H stretch (amide A at 3270 cm$^{-1}$) and overtones or combinations (amide B at 3107 cm$^{-1}$) of amide II vibrations found in the 1500-1600 cm$^{-1}$ region [20, 21]. The large and broad band between 3000 and 2800 cm$^{-1}$ is representative of the C-H stretch of $\text{H}_2\text{O-COO – AEIO}$. Looking a bit more deeply into the carbonyl region (between 1775 cm$^{-1}$ and 1520 cm$^{-1}$), 4 strong bands are displayed. The distinctive bands in this region can be explained by different moieties absorbance. Figure 5.15 is a snapshot on this particular region.
Figure 5.15: Zoom on the carbonyl region (1775 cm$^{-1}$ to 1525 cm$^{-1}$) of H$_2$O-COO – AEIO

The two bands at 1734 cm$^{-1}$ and 1679 cm$^{-1}$ have already been discussed (in Chapter Three section 2.3.2 and Chapter Five section 2.2. respectively) and are characteristic respectively to C=O stretch of ester moieties and C=O stretch of the imidazolidone ring. The band at 1624 cm$^{-1}$ which is not present in the AEIO or H$_2$O-COOH spectra. It is characteristic of the amide I absorbance in proteins structure [12, 14-15]. In addition, the band at 1565 cm$^{-1}$ is representative of a combination between N-H bending and C-N stretching of amide moieties. It is another indication of the presence of amide groups in the structure of H$_2$O-COO-AEIO. Finally, in the case of secondary amides, the N-H out-of plane band is a sharp band which can be visualised on Figure 5.14 [17].
5.3.3.1. Evidence of hydrogen bonding in H$_2$O-COO – AEIO

5.3.3.1.1. Temperature dependent FTIR

Even though the presence of hydrogen bonding in H$_2$O-COO-AEIO couldn’t be detected via NMR experiments, some temperature dependent FTIR experiments were carried out to evidence the presence of hydrogen bonding interactions in the material. An aqueous solution of H$_2$O-COO – AEIO (5 g/L) was deposited on a glass slide and dried under vacuum overnight at 60 °C. The compound was heated up from room temperature to 50, 60, 70, 80, 90 and 100 °C and the corresponding FTIR spectra (in ATR mode) were collected. The carbonyl region (1800 to 1500 cm$^{-1}$) and N-H stretch region (3700 to 3100 cm$^{-1}$) were of particular interest in order to detect the changes in hydrogen-bonding as a function of the temperature. Figure 5.16 displays the evolution of the spectra of the H$_2$O-COO – AEIO compound along with the increase in temperature.

![Temperature-dependent FTIR spectra of H$_2$O-COO - AEIO](image)

Figure 5.16: Temperature-dependent FTIR spectra of H$_2$O-COO - AEIO
Chapter Five – Hydrogen bonded dendritic supramolecular network

The intensity of the strong band at 3372 cm\(^{-1}\), which has been assigned to the hydrogen-bonded N-H stretch of amide moieties [22-24], can be seen to decrease with increasing temperatures due to the weakening of hydrogen-bonding as reported by Wu [25].

Looking at the carbonyl region, the characteristic bands of the imidazolidone ring at 1679 cm\(^{-1}\) and the amide I at 1624 cm\(^{-1}\) displayed a reverse trend with the increase of temperature. The decrease of frequency of the amide I band in addition to the down shift of the N-H stretch is an indication of the weakening of the hydrogen-bonding breakage with the increasing temperature. The down shifts of both characteristic amide bands (I and II at ~1630 and 1570) have already been reported by Mishakina et al. [26] in N-methylacetamide. On the other hand, the imidazolidone C=O stretch displayed a shift towards higher wavelengths and the intensity of the stretch was also found to increase. This phenomenon has been reported by Yang et al. [27] in supramolecular elastomers based on linear carboxyl-terminated polydimethylsiloxane oligomers. Yang showed that in this particular system, as the hydrogen bonding weakened with an increase in temperature the frequency of the C=O stretch was observed to increase. The difference of behaviours between the C=O stretch of the amide bonds and C=O stretch of the imidazolidone can be explained as IR spectroscopy is sensitive to backbone conformation, and degree and strength of hydrogen bonding to amide C=O groups as reported by Jackson et al. [28].

Table 5.7 summarises the frequency shifts of the characteristic bands.

