JUST	IFICATION AND INTEREST OF THE WORK	1
INTR	ODUCTION	9
I.	Edible films and coatings to prevent the detrimental effect	
	of oxygen on food quality: possibilities and	
	limitations	23
II.	Recent patents on the use of antioxidant agents in food	63
OBJE	CTIVES	119
RESU	LTS AND DISCUSSION	
III.	Effect of basil and thyme essential oils and	
	homogenization conditions on properties of chitosan based	
	films	123
IV.	Pork meat product preservation by using chitosan films	
	containing essential oils	165
V.	Properties of wheat starch film-forming dispersions and	
	films as affected by chitosan addition	213

v 1.	Effect of antioxidant incorporation on the properties of	
	wheat starch-chitosan films	269

i

VII.	Physical, structural and antimicrobial properties of poly	
	vinyl alcohol-chitosan biodegradable films	305
VIII.	Physicochemical and antimicrobial properties of extruded	
	polylactic acid films as affected by chitosan	
	addition	349
CON	CLUSIONS	391

ii

TABLES

Table I.1. Oxygen permeability of edible and synthetic films	29
Table I.2. Measurement of the antioxidant capacity of	
disintegrated edible films	34
Table I.3. Peroxide value (PV) development in sunflower oil	
unprotected, protected with aluminium foil or with sodium	
caseinate (SC) films incorporated with cinnamon (SC-C) or ginger	
(SC-G) essential oils	40
Table I.4. Application of antioxidant edible films to nuts	45
Table I.5. Application of antioxidant edible films to meat and fish	
products	48
Table I.6. Application of antioxidant edible films to fruits and	
vegetable products	50
Table II.1. Composition of some essential oils	82
Table III.1. Average diameter $d_{3,2}$, maximum peak in size	
distributions and ζ -potential. Average values and standard	
deviations, in brackets	142

iii

Table III.2. Water vapour permeability (WVP) and Gloss (60°) of
the films at 58-100%RH gradient and 5°C. Average values and
standard deviations, in brackets
Table IV.1: Thickness (mm), oxygen transference rate (cm ³ m ⁻²
day ⁻¹) and Oxygen permeability (OP, cm ³ mm m ⁻² atm ⁻¹ day ⁻¹), at
refrigerated conditions and intermediate relative humidity (10°C-
58%RH) of all film formulations and both homogenization
procedures (rotor-stator: H1; or additionally microfluidized: H2).
Average values and standard deviations in
brackets 188
brackets
Table IV.2. Oxygen transference rate $(cm^3 m^{-2} day^{-1})$ and oxygen
Table IV.2. Oxygen transference rate $(cm^3 m^{-2} day^{-1})$ and oxygen permeability $(cm^3 mm m^{-2} atm^{-1} day^{-1})$ of films formulated with
Table IV.2. Oxygen transference rate $(\text{cm}^3 \text{ m}^{-2} \text{ day}^{-1})$ and oxygen permeability $(\text{cm}^3 \text{ mm m}^{-2} \text{ atm}^{-1} \text{ day}^{-1})$ of films formulated with pure chitosan (CH), chitosan with basil essential oil 1:1 w/w
Table IV.2. Oxygen transference rate (cm ³ m ⁻² day ⁻¹) and oxygen permeability (cm ³ mm m ⁻² atm ⁻¹ day ⁻¹) of films formulated with pure chitosan (CH), chitosan with basil essential oil 1:1 w/w (CH:B _{1.0}) and chitosan with thyme essential oil 1:1 w/w (CH:T _{1.0}).
Table IV.2. Oxygen transference rate (cm ³ m ⁻² day ⁻¹) and oxygenpermeability (cm ³ mm m ⁻² atm ⁻¹ day ⁻¹) of films formulated withpure chitosan (CH), chitosan with basil essential oil 1:1 w/w(CH:B _{1.0}) and chitosan with thyme essential oil 1:1 w/w (CH:T _{1.0}).Averagevaluesandstandarddeviationsin

iv

formulations and homogenization procedures. Average values and	
standard deviations in brackets. Initial conditions are in the	
text	196
Table V.1. ζ-potential and rheological parameters (K, n and	
apparent viscosity at 100s ⁻¹) of all FFD	234
Table V.2. Thickness, gloss at 60° and roughness parameters (Ra,	
Rq and ISAD) of the films	240
Table V.3. Tensile properties (EM, TS and E%) of all films	
equilibrated at 58% RH. Mean values and 95% LSD intervals in	
brackets	246
Table V.4. Moisture content (MC) of films stored at 5°C-58%RH	
and 25°C-58%RH. Water vapour permeability (WVP) of the films	
at 58-100% RH and 5°C and 25°C	252
Table V.5. Oxygen permeability (OP) of the films at 58-100% RH	
and 10°C and 25°C	254
Table VI.1. Roughness parameters (Ra, Rq and ISAD) and gloss	
at 60° of the films. Mean values and standard deviation in	
brackets	291

