# CONTENTS

<table>
<thead>
<tr>
<th>Content</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>Declaration</td>
<td>iv</td>
</tr>
<tr>
<td>Certificate of supervisor</td>
<td>v</td>
</tr>
<tr>
<td>Certificate of examiners</td>
<td>vi</td>
</tr>
<tr>
<td>Preface</td>
<td>vii</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>viii</td>
</tr>
<tr>
<td>Contents</td>
<td>x</td>
</tr>
<tr>
<td>List of Abbreviations and Symbols</td>
<td>xix</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xxi</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xxiii</td>
</tr>
<tr>
<td>List of Schemes</td>
<td>xxviii</td>
</tr>
</tbody>
</table>

## Chapter 1

**General introduction**

1.1. Introduction 2
1.2. Background 5
1.3. Classification of SMP 6
1.4. Classification of polymer nanocomposites 8
1.5. Materials and methods 8
   1.5.1. Materials 8
   1.5.2. Nanomaterials 11
   1.5.3. Method 14
   1.5.3.1. Preparation of polyurethane 14
   1.5.3.2. Preparation of polymer nanocomposite 14
1.6. Characterization 16
   1.6.1. Nuclear magnetic resonance (NMR) spectroscopy 16
1.6.2. X-ray diffraction (XRD) study ................................. 17
1.6.3. Fourier transformed infrared spectroscopy (FTIR) .......... 17
1.6.4. Scanning electron microscopy (SEM) ......................... 17
1.6.5. Transmission electron microscopy (TEM) .................... 18
1.6.6. Thermo-gravimetric analysis (TGA) .......................... 18
1.6.7. Differential scanning calorimetry (DSC) ..................... 18
1.6.8. Raman spectroscopy ........................................... 19
1.6.9. Vibrating sample magnetometric study ....................... 19
1.6.10. Biodegradation testing ........................................ 19
1.6.11. Testing for shape memory behaviour ......................... 19

1.7. Property .................................................................. 21
  1.7.1. Mechanical property ........................................... 21
  1.7.2. Thermal property ............................................... 22
  1.7.3. Magnetic property ............................................. 22
  1.7.4. Biodegradation behaviour .................................... 22
  1.7.5. Shape memory property ...................................... 23

1.8. Applications of shape memory polymers .......................... 24
1.9. Short review on shape memory polyurethane nanocomposites 27
1.10. Scopes and objectives of the present investigation .......... 32
1.11. Plans of the present work ......................................... 33

References ..................................................................... 35

Chapter 2

Vegetable oil based hyperbranched polyurethanes

2A. Effect of Different Vegetable Oils ............................... 46
2A.1. Introduction ......................................................... 46
2A.2. Experimental ....................................................... 47
  2A.2.1. Materials ....................................................... 47
  2A.2.2. Preparation of monoglyceride of the oil .................. 48
  2A.2.3. Synthesis of hyperbranched polyurethane ............... 49
2A.2.4. Instrumentation
2A.2.5. Shape memory behavior testing

2A.3. Results and discussion
2A.3.1. Infrared spectroscopic study
2A.3.2. XRD study
2A.3.3. NMR study
2A.3.4. Thermal property
2A.3.5. Mechanical property
2A.3.6. Shape memory study

2A.4. Conclusion

2B. Effect of vegetable oil content
2B.1. Introduction

2B.2. Experimental
2B.2.1. Materials
2B.2.2. Synthesis of hyperbranched polyurethane
2B.2.3. Instrumentation

2B.3. Results and discussion
2B.3.1. Infrared spectroscopic study
2B.3.2. NMR study
2B.3.3. XRD study
2B.3.4. Morphological study
2B.3.5. Thermal property
2B.3.6. Mechanical property
2B.3.7. Chemical resistance
2B.3.8. Shape memory property

2B.4. Conclusion

2C. Effect of multifunctional component
2C.1. Introduction

2C.2. Experimental
2C.2.1. Materials
2C.2.2. Preparation of hyperbranched polyurethane 71
2C.2.3. Instrumentation 72

2C.3. Results and discussion 72
2C.3.1. Infrared spectroscopic study 72
2C.3.2. NMR study 73
2C.3.3. X-ray diffraction study 74
2C.3.4. Thermal property 75
2C.3.5. Mechanical property 77
2C.3.6. Shape memory property 78
2C.3.7. Chemical resistance 79

2C.4. Conclusion 80
References 81

Chapter 3

Modified hyperbranched polyurethane

3.1. Introduction 86
3.2. Experimental 87
3.2.1. Materials 87
3.2.2. Preparation of hyperbranched polyurethane 87
3.2.3. Modification of hyperbranched polyurethane with epoxy resin 87
3.2.4. Broth culture technique for biodegradation 88
3.2.5. Instrumentation 88
3.3. Results and discussion 89
3.3.1. Curing study 89
3.3.2. Infrared spectroscopic study 91
3.3.3. X-ray diffraction study 91
3.3.4. Morphology study 93
3.3.5. Thermal property 94
3.3.6. Mechanical property 96
3.3.7. Chemical resistance 97