Table 5.7: Evolution of the characteristic bands of absorption involved in the hydrogen bonding of H\(_2\)O-COO – AEIO as a function of temperature

<table>
<thead>
<tr>
<th>Band</th>
<th>N-H</th>
<th>C=O imidazolidone</th>
<th>C=O Amide I</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>3273.59</td>
<td>1670.59</td>
<td>1626.79</td>
</tr>
<tr>
<td>50</td>
<td>3268.82</td>
<td>1675.03</td>
<td>1625.93</td>
</tr>
<tr>
<td>60</td>
<td>3264.05</td>
<td>1676.08</td>
<td>1624.00</td>
</tr>
<tr>
<td>70</td>
<td>3261.76</td>
<td>1677.70</td>
<td>1623.01</td>
</tr>
<tr>
<td>80</td>
<td>3260.52</td>
<td>1678.70</td>
<td>1622.70</td>
</tr>
<tr>
<td>90</td>
<td>3259.28</td>
<td>1679.51</td>
<td>1622.40</td>
</tr>
<tr>
<td>100</td>
<td>3258.22</td>
<td>1679.94</td>
<td>1621.75</td>
</tr>
</tbody>
</table>
In order to visualise the hydrogen-bonding between the N-H and C=O moieties of H$_2$O-COO$^-$ AEIO, 2 Dimensional (2D) FTIR was employed.

### 5.3.3.2. 2D FTIR

#### 5.3.3.2.1. Introduction

Two dimensional correlation spectroscopy (2DCos) is a powerful tool for spectral analysis. It is able to reveal correlations between spectral changes resulting from the application of an external impulse such as pH, temperature or concentration. The spectra are processed by a correlation function into a 2D spectra [29-30]. Two different part of this spectra exist: the synchronous which consist of simultaneous or coincidental changes and asynchronous which represents sequential or successive changes of measured spectral series. In this work, the main focus will be on synchronous spectra in order to determine the different correlation as source of hydrogen bonding.

In a synchronous 2D spectrum, simultaneous or coincidental changes are represented by cross peaks located at the off—diagonal positions. Those changes can be interpreted as coupled or related groups. A correlation square is constructed in between the cross peaks and the diagonal in order to show the existence of true correlations [31]. The sign of a synchronous cross peak is dependent on the evolution of the moieties coordinates as function of the external stimuli. If the spectral intensity is positive, both moieties are evolving together (either increase or decrease of the relative intensities of the characteristic bands); however, if it becomes negative, one is increasing whilst the other one is decreasing.

#### 5.3.3.2.2. Analysis

The 2D correlation analysis was carried out on the series of spectra presented above in Figure 5.17 using the software 2D Shige, version1.3 (Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004-2005). The synchronous spectra was analysed in order to determine the direct change of behaviour and bonding between carbonyl and amide moieties.
Chapter Five – Hydrogen bonded dendritic supramolecular network

Figure 5.17 displays the synchronous 2D correlation spectrum of H$_2$O–COO – AEIO where warm colours (red) are defined as positive intensities, while cool colours (blue) are defined as negative ones. The 2DCos spectrum of H$_2$O–COO – AEIO was plotted in the regions of interest: amide N-H stretch (3800 cm$^{-1}$ to 3100 cm$^{-1}$) and the carbonyl region (1800 cm$^{-1}$ to 1500 cm$^{-1}$) where the hydrogen bonding can be monitored.

![Figure 5.17: Synchronous 2D correlation spectrum of H$_2$O–COO – AEIO in the regions of interest: amide N-H stretch (3800 cm$^{-1}$ to 3100 cm$^{-1}$) and the carbonyl region (1800 cm$^{-1}$ to 1500 cm$^{-1}$)](image)

The 2DCos results clearly show two types of correlations represented in the figure above represented by correlation square A and correlation square B. Both cross peaks have negative intensities which correlate with the 1D FTIR observation as the N-H stretch band intensity is decreasing whilst the C=O stretch of both the amide and imidazolidone are increasing. As expected, the main source of hydrogen bonding can be detected between the N-H and the
carbonyl of the amide bond at 1620 cm$^{-1}$ (correlation square A) and the N-H and the imidazolidone ring at 1680 cm$^{-1}$ (correlation square B).

5.4. Self-healing behaviour

Self-healing tests were carried out by initiating a thin crack using a razor blade on samples deposited on a glass slide (Figure 5.18, left). The self-healing potential of these materials was investigated. The film was left at room temperature under a microscope, and the sample was found to self-repair without any external stimuli after 5 min as shown on Figure 5.18.

Figure 5.18: H$_{2}$O-COO – AEIO sample just after crack initiation (left) and after 5 min at room temperature (right)

In this work, the self–healing ability of the dendritic network was expected as per the work of Cordier et al. [3]. The self-healing process is most probably due to intra or inter molecular hydrogen bonding facilitated by the presence of imidazolidone at the surface of the dendrimer.
5.5. Conclusions