۷

Table VI.2. Lightness (L^*) , hue (h^*_{ab}) , chroma (C^*_{ab}) and	
whiteness index (WI) values of the film. Average values and	
standard deviations in brackets	293
Table VI.3. Tensile properties (Elastic modulus: EM, tensile	
strength: TS and deformation: E %, at break) and thickness of all	
films equilibrated at 58% RH. Mean values and standard	
deviations in brackets	296
Table VI.4. Moisture content (MC, g water/g dry film) of films	
equilibrated at 25°C-53% RH. Water vapor permeability (WVP,	
g•mm•kPa ⁻¹ •h ⁻¹ •m ⁻²) of the films at 58–100% RH and 25°C and	
Oxygen permeability (OP, $cm^3 \cdot mm^{-2} \cdot atm^{-1} \cdot day^{-1}$) at 25°C-53%	
RH. Mean values and standard deviation in brackets	298
Table VI.5. Trolox equivalent antioxidant capacity (TEAC) of the	
incorporated antioxidant compounds, expressed as the amount	
(mg) of the compound which gives the same absorbance reduction	
as 1mM Trolox solution	299

vi

Table VII.1. Thickness, tensile properties (E_{young} , TS and E%)	
and WVP of the films. Average values and standard deviations, in	
brackets. The same superscript means homogeneous group in LSD	
test	320
Table VII.2. Thermal characteristics of PVA, CH and PVA:CH	
blend films	336
Table VIII.1. Thermal properties of pure PLA and PLA:CH	
composite films (first heating scan): Glass transition temperature	
(T_g) ; crystallization temperature (T_c) ; enthalpy of	
crystallization (ΔH_c); Melting temperature (Tm); Enthalpy of	
melting (ΔH_m); crystallinity degree (X)	373
Table VIII.2. Tensile properties and water vapour permeability	
(WVP) at 10°C and 58-100%RH gradient of pure PLA and	
PLA:CH composite films. Average values and standard	
deviations, in brackets	376

vii

FIGURES

Figure I.1. Methacrylate cell used to test the antioxidant activity	
of stand-alone films	38
Figure II.1. Natural antioxidant solid line black plant extract	68
Figure II.2. Chemical structure of α , β , γ and δ tocopherols	72
Figure II.3. Flavone (2-phenyl-1,4-benzopyrone) skeleton	73
Figure II.4. Chemical structure of resveratrol	76
Figure II.5. Chemical structure of anthocyanins	77
Figure II.6. Chemical structure of some carotenoids: β -carotene,	
cryptoxanthin and lycopene	79
Figure II.7. Chemical structure of chitosan	86
Figure III.1. Particle size distribution in terms of volume of film-	
formulations with basil (B) or thyme (T) essential oils, at 1%	
concentration in the film-forming dispersion	138
Figure III.2. Typical flow curves, at 25°C, of the film forming	
dispersions homogenised in rotor-stator (H1: dashed lines) or	
additionally microfluidized (H2: continuous lines)	146

viii

Figure III.3. Scanning electron microscopy micrographs of the	
cross section of films submitted to H1 and H2 homogenization	
process	149
Figure III.4. Typical true stress (σ) vs. Hencky strain (ϵ_{H}) curves	
obtained in tensile tests carried out on some composite films	
submitted to H1 (dotted lines) and H2 (solid lines)	
homogenization processes	153
Figure III.5. Mechanical properties of the films: a)Elastic	
modulus b)tensile strength and c)percentage of elongation (%E) at	
break. Mean values and 95% LSD intervals	154
Figure IV.1. Progression of the peroxide value (PV) of fat	
samples covered with the edible films (CH = chitosan, CH:B =	
chitosan and basil essential oil 1:1 w/w, CH:T = chitosan and	
thyme essential oil 1:1 w/w), and those unprotected, over storage	
at (a) 40°C and 43%HR and (b) 40°C and 83%RH. The dotted line	
represents the initial PV of the fat. Mean values and standard	
deviation. Different letters (^{a, b, c}) indicate significant differences	
(p<0.05)	193

ix

Figure IV.2. Microbial counts of minced pork meat samples	
coated with chitosan-based edible films. Evolution during storage	
at 10°C. Mean values and 95% LSD intervals. Control = non-	
coated samples	198
Figure IV.3. Microbial counts of minced pork meat samples	
inoculated with L. innocua or E. coli coated with chitosan-based	
edible films. Evolution during storage at 10°C. Mean values and	
95% LSD intervals. Control = non-coated samples	200
Figure V.1. Typical ζ -potential distributions of pure polymers and	
CH-WS film-forming dispersions. CH: chitosan. WS: wheat	
starch. The percentage of each polymer in the film-forming	
dispersion is indicated as a subscript	231
Figure V.2. Scanning electron microscopy (SEM) images of	
cross-sections of the films. CH: chitosan. WS: wheat starch. The	
percentage of each polymer in the film-forming dispersion is	
indicated as a subscript	237
Figure V.3. AFM images of surface topography of films from	
pure polymers and selected CH-WS blends. CH: chitosan. WS:	

