

## TABLE OF CONTENTS

---

Abstract .....	9
Resumen .....	11
Resum .....	13
Motivation .....	15
Aim and thesis outline .....	17
Overview of the thesis .....	19
List of contributions of this thesis .....	20
Table of contents .....	23

### CHAPTER 1. INTRODUCTION TO SHAPE-MEMORY POLYMERS

1. Shape-memory polymers (SMPs) .....	33
1.1. General concept .....	33
1.2. Thermally activated shape-memory polymers .....	36
1.3. Molecular mechanism of the shape-memory effect and thermomechanical characterization .....	36
1.4. Types of shape-memory polymers .....	39
1.5. Biomedical applications of shape-memory polymers .....	43
2. Biodegradable shape-memory polymers .....	47
2.1. Soft biodegradable polymers (elastomers) .....	49
2.1.1. Physically crosslinked (Thermoplastic) elastomers .....	50
2.1.1.1. Tailoring the shape-memory effect .....	51
2.1.2. Chemically crosslinked elastomers .....	53
2.1.2.1. Poly(polyol sebacate) family .....	53
2.2. Limitations of SMPs for biomedical applications .....	57
3. Electrospinning .....	63
3.1. Mechanism and set-up .....	63

3.2. Electrospinning of biodegradable nanofibers .....	66
4. Shape-memory polymer composites (SMPCs) .....	69
4.1. Biodegradable nanocomposites with shape-memory effect in the biomedical field .....	71
4.2. Nanofillers as reinforcement of biodegradable elastomeric matrices .....	73
4.2.1. Cellulose nanocrystals as potential filler for biodegradable elastomeric matrices .....	74
4.2.2. Nanofibers as potential filler for biodegradable elastomeric matrices .....	76
5. References in this chapter .....	79

## **CHAPTER 2. WORKFLOW, MATERIALS, METHODS AND EXPERIMENTAL TECHNIQUES**

1. Experimental Workflow .....	103
1.1. Selection of the polymer matrix .....	104
1.2 Selection of the fillers .....	105
1.3. Filler incorporation .....	106
1.4. Characterization of nanocomposites .....	106
2. Materials and methods .....	107
2.1. Materials .....	107
2.2. Sample preparation methods .....	109
2.2.1. Synthesis of poly(mannitol sebacate) pre-polymers .....	109
2.2.2. Isolation of cellulose nanocrystals (CNCs) .....	111
2.2.3. Production of nanofiber mats .....	112
<i>2.2.3.1. Implementation of solution, electrospinning parameters and PLA:HA ratios to obtain neat PLA and PLA:HA mats .....</i>	112

<i>2.2.3.2. Experimental procedure</i>	.....	115
<i>2.2.4. Preparation of nanoparticulate reinforced composites (PMS/CNC)</i>	.....	117
<i>2.2.5. Preparation of electrospun nanofiber reinforced composites (PMS/NF-PLA)</i>	.....	118
<b>3. Experimental techniques</b>	.....	<b>123</b>
<i>3.1. Gel permeation chromatography (GPC)</i>	.....	124
<i>3.1.1. Fundamentals</i>	.....	124
<i>3.1.1.1. Detection system</i>	.....	126
<i>3.1.2. Calculation methods and experimental procedure</i>	.....	129
<i>3.2. Nuclear magnetic resonance spectroscopy (NMR)</i>	.....	131
<i>3.2.1. Fundamentals</i>	.....	131
<i>3.2.1.1. Structural determination</i>	.....	134
<i>3.2.2. Experimental procedure</i>	.....	136
<i>3.3. Fourier transform infrared analysis (FT-IR)</i>	.....	137
<i>3.3.1. Fundamentals</i>	.....	137
<i>3.3.2. Experimental procedure</i>	.....	142
<i>3.4. X-ray diffraction (XRD)</i>	.....	143
<i>3.4.1. Fundamentals</i>	.....	143
<i>3.4.2. Calculation methods</i>	.....	145
<i>3.4.3. Experimental procedure</i>	.....	146
<i>3.5. Scanning electron microscopy (SEM)</i>	.....	147
<i>3.5.1. Fundamentals</i>	.....	147
<i>3.5.2. Experimental procedure</i>	.....	149
<i>3.6. Transmision electron microscopy (TEM)</i>	.....	149
<i>3.6.1. Fundamentals</i>	.....	149
<i>3.6.2. Experimental procedure</i>	.....	152
<i>3.7. Differential scanning calorimetry (DSC)</i>	.....	153
<i>3.7.1. Fundamentals</i>	.....	153

3.7.2. Calculation methods	.....	154
3.7.3. Experimental procedure	.....	156
3.8. Thermogravimetry (TGA)	.....	157
3.8.1. Fundamentals	.....	157
3.8.2. Experimental procedure	.....	159
3.9. Tensile testing	.....	159
3.9.1. Fundamentals	.....	159
3.9.2. Experimental procedure	.....	161
3.10. Dynamical mechanical thermal analysis (DMTA)	.....	162
3.10.1. Fundamentals	.....	162
3.10.2. DMTA instrumentation	.....	167
3.10.3. Experimental procedure	.....	168
3.10.4. DMTA set-up for shape-memory characterization	.....	169
3.11. Swelling and degradation studies in simulated body fluid (SBF)	.....	170
3.12. Conductometric titration	.....	172
4. References in this chapter	.....	175

### **CHAPTER 3. CONTRIBUTION I**

<i>Mechanical properties and degradation studies of Poly(mannitol sebacate)/Cellulose nanocrystal nanocomposites</i>	.....	179
<i>Supporting Information: Mechanical properties and degradation studies of Poly(mannitol sebacate)/ Cellulose nanocrystal nanocomposites</i>	.....	217

## **CHAPTER 4. CONTRIBUTION II**

<i>Electrospinning of biodegradable Polylactice/Hydroxyapatite nanofibers: study on the morphology, crystalline structure and thermal stability</i> .....	225
---	-----

## **CHAPTER 5. CONTRIBUTION III**

<i>Mechanical and shape-memory properties of Poly(mannitol sebacate)/Cellulose nanocrystal nanocomposites</i> .....	249
<i>Supporting Information: Mechanical and shape-memory properties of Poly(mannitol sebacate)/Cellulose nanocrystal nanocomposites</i> .....	279

## **CHAPTER 6.I CONTRIBUTIONS IV AND V**

<i>A comparative study of the mechanical, shape-memory, and degradation properties of fiber- and particulate-reinforced Poly(mannitol sebacate) nanocomposites</i> .....	295
<i>Supporting Information: A comparative study of the mechanical, shape-memory, and degradation properties of fiber- and particulate- reinforced Poly(mannitol sebacate) nanocomposites</i> .....	331

## **CHAPTER 6.II COMPLEMENTARY SHAPE-MEMORY STUDIES**

<i>Complementary shape-memory studies</i> .....	337
---	-----

## **CHAPTER 7. CONCLUSIONS AND FUTURE RESEARCH LINES**

1. Conclusions .....	347
2. Future research lines .....	353

## **GLOSSARIES**

List of figures .....	357
List of tables .....	365

## **EPILOGUE**

Agradecimientos y dedicatorias .....	369
--------------------------------------	-----