Chapter 4

Hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites

4A. Hyperbranched thermoplastic polyurethane/Fe$_3$O$_4$ nanocomposites
4A.1. Introduction
4A.2. Experimental
   4A.2.1. Materials
   4A.2.2. Preparation of Fe$_3$O$_4$ nanoparticles
   4A.2.3. Preparation of hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposite
   4A.2.4. Instrumentation
4A.3. Results and discussion
   4A.3.1. FTIR study
   4A.3.2. X-ray diffraction study
   4A.3.3. TEM study
   4A.3.4. Thermal property
   4A.3.5. Mechanical property
   4A.3.6. Magnetic property
   4A.3.7. Shape memory property
4A.4. Conclusion

4B. Hyperbranched polyurethane/Fe$_3$O$_4$ thermosetting nanocomposites
4B.1. Introduction
4B.2. Experimental
   4B.2.1. Materials
   4B.2.2. Preparation of Fe$_3$O$_4$ nanoparticles
   4B.2.3. Preparation of hyperbranched polyurethane/Fe$_3$O$_4$ thermosetting nanocomposite

References
Chapter 5

Hyperbranched polyurethane/MWCNT nanocomposites

5A. Hyperbranched thermoplastic polyurethane/triethanolamine functionalized MWCNT nanocomposites
5A.1. Introduction 132
5A.2. Experimental 133
5A.2.1. Materials 133
5A.2.2. Modification of MWCNT 133
5A.2.3. Preparation of hyperbranched polyurethane/TEA-f-MWCNT nanocomposites 133
5A.2.4. Instrumentation 134
5A.3. Results and discussion 134
5A.3.1. FTIR study 134
5A.3.2. Raman spectroscopic study 136
5A.3.3. X-ray diffraction study 136
5A.3.4. Morphology study 137
5A.3.5. Thermal property 139
5A.3.6. Mechanical property 139
5A.3.7. Shape memory property 142
5A.4. Conclusion 144

5B. Hyperbranched thermosetting polyurethane/triethanolamine functionalized MWCNT nanocomposites 145
5B.1. Introduction 145
5B.2. Experimental 146
   5B.2.1. Materials 146
   5B.2.2. Modification of MWCNT 146
   5B.2.3. Preparation of hyperbranched thermosetting polyurethane/TEA-f-MWCNT nanocomposites 146
   5B.2.4. Instrumentation 146
5B.3. Results and discussion 147
   5B.3.1. Curing study 147
   5B.3.2. FTIR study 147
   5B.3.3. XRD study 149
   5B.3.4. Morphology study 150
   5B.3.5. Thermal property 152
   5B.3.6. Mechanical property 152
   5B.3.7. Shape memory property 155
5B.4. Conclusion 156
References 157

Chapter 6

Fe₃O₄ nanoparticles decorated MWCNT/hyperbranched polyurethane nanocomposites

6A. Fe₃O₄ nanoparticles decorated MWCNT/hyperbranched polyurethane thermoplastic nanocomposites 160
6A.1. Introduction 160
6A.2. Experimental 160
6A.2.1. Materials 160
6A.2.2. Preparation of Fe$_3$O$_4$ decorated MWCNT (Fe$_3$O$_4$-MWCNT) 161
6A.2.3. Preparation of Fe$_3$O$_4$-MWCNT/hyperbranched polyurethane nanocomposites 161
6A.2.4. Instrumentation 162
6A.3. Results and discussion 162
6A.3.1. FTIR study 162
6A.3.2. Raman spectroscopic study 163
6A.3.3. X-ray diffraction study 165
6A.3.4. Morphology study 166
6A.3.5. Thermal property 168
6A.3.6. Mechanical property 169
6A.3.7. Shape memory property 170
6A.4. Conclusion 171
6B. Fe$_3$O$_4$ nanoparticles decorated MWCNT/hyperbranched polyurethane thermosetting nanocomposites 172
6B.1. Introduction 172
6B.2. Experimental 172
6B.2.1. Materials 172
6B.2.2. Preparation of Fe$_3$O$_4$-MWCNT nanohybrid 173
6B.2.3. Preparation of thermosetting hyperbranched polyurethane/Fe$_3$O$_4$-MWCNT nanocomposites 173
6B.2.4. Instrumentation 173
6B.3. Results and discussion 174
6B.3.1. Curing study 174
6B.3.2. FTIR study 175
6B.3.3. X-ray diffraction study 175
6B.3.4. Magnetic property 175
6B.3.5. Morphology study 178
6B.3.6. Thermal property 178
6B.3.7. Mechanical property 180
6B.3.8. Shape memory property 183
6B.4. Conclusion 184
References 185