х

wheat starch. The percentage of each polymer in the film-forming	
dispersion is indicated as a subscript	239
Figure V.4. Typical true stress (σ) vs. Hencky strain (ϵ_{H}) curves	
obtained in tensile tests carried out on pure biopolymer and WS-	
CH blend films a) after 7 days of storage, b) after 90 days of	
storage. CH: chitosan. WS: wheat starch. The percentage of each	
polymer in the film-forming dispersion is indicated as a	
subscript	242
Figure V.5. Effect of storage time on mechanical properties of	
pure wheat starch films. Mean values and standard deviation.	
Different letters indicate 95% significant differences	249
Figure V.6: Total aerobial and coliform counts of non-coated	
minced pork samples (control) and samples coated with WS, CH	
and WS-CH blend films. Mean values and 95% LSD intervals.	
Dashed line indicates initial counts in minced meat samples. CH:	
chitosan. WS: wheat starch. The percentage of each polymer in	
the film-forming dispersion is indicated	256

xi

Figure VI.1. Scanning electron microscopy micrographs of the	
film surface	288
Figure VI.2. Scanning electron microscopy micrographs of the	
cross-sections of the films	289
Figure VI.3. Typical AFM images of the surface topography of	
the films	290
Figure VI.4. Typical spectra of internal transmittance (Ti) of the	
films	294
Figure VII.1. Field emission scanning electron microscopy	
(FESEM) images of cross-sections of the films. PVA: Polyvinyl	
alcohol, CH: chitosan	322
Figure VII.2a. FTIR spectra for pure PVA, pure CH and	
PVA:CH blend films	325
Figure VII.2b. UV-VIS spectra for pure PVA and PVA:CH	
blend films	326
Figure VII.3. Typical true stress (σ) vs. Hencky strain (ϵ_{H}) curves	
obtained in tensile tests carried out on pure PVA, pure CH and	
PVA:CH blend films	327

xii

Figure VII.4. a) TG and b) DTG typical curves of pure PVA, pure	
CH and PVA:CH blend films	333
Figure VII.5. DSC thermograms a) Cooling scan and b) Second	
heating scan for pure PVA and PVA:CH blend films	334
Figure VII.6. Microbial counts of minced pork meat samples	
coated with PVA:CH films after 7 days storage at 10°C. Mean	
values and 95% LSD intervals. Control = non-coated samples.	
Different letters indicate significant differences (p<0.05) due to	
film formulation (^{a, b, c})	338
Figure VIII.1. Images of pure PLA films and PLA:CH composite	
films. PLA: Polylactic acid, CH: chitosan. The percentage of each	
polymer is indicated as a subscript	363
Figure VIII.2. UV-VIS spectra of pure PLA and PLA:CH	
composite films. PLA: Polylactic acid, CH: chitosan. The	
percentage of each polymer is indicated as a subscript	364
Figure VIII.3. Field emission scanning electron microscopy	
(FESEM) images of different granulometries of chitosan: a) G1	
and b) G2	365

xiii

Figure VIII.4a. Field emission scanning electron microscopy	
images of the surface of PLA and PLA:CH composite films.	
Polylactic acid, CH: chitosan. The percentage of each polymer in	
the film is indicated as a subscript	367
Figure VIII.4b. Scanning electron microscopy images of the	
cross-sections of PLA and PLA:CH composite films. Polylactic	
acid, CH: chitosan. The percentage of each polymer in the film is	
indicated as a subscript	368
Figure VIII.5. a) TG and b) DTG curves of PLA and different	
PLA:CH composite films. PLA: Polylactic acid, CH: chitosan.	
The percentage of each polymer is indicated as a subscript	370
Figure VIII.6. First heating DSC scan for pure PLA and PLA:CH	
composite films. PLA: Polylactic acid, CH: chitosan. The	
percentage of each polymer is indicated as a subscript	372
Figure VIII.7. Typical true stress (σ) vs. Hencky strain ($\epsilon_{\rm H}$)	
curves obtained in tensile tests carried out on PLA and PLA:CH	
composite films. PLA: Polylactic acid, CH: chitosan. The	
percentage of each polymer is indicated as a subscript	374

xiv

Figure VIII.8. Microbial counts of minced pork meat samples	S:
coated with PLA and PLA:CH after 10 days of cold-storage. Mean	
alues and 95% LSD intervals. Control = non-coated samples.	378
Initial count is indicated by the dashed line	

xv