## **Contents**

Abstract Resumen		
		Resum
1. Introduction	1	
1.1 Dentin	1	
1.1.1 Structure and composition	1	
1.1.2 Dentinogenesis and dentinogenic responses to injury	4	
1.1.3 Dentin/pulp therapies	6	
1.1.4. Tissue engineering applied to the regeneration of pulp and de-	entin in	
endodontics	7	
1.2 Bioactivity	11	
1.2.1 Requirement for bone bonding: in vivo bioactivity	11	
1.2.2 Biomimetic in vitro test for predicting the in vivo bioactivity	12	
1.2.3 Mechanism of apatite formation on bioactive glasses	16	
1.2.4 Biomimetic approaches to bioactive materials for hard tissue		
engineering: bioactive hybrids and bioactive surface functionalization	20	
1.3 Polymer/silica nanohybrids obtained by sol-gel process	24	
1.4 Purpose of the study	29	
2. Materials and methods	31	
2.1 Materials	31	
2.1.1 Bulk samples	31	
2.1.2 Scaffolds of tubular parallel channels	34	
2.2 In vitro test of bone bonding ability in SBF	35	
2.3 Surface treatments prior to the immersion in SBF	37	
2.4 Experimental techniques	38	
2.4.1 Fourier-Transform Infrared Spectrometry (FTIR)	38	
2.4.2 Scanning Electron Microscopy (SEM)	38	
2.4.3 Energy Dispersive X-ray Spectroscopy (EDS)	38	

	2.4.4 Thermogravimetric Analysis (TGA)	39
	2.4.5 Pyrolysis	39
	2.4.6 Specific volume	39
	2.4.7 Porosity	40
	2.4.8 Transmission Electron Microscopy (TEM)	41
	2.4.9 Solvent uptake	41
	2.4.10 Contact angle measurements	42
	2.4.11 Differential Scanning Calorimetry (DSC)	43
	2.4.12 Dynamic-Mechanical Spectroscopy (DMS)	44
	2.4.13 Compression tests	44
	2.4.14 X-Ray Diffraction (XRD)	44
3.	. Results	45
	3.1 Structure of SiO <sub>2</sub> in the P(EMA-co-HEA) matrix	45
	3.1.1 Fourier-Transformed Infrared Analysis	45
	3.1.2 Energy Dispersive X-ray Spectroscopy	48
	3.1.3 Thermogravimetric Analysis	49
	3.1.4 Pyrolysis	51
	3.1.5 Transmission Electron Microscopy	52
	3.1.6 Solvent uptake	54
	3.2 Characterization of P(EMA-co-HEA)/SiO <sub>2</sub> nanocomposites	56
	3.2.1 Dynamic-Mechanical Spectroscopy	56
	3.2.2 Specific volume	59
	3.2.3 Surface tension	60
	3.2.4 Differential Scanning Calorimetry	61
	3.2.5 Compression tests	63
	3.3 Bioactivity of P(EMA-co-HEA)/SiO <sub>2</sub> nanocomposites	65
	3.3.1 Characterization of the apatite formed on the substrates in SBF	65
	3.3.2 Structural changes of the nanocomposites in the SBF	76
	3.4 Surface treatments as a means of reducing the apatite nucleation	
	induction times	81
	3.4.1 Surface structural changes of the substrates due to the NaOH treatment	81
	3.4.2 Characterization of the apatite formed on the NaOH-treated substrates	84
	3.4.3 Surface structural changes of the substrates due to the CaP treatment	86
	3.4.4 Characterization of the apatite formed on the CaP-treated substrates	89
	3.5 Bioactive P(EMA-co-HEA)/SiO <sub>2</sub> scaffolds mimicking natural dentin	
	structure	91
	Del de Contra C	

3.5.1 Structure of the P(EMA-co-HEA)/SiO nanohybrid scaffolds	91
$3.5.2$ Characterization of the nanohybrid P(EMA- $co\text{-HEA})/\text{SiO}_{\text{\tiny s}}$ scaffolds	93
$3.5.3$ Bioactivity of the P(EMA- $co\mbox{-HEA})/15$ wt% SiO $_{\mbox{\tiny ,}}$ nanohybrid scaffolds	95
4. Discussion	99
4.1 On the structure of $\mathrm{SiO}_2$ in the P(EMA- $co$ -HEA) polymeric matrix	99
4.2 Characterization of P(EMA- $co$ -HEA)/SiO $_2$ nanocomposites	103
4.3 Bioactivity of P(EMA- $co$ -HEA)/SiO $_2$ nanocomposites	107
4.3.1 On the morphology and composition of the apatite formed on the	.e
substrates in SBF	107
4.3.2 On the structural changes of the nanohybrids when immersed in SBF	111
4.4 Surface treatments as a means of reducing the apatite nucleation	n
induction times	115
$4.5~\mathrm{P(EMA-}\textit{co-HEA})/\mathrm{SiO_2}$ scaffolds mimicking natural dentin structure:	
structure, characterization and bioactivity	118
5. Conclusions	121
6. Appendix: Biological response	129
6.1 Culture in vitro	129
6.2 Subcutaneous implants in vivo	132
References	135
Glossary	151