In this chapter, the NMR and FTIR characterisation of the self-healing precursor 1-(2-aminoethyl)-2-imidazolidone (AEIO) was achieved. The functionalisation of the carboxylic acid terminated dendrimer H₂O-COOH with AEIO was successfully achieved and characterised with 1D/2D NMR and 1D/2D FTIR. The complete structure assignment was studied with 1D and 2D NMR and confirmed via 1D FTIR. The possible presence of unreacted AEIO could be observed in some of the NMR spectra. The presence of hydrogen bonding in the H₂O-COOH-AEIO material couldn’t be noticed via NOE experiments, nevertheless 2Dcos (FTIR) experiments revealed the interactions (i.e. hydrogen bonding) between the N-H moieties and both carbonyl of the amide and imidazolidone functionalities. Finally, the self-healing behaviour of the hydrogen-bonded supramolecular was successful without any external stimuli and/or swelling into a solvent self-healing process as a result of the intermolecular hydrogen bonding facilitated by the presence of imidazolidone.
Chapter Five – Hydrogen bonded dendritic supramolecular network

5.6. References


[8] Qing, N.; Colebrook, L. D.; Edward, J. T.; Kon, A.; Chubb, F. L., Reactions of α-phenylglycinamide with some carbonyl compounds. Formation of 5,7-diisopropyl-8,8-dimethyl-2-oxo-3-phenylimidazolidino-[1,2-c]-tetrahydro-[1,3]-oxazine, and determination of structure and stereochemistry by nuclear Overhauser effect difference measurements. *Canadian Journal of chemistry* 1989 67 (10)


Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers
6.1. Introduction

Nitrile-butadiene rubber is an oil-resistant synthetic rubber produced from a copolymer of acrylonitrile and butadiene. NBR’s are mainly used in fuel hoses, gaskets and rollers, and other products where oil resistance is required [1, 2]. In the production of NBR’s, acrylonitrile (CH$_2$=CH-CN) and butadiene (CH$_2$=CH-CH=CH$_2$) are emulsified in water and then polymerized through the action of free-radical initiators [3]. The amount of acrylonitrile present in the final commercial products varies from 15 to 50 percent [4]. With increasing acrylonitrile content of the rubber, higher strength, greater resistance to swelling by hydrocarbon oils, and lower permeability to gases can be attained (Figure 6.1). On the other hand, the rubber becomes less flexible and displays much lower glass transition temperature [5].

![Figure 6.1: Examples of NBR products [4]](image)

Block copolymer elastomers such as NBR’s are generally characterised by relatively weak inter-chain interactions within molecules. Tailoring the physical characteristics of NBR molecules can be achieved by introducing functional monomers onto the backbone of the rubber [6-8]. Incorporation of carboxyl bearing monomers has been shown to increase tensile strength as a result of intra- and intermolecular interactions. Further to that carboxylic acid groups can be employed as crosslinking points or attachment points onto other molecules or surfaces [9-12].

Commercially available carboxylated nitrile rubbers (NBR) are ter-polymers of acrylonitrile, butadiene, and typically acrylic or methacrylic acid monomers. The pendant carboxylic acid functionalities present in along the backbone of the polymer provide a useful site to apply the
versatile neutralisation methodology reported in Chapter Four in order to create an ionic supramolecular network.

![Figure 6.2: Commercially available carboxylated NBR (Nipol DN601) used in this work.](image)

This Chapter will be dedicated to the development of metallosupramolecular elastomers based on zinc counter-ions. The neutralisation of the Nipol DN601 (Figure 6.2), a commercially available carboxylated NBR material, ter-polymer of acrylonitrile (20 wt%), butadiene (72.5 wt%) and carboxylated butadiene (7.5 wt%) with zinc hydroxide will be first described. We used the same liquid-solid diffusion methodology to what has been reported in Chapter Four. The neutralised materials will be characterised using FTIR analysis. Because the exact structure and sequence of the co-polymers of the starting material is protected by patent laws, no attempt was made at elucidating the structure of these materials using more sophisticated spectroscopic technique such as NMR. The assessment of self-healing capabilities of the zinc-based metallosupramolecular elastomers alone or in a blend with an aerospace grade epoxy resin was investigated showing some very promising results.

### 6.2. Metallosupramolecular elastomers based on zinc counter ions

The pendant carboxylic acid groups contained in the NBR compound were neutralised at four levels using zinc hydroxide Zn(OH)$_2$ via a solid-liquid diffusion in THF. The 4 levels correspond to the neutralisation of 25, 50, 75 and 100% of the total available carboxylic acids present in
Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers

the NBR backbone. The resulting materials are referred to here as NBR – 0.25Zn, NBR – 0.50Zn, NBR – 0.75Zn and NBR – Zn.

An example of protocol used for the neutralisation of one quarter of the total carboxylic acids available in the NBR backbone is as follow: 5.0 g (0.14 mmol) of NBR was dissolved in 25 mL THF for 1h at room temperature. After total dissolution of the NBR, 8.5 mg (0.09 mmol) of freshly prepared Zn(OH)₂ powder was added to the solution and left under high agitation (1300 rpm) till complete disappearance of the Zn(OH)₂.

All neutralisations were achieved following the same protocol only using different quantities of Zn(OH)₂. The amount of Zn(OH)₂ were calculated based on a reported molecular weight of approximately 35,000 g.mol⁻¹ [4].