Chapter 7

Conclusions and future directions

7.1. Summary and conclusions 189
7.2. Future directions 191
List of Publications 192
Conference/symposium 193
LIST OF ABBREVIATIONS AND SYMBOLS

b.p. boiling point

\( \text{cm}^3 \) cubic centimeter

\( \text{cm} \) centimeter(s)

CNTs carbon nanotubes

DSC differential scanning calorimetry

ºC degree centigrade

FTIR fourier transform infrared spectroscopy

\( F_w \) formula weight

\( g \) gram(s)

\( \text{kg} \) kilogram(s)

\( h \) hour(s)

\( H_c \) coercivity

\( m \) meter(s)

\( \text{min} \) minute(s)

\( \text{mL} \) milliliter

\( \text{mm} \) millimeter

\( \text{mol} \) mole

\( \text{m.p.} \) melting point

MPa megapascal

\( M_n \) number average molecular weight

\( M_r \) remanence magnetization

\( M_w \) weight average molecular weight

MWCNT multi walled carbon nanotubes

NMR nuclear magnetic resonance

\( \text{nm} \) nanometer(s)

OD optical density

ppm parts per million

s second(s)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>UTM</td>
<td>universal testing machine</td>
</tr>
<tr>
<td>v</td>
<td>volume</td>
</tr>
<tr>
<td>wt</td>
<td>weight</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>micrometer</td>
</tr>
<tr>
<td>$\mu$L</td>
<td>microliter</td>
</tr>
<tr>
<td>%</td>
<td>percentage</td>
</tr>
<tr>
<td>$\theta$</td>
<td>scattering angle</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1.1: Comparison of the properties of SMP and SMA
Table 1.2: Diisocyanates used for the synthesis of polyurethanes
Table 1.3: Macroglycols used for the synthesis of polyurethanes
Table 1.4: Chain extender used for the synthesis of polyurethanes
Table 2A.1: Structure and composition of fatty acid of the vegetable oil
Table 2A.2: Composition (mmol) of reactant
Table 2A.3: Mechanical properties of the hyperbranched polyurethanes
Table 2A.4: Shape memory behavior of hyperbranched polyurethanes
Table 2B.1: Composition (mol) of reactant
Table 2B.2: Mechanical properties of the hyperbranched polyurethanes
Table 2B.3: Chemical resistance as changes of weight (g) of hyperbranched polyurethanes
Table 2B.4: Shape memory properties of hyperbranched polyurethanes
Table 2C.1: Composition (mmol) of reactant
Table 2C.2: FTIR spectral data of the hyperbranched polyurethanes
Table 2C.3: Thermal properties of hyperbranched polyurethanes
Table 2C.4: Mechanical properties of the hyperbranched polyurethanes
Table 2C.5: Shape memory properties of hyperbranched polyurethanes
Table 2C.6: Chemical resistance as changes of weight (g) of hyperbranched polyurethanes
Table 3.1: Composition and curing time of modified hyperbranched polyurethane at 120 °C
Table 3.2: Mechanical properties of unmodified and modified hyperbranched polyurethanes
Table 3.3: Chemical resistance as changes of weight (g) of unmodified and modified hyperbranched polyurethanes
Table 3.4: Shape memory properties of hyperbranched polyurethane and modified hyperbranched polyurethane
Table 4A.1: Mechanical properties of hyperbranched polyurethane and the nanocomposites
Table 4A.2: Shape memory behaviors of hyperbranched polyurethane and the nanocomposites
Table 4B.1: Composition and curing time of the nanocomposites at 120 °C
Table 4B.2: Melting temperature and melting enthalpy of the thermosetting nanocomposites
Table 4B.3: Mechanical properties of hyperbranched polyurethane and the thermosetting nanocomposites
Table 4B.4: Shape memory behaviors of hyperbranched polyurethane and the nanocomposites
Table 5A.1: Mechanical properties of hyperbranched polyurethane and its nanocomposites
Table 5A.2: Shape memory behaviors of hyperbranched polyurethane and its nanocomposite at different microwave output powers*
Table 5B.1: Composition and curing time of the nanocomposites at 120 °C
Table 5B.2: Mechanical properties of hyperbranched polyurethane and the nanocomposites
Table 6A.1: Mechanical properties of hyperbranched polyurethane and its nanocomposites
Table 6B.1: Compositions and curing time of the nanocomposites at 120 °C
Table 6B.2: Thermal behaviors of the hyperbranched polyurethane and its nanocomposites
Table 6B.3: Mechanical properties of hyperbranched polyurethane and its thermosetting nanocomposites