6.2.1. FTIR characterisation

The FTIR spectra of the various zinc-based metallosupramolecular elastomers formed after neutralisation are shown in Figure 6.3. The spectra have been resumed to the carbonyl absorbing region between 1800 cm⁻¹ and 1500 cm⁻¹.

Figure 6.3: FTIR of zinc-based metallosupramolecular elastomers in the carbonyl region
Similarly to what has been reported in Chapter Four section 2.4, the FTIR spectrum shows that the band characteristic to carboxylate group at 1580 cm\(^{-1}\) is increasing in intensity with increasing degree of neutralisation whilst the carboxylic band at 1735 cm\(^{-1}\) decreases (data normalised at 2200 cm\(^{-1}\) corresponding to the stretching vibrations of the nitrile bond). It can be seen that comparably to what has been seen in Chapter Four, the carboxylate band is displaying separate bands corresponding to the coordination state of the cation Zn\(^{2+}\), namely Carboxylate/Zn\(^{2+}\) (T) and Carboxylate/Zn\(^{2+}\) (H). The experimental degree of neutralisation of the rubber can be determined by equation 6.1 [15 - 16].

\[
D_{\text{Neutralisation}} = \left(1 - \frac{A_{\text{NBR}}}{A_{1700}}\right) \times 100
\]

**Equation 6.1: Equation to determine the degree of neutralisation of zinc-based metallosupramolecular elastomers**

Where \(A_{\text{NBR}}\) is the absorbance of the starting NBR at 1700 cm\(^{-1}\) and \(A_{1700}\) are the absorbance of the neutralised compound at 1700 cm\(^{-1}\).

Table 6.1 presents the difference between the theoretical and experimental degree of neutralisation for the four samples. The absorbance \(A_{\text{NBR}}\) of the carboxyl moiety (1700 cm\(^{-1}\)) for the starting NBR was 5.614. It can be seen that the theoretical and experimental data matched up.

**Table 6.1: Difference between theoretical and experimental zinc degree of neutralisation**

<table>
<thead>
<tr>
<th>Degree of neutralisation (%)</th>
<th>Degree of neutralisation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical</strong></td>
<td><strong>Experimental</strong></td>
</tr>
<tr>
<td>NBR – 0.25Zn</td>
<td>25</td>
</tr>
<tr>
<td>NBR – 0.50Zn</td>
<td>50</td>
</tr>
<tr>
<td>NBR – 0.75Zn</td>
<td>75</td>
</tr>
<tr>
<td>NBR – Zn</td>
<td>100</td>
</tr>
</tbody>
</table>
Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers

The carboxylate band at 1600 cm\(^{-1}\) was deconvoluted and the area under the curve of the two absorption bands at 1610 cm\(^{-1}\) and 1585 cm\(^{-1}\) were separately quantified so that the tetra to hexa ratios could be calculated. The quantitative analysis results showing the relative percentage ratios in the samples as a function of the neutralisation are displayed in Table 6.2.

Table 6.2: Quantitative analysis of the tetra and hexa ratios present in the various materials from peak deconvolution.

<table>
<thead>
<tr>
<th>Association</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR – 0.25Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (T)</td>
<td>1610</td>
<td>100.0</td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (H)</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>NBR – 0.50Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (T)</td>
<td>1607</td>
<td>72.8</td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (H)</td>
<td>1585</td>
<td>27.2</td>
</tr>
<tr>
<td>NBR – 0.75Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (T)</td>
<td>1608</td>
<td>49.9</td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (H)</td>
<td>1588</td>
<td>50.1</td>
</tr>
<tr>
<td>NBR – Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (T)</td>
<td>1608</td>
<td>28.3</td>
</tr>
<tr>
<td>Carboxylate/Zn(^{2+}) (H)</td>
<td>1586</td>
<td>71.7</td>
</tr>
</tbody>
</table>

The band wavenumber measured for each type of coordination was found to relatively unchanged with the increase in the degree of neutralisation and conformed to the literature [16 - 17]. Looking closely at the trends it can be observed that the relative percentage of tetra-coordination decreased with increasing degree of neutralisation (from 100% to 28%) whilst the relative percentage of hexa-coordination increases from 0% to 72%. Our results are consistent with Coleman [16] and Gao [18] who also measured an increase of the hexa-coordinated of zinc ions present in ethylene methacrylic acid copolymer (EMAA) ionomers as a function of the neutralisation.
6.3. **Self-healing ability**

6.3.1. **Neat zinc-based metallosupramolecular elastomer**

Self-healing tests were carried out by initiating a thin crack using a razor blade of neutralised samples deposited on a glass slide after being dried at 60°C under vacuum overnight. Figure 6.4 shows that the neat NBR sample did not self-repair at room temperature. Heat treatment (100 °C for 30 min) was also trialled but it did not help the self-healing of this material (not shown here). On the other hand, all neutralised samples were found to exhibit healing behaviour at room temperature without the help of external stimuli. The NBR – 0.75Zn sample shown in Figure 6.4 was found to self-repair at room temperature and crack closure was observed in less than 5 minutes. The ability of the zinc-based metallosupramolecular elastomers to self-repair can be explained by the various associations between zinc counter-ions and the carboxylate moieties of the NBR. Ionic hopping and rearrangements after fracture has been for instance reported by Speck et al. [19 - 20] where...
carboxylated nitrile rubber associated with zinc were found to exhibit self-healing ability leading to a recovery of tensile strength of up to 50%.

Similarly of what has been reported in Chapter Four Section 4.2.4., the mechanism involved during the self-healing process of the zinc-based metallosupramolecular elastomers was studied via a FTIR dynamic study on a NBR – 0.75Zn sample. The same trend was observed with the appearance of a third band at 1537 cm\(^{-1}\) (Figure 6.5) representing the association of the carboxylate group with tetra-coordinated Zn\(^{2+}\) ions coupled with hydrogen bonding between the carboxylate groups and carboxylic groups (Carboxylate/Zn\(^{2+}\)/-COOH).

Upon healing of the crack, this characteristic band is found to disappear gradually. Similarly to what was reported for the dendrimer, this specific association of the carboxylate moieties with zinc ions and carboxylic acid groups is only present during the transition mode. Before the crack and after complete healing (equilibrium mode), this state of coordination is not present (Figure 6.6).

**Figure 6.5: Example of deconvolution in the carboxylate region during the self-healing process at t = 1min (NBR - 0.75Zn is presented here)**
6.3.2. Composite Application

It has already been widely reported that NBR rubbers can be used as toughening agents for composites application in combination with epoxies [21 – 24]. This work therefore looked at the possibility of using the studied zinc-based metallosupramolecular elastomers as potential toughening and self-healing agents for composite applications.

The next stage of this work involved the blending of zinc-based metallosupramolecular elastomers with an aerospace grade epoxy resin, diglycidyl ether of bisphenol F (DGEBF, EPON 862). The toughening and self-healing properties were studied on these materials using a compact tension methodology [25 – 26].

Following is a short experimental description of the method used to cast the epoxy/zinc-based metallosupramolecular elastomer samples. The epoxy DGEBF was heated at 80 degrees for 30 min to reduce its viscosity before adding 4 wt% total ratio of the neat liquid rubber (DN601) or the zinc-based metallosupramolecular elastomers. The hardener (Epikure W) was then added and mixed for an additional 30 min at the same temperature. The mixture was
then degased in a vacuum oven at 80 °C for 30 min. The final homogeneous solution was then poured into degassed silicone moulds and put into an oven at 100 degrees for 5h.

It is important to point out at this point of the text that only the unmodified liquid rubber as well as the NBR – 0.25Zn sample (i.e. rubber having the lowest degree of neutralisation, 25%) were found to be miscible after 15h in solution with the DGEBF resin. At higher degrees of neutralisation the NBR – 0.5Zn, NBR – 0.75Zn and NBR –Zn samples were not miscible in DGEBF even after extended period of mixing times of up to 7 days. Attempts were made at using THF as a solvent for casting the compact samples. However given the large volume of THF needed to dissolve ~ 30 grams of resin (>100ml), the samples were found to degrade after extended period of drying in order to remove the THF solvent at 80 °C under vacuum. We also found that the THF had severe plasticising effects. No further attempts was made at dissolving the epoxy DGEBF and the zinc-based metallosupramolecular elastomers in THF. Therefore only the fracture toughness and the self-healing properties of the epoxy sample containing the NBR – 0.25Zn ionic network will be reported here.

We also found that by increasing the curing temperature in order to speed up the curing process, the zinc ions would then catalysed a reaction with the pendant carboxylic acid groups resulting in the release of CO₂ [27 – 28]. The casted samples produced above 100 °C were found to be very bubbly and unusable (Figure 6.7).

![Figure 6.7: Compact tension sample cured at 150 degrees showing a very porous structure as a result of zinc catalysed CO₂ release.](image)

Solid compact tension sample were obtained as per the British standard [25] or the ASTM standard E1820-13 [26] (Figure 6.8).
In order to determine the toughening and self-healing properties of the materials, a fracture mechanic test was employed as described by Jones et al. [39]. A pre-crack of 1 mm was applied with a razor-cut on each sample prior to testing to initiate the crack and then the sample was subjected to a tensile test till the crack reached the hole. The maximum of energy necessary to propagate the crack is monitored and used to determine the fracture toughness of the system following the equation below (Equation 6.2):

$$K_{IC} = \frac{P_{Max}}{B \times \sqrt{W}} \times f(x)$$

**Equation 6.2: Fracture toughness ($K_{IC}$) equation for a compact tension sample following the ASTM E1820-13 [26]**

Where:
- $P_{Max}$ is the maximal force obtained before failure
- $B$ is the thickness
- $W$ is the specimen width
- $f(x)$ is a constant depending on the initial crack length and width of the specimen

Six samples were tested per batch and the average fracture toughness was calculated. Figure 6.9 presents the fracture toughness results tests of the neat DGEBF, DGEBF/NBR and DGEBF/NBR – 0.25Zn samples.
Figure 6.9: Fracture toughness results for the neat epoxy resin, epoxy resin/DN601 system and epoxy resin/DN601-25% Zn system

The fracture toughness of the neat DGBEF epoxy system was found to be increased by ~150% after incorporation of 4wt% of the liquid NBR (DN601). This was expected as NBR have already been reported to be effective toughening agents [21 - 24]. Nonetheless, the measured fracture toughness was found to be further increased by 210% after incorporation of the ionic NBR - 0.25Zn material.

In order to assess the self-healing behaviour of the different systems, the two sides of the compact tension samples were put back together and placed in an oven at 100 °C overnight and retested the following day. Table 6.3 shows the compact tension before fracture toughness testing, and after testing followed by a heat treatment.
Table 6.3: Compact tension samples of the different systems before the test, after the test and after heat treatment

<table>
<thead>
<tr>
<th></th>
<th>DGEBF</th>
<th>DGEBF/NBR</th>
<th>DGEBF/NBR – 0.25Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before the test</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>After the test</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>After heat treatment</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 6.10: Compact tension sample of DGEBF/NBR – 0.25Zn after heat treatment (overnight at 100 ºC)
Whilst the neat epoxy sample and the epoxy resin/unmodified NBR systems showed no visual sign of healing, all the DGEBF/NBR – 0.25Zn compact sample was found to present a crack closure as shown in Figure 6.8. The DGEBF/NBR – 0.25Zn compact samples were found to recover a fracture toughness of around 1.29 MPa.m$^{1/2}$ (+/- 0.18) which is an average of 24.8% recovery of the mechanical properties. It is important to highlight that the self-healing properties of NBR – 0.25Zn were translated to the epoxy blend even though as little as 4 wt% of NBR – 0.25Zn was incorporated into the epoxy resin. The apparent healing of the systems could be explained by molecular rearrangement of the NBR with the zinc cations with temperature as explained in the previous section. The DSC thermal analysis study (Appendix I) carried out on the samples showed that the $T_g$ was not affected after incorporation of the zinc-based metallosupramolecular elastomers into the epoxy resin (all $T_g$ were found to be displayed around 105-110 °C). This also showed that with addition of the ionic NBR – 0.25Zn into the epoxy resin no plasticisation effect was observed and importantly the thermo-mechanical properties were unaffected. The dispersion of NBR - 0.25Zn into the epoxy matrix could be observed by SEM (Figure 6.11).

Figure 6.11: SEM image of DGEBF/NBR – 0.25Zn compact tension sample in the crack region. Highlighted are cavities left by pulled out NBR – 0.25Zn globules (size between 150 and 250 nm). A homogeneous fine dispersion of NBR – 0.25Zn globules is visible throughout the sample.
Globules of NBR were found in low concentration into the matrix which could explain that only 25% of the mechanical properties could be retrieved after heat treatment of the compact tension samples.

6.3.3. NBR Blends

NX775 is a high molecular weight, tough, oil and fuel resistant [30] NBR currently used as an additive for applications such as high-performance injection moulding products, rolls, calendered belting or extruded hose. The idea of the work presented in this section was to blend this compound with the zinc-based metallosupramolecular elastomer and see if a self-healing blend could be developed.

NX775 was dissolved into THF overnight and a 1 to 1 weight ratio of the zinc-based metallosupramolecular elastomers developed in 6.2 above were added under agitation for another 24h at 60 ºC. The THF was evaporated at 60 ºC under vacuum in order to obtain a dry compound. The final products were soft sponge-like materials.

Self-healing tests were achieved by cutting the blend materials into two halves using a sharp razor and put the two halves together applying a slight manual pressure in order to initiate the healing process at room temperature. A visual example of the self-healing test in the case of NX775/NBR – 0.75Zn material is displayed in Figure 6.12.

Figure 6.12: Neat NX775 material (top) showing no self-healing and NX 775/NBR – 0.75Zn blend (bottom) showing self-healing
We found that blends of NX775 with any of the zinc-based metallosupramolecular elastomers exhibited self-healing behaviour and the two halves were able to “stick” together. All materials displayed efficient and fast (<1 minute) self-healing behaviour.

6.4. Conclusions

In this chapter, it was demonstrated that the versatile neutralisation method presented in Chapter 4 could be used on an engineering product such as a nitrile butadiene rubber. The neutralisation of the NBR using zinc hydroxide was found to be a quick and efficient way to produce zinc-based metallosupramolecular elastomers having the ability to effectively self-repair due to molecular rearrangement between the zinc counter-ions and the carboxylate moieties of the carboxylated NBR. Both the metallosupramolecular elastomers and zinc-based metallosupramolecular dendrimers based on zinc interactions were found to show the same self-healing efficiency. It has also been shown that the introduction of the ionic NBR-0.25Zn rubber into an aerospace grade epoxy resin improved significantly its toughness and also provided some self-healing properties. The ability to transfer the neutralisation method from one polymer (dendrimer) to another (natural rubber) was found to be particularly important when one compound is found to be incompatible with the matrix. In addition, the blend of zinc-based metallosupramolecular elastomers with a NBR matrix was also found to exhibit autonomous self-healing properties at room temperature which makes it of high interest for applications such as seals, hoses, belts where durability is a key factor.
Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers

6.5. References


Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers


Chapter Six – Preliminary work on self-healing zinc-based metallosupramolecular elastomers


Chapter Seven – General conclusions and recommendations for future work
Chapter Seven – General conclusions and recommendations for future work

The scope of the thesis was to develop an autonomous self-healing system based on dendrimers. The research hypothesis was that the high degree of branching (3D) and abundant number of surface functionalities displayed by dendrimers could facilitate the inter- and intra-molecular interactions needed for efficient self-healing mechanisms. In order to investigate this hypothesis, the research strategy presented in this thesis focused on the development of supramolecular dendritic networks using the ionic or hydrogen bonding self-healing approaches. The research was validated based on the experimental observations and the collective outcomes of this work presented some results which could be of significance to the industry.

7.1. Summary of the research findings

The research work began (Chapter Three) with the functionalisation of a second generation hydroxyl terminated dendrimer (H20) to yield a carboxylic acid terminated dendrimer (H20-COOH). This was a very important step of the work as this material was used as a precursor for the development of the development of the various ionic and hydrogen supramolecular networks.

The neutralisation of the carboxylic acid terminated dendrimer H20-COOH with a base to yield a range of carboxylate terminated supramolecular ionic dendrimers, was first investigated. The research strategy aimed to understand the effect of both the valency of the counter-ions and the degree of neutralisation (e.g. number of surrounding counter-ions) on the self-healing behaviour of these ionic supramolecular networks. The results reported in this thesis focussed on the carboxylate terminated ionic dendrimers based mono-valent sodium (Na+) or a divalent zinc (Zn2+) counter-ions.

In Chapter Three, the carboxylate interactions with the mono-valent sodium (Na+) counter-ions was shown to induce strong electrostatic interactions, and this effect was more pronounced with the increasing degree of neutralisation. This phenomena also correlated to the hindering of the Na+ ion hopping mechanisms caused by strong electrostatic interactions and contraction of the chains, which has co-occurred with a gradual increase in the glass
transition of the neutralised materials. As a result no positive influence was observed on the self-healing potential of the sodium based ionic dendrimers.

In Chapter Four we used a versatile liquid-solid diffusion process to produce the zinc-based metallosupramolecular dendrimers. The presence of bivalent zinc (Zn$^{2+}$) counter-ions was shown to lead to various modes of inter or intra molecular electrostatic interactions with the terminal carboxylate groups as a result of the possible states of coordination undertaken by the zinc ions (tetra and hexa type of coordinations). The successful autonomous and efficient (< 5 minutes) self-healing ability of the zinc-based metallosupramolecular dendrimers was observed in thin films after crack opening. During the healing process, infra-red analysis data at the crack interface revealed the dynamic changes in the coordination states of the zinc ions observed. It was found that a transitional mode of association between the carboxylate and tetra-coordinated zinc ions coupled with hydrogen bonding between carboxylate and carboxylic groups (at 1537 cm$^{-1}$) appeared at the crack interface, but disappeared after repair. It is therefore believed that this particular transitional mode of association and interaction must be responsible for the mechanism of self-healing of the zinc-based metallosupramolecular dendrimers. These possible changes in inter/intra molecular modes of interactions and molecular re-arrangement were attributed to the success of this self-healing approach. Additionally, we showed that the self-healing ability of these materials could be transferred using thermal heat to poly(lactic acid) when blended at 5 wt% ratio. This lead to the interesting conclusion that zinc-based metallosupramolecular dendrimers could be used as self-healing agents in combination with other thermoplastics such as PLA.

The research was followed by investigating the hydrogen bonded approach particularly looking at imidazolidone interactions. The functionalization of the carboxylic acid terminated dendrimer H$_{20}$-COOH with a 1-(2-aminoethyl)-2-imidazolidone (AEIO) yielding the hydrogen bonded supramolecular dendritic network (H$_{20}$-COO – AEIO) was described. The presence of hydrogen-bonding in the supramolecular networks between the imidazolidone moieties and with the amide bonds was also verified using 2 dimensional FTIR. In thin casted film after crack opening, these networks displayed effective and autonomous self-healing at room temperature without the need for external help.
Chapter Seven – General conclusions and recommendations for future work

The final experimental Chapter focused on adapting the previous lessons learnt to an engineering product of interest: a carboxylated Nitrile Butadiene Rubber (NBR). Because of the versatility of the liquid-solid diffusion process previously used to yield the zinc-based metallosupramolecular dendrimers (Chapter Four), this method was adopted in Chapter Six in order to produce a range of metallosupramolecular rubber networks. We found that the methodology worked very well producing zinc-based metallosupramolecular elastomers capable of rapid and efficient self-repair. Very importantly (and although the results were confined to only one type of metallosupramolecular elastomer e.g. NBR-0.25 Zn) it was demonstrated that by using as little as 4 wt% of the ionic NBR network in a blend with an aerospace grade epoxy resin, a combined toughening and self-healing actions were observed (~50% and 25% observed in CT test samples). This result is in our opinion of high interest for composite applications where strength, toughness and durability are critical.

7.2. Recommendations for future work

The collective outcomes of this work presented some results which could be of significance to the composite industry.

This project was focused on the self-healing behaviour of dendrimers based on ionic or hydrogen-bonded supramolecular interactions. The findings of the study showed that the valency of the counter-ion employed to create the various studied ionic dendrimers was of importance and only self-healing could only be achieved using divalent counter-ions. The results here are confined to two types of valency and the study should be extended to include other types of divalent or trivalent counter-ions such as Co^{2+}, Mn^{2+}, Al^{3+}. The changes in coordinations of the counter-ions and changes in modes of inter/intra molecular re-arrangement could be investigated to further expand our understanding of the self-healing mechanisms in these ionic dendrimers.

Also it was demonstrated that self-healing properties could be translated from the neat zinc-based metallosupramolecular dendrimer to its blend with PLA with concentration as low as 4wt%, although the self-healing process required a heat treatment. The ionic dendrimer to PLA ratios could be varied in order to improve the self-healing action of the ionic dendrimer. The use of another matrix such as an epoxy resin could be of interest.
Chapter Seven – General conclusions and recommendations for future work

Following the same approach, the self-healing abilities of zinc-based metallosupramolecular rubber in a blend with aerospace grade epoxy resin could be improved by increasing the concentration of the metallosupramolecular rubber. The result of our study was limited to 4wt% of the metallosupramolecular rubber in epoxy. An increase in concentration could be investigated and the effect of metallosupramolecular rubber concentration mechanical/thermal properties as well as self-healing efficiency would be of interest.
Appendix

Appendix A: $^1$H NMR spectrum of Boltorn $\text{H}_2\text{O}$

Figure A.1: $^1$H NMR spectrum of $\text{H}_2\text{O}$ in $\text{CD}_3\text{COCD}_3$ (*)
Appendix B: $^{13}$C NMR spectrum of Boltorn H$_{20}$

![Figure B.2: $^{13}$C NMR spectrum of H$_{20}$ in CD$_3$COCD$_3$ (*)](image)
Appendix C: $^1$H NMR spectrum of H$_{20}$-COOH after an excess of sodium hydroxide was added

Figure C.3: $^1$H NMR spectrum of H$_{20}$-COOH after addition of an excess of sodium hydroxide in CD$_3$COCD$_3$ (*)
Appendix D: C1s XPS of sodium based ionic dendrimer

Figure D.4: C1s XPS spectrum of $\text{H}_2\text{O}^-\text{COO}^- - 0.25\text{Na}$

Figure D.5: C1s XPS spectrum of $\text{H}_2\text{O}^-\text{COO}^- - 0.75\text{Na}$
Appendix E: C1s XPS spectra of zinc-based metallosupramolecular dendrimer

Figure E.6: C1s XPS spectrum of H$_2$O$_2$-COO – 0.75Zn

Figure E.7: C1s XPS spectrum of H$_2$O$_2$-COO – Zn
Appendix F: DEPT NMR spectrum of $\text{H}_2\text{O}$-COO – 0.50Zn in the carbonyl region after diffusion

Figure F.8: DEPT NMR of $\text{H}_2\text{O}$-COO – 0.50Zn after 192h of diffusion into $\text{D}_2\text{O}$
Appendix G: FTIR deconvolution of zinc-based metallosupramolecular dendrimer in the carboxylate region

Figure G.9: FTIR deconvolution of H$_{2}$O-COO – 0.25Zn

Figure G.10: FTIR deconvolution of H$_{2}$O-COO – 0.50Zn
Figure G.11: FTIR deconvolution of $\text{H}_2\text{COO}^- - \text{Zn}$
Appendix H: $^{13}$C NMR of AEIO

Figure H.12: $^{13}$C NMR of AEIO in D$_2$O
Appendix I: Glass transition temperature of DGEBF, DGEBF/NBR and DGEBF/NBR – 0.25Zn compact samples after curing

Figure I.13: Glass transition temperatures of DGEBF, DGEBF/NBR and DGEBF/NBR – 0.25Zn compact tension samples after curing