## **UNIVERSIDAD INTERNACIONAL MENÉNDEZ PELAYO**





# CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS INSTITUTO DE CIENCIA Y TECNOLOGÍA DE POLÍMEROS

# DESARROLLO DE NUEVOS NANOCOMPUESTOS BIODEGRADABLES BASADOS EN MEZCLAS DE ÁCIDO POLILÁCTICO Y CAUCHO NATURAL

## **NATACHA BITINIS**

Ingeniero Químico

**Tesis doctoral** 

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# DEVELOPMENT OF NEW BIODEGRADABLE NANOCOMPOSITES BASED ON POLY(LACTIC ACID)/NATURAL RUBBER BLENDS

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### TABLE OF CONTENTS

Table of contents	i
List of symbols and abbreviations	vii
List of figures	xi
List of tables	xvii
Abstract	xix
Sumario	xxi
Chapter I. Introduction	1
I.1. Context of the thesis	3
I.2. Objectives of the study	4
I.3. Overview of the thesis	6
Chapter II. Literature review	7
II.1. Biopolymers	9
II.2. Poly(lactic acid) (PLA)	11
II.2.1. Production process	11
II.2.2. PLA properties	13
II.2.2.1. PLA strengths	13
II.2.2.2. PLA weaknesses	16
II.3. Improvement of the mechanical properties of PLA	19
II.3.1. Addition of plasticisers	19
II.3.2. Copolymerisation	21
II.3.3. Blending with other polymers	22
II.3.3.1. Blending with biodegradable polymers	22
II.3.3.2. Blending with non-biodegradable petroleum based polymers	25
II.3.3.3. Blending with elastomers	25
II.3.4. Blending with natural rubber (NR)	26

II.4. PLA bionanocomposites	29
II.4.1. Nanoparticle classifications	29
II.4.2. Methods of preparation of PLA nanocomposites	35
II.4.2.1. PLA layered silicate nanocomposites	35
II.4.2.2. PLA bionanoparticle nanocomposites	37
II.4.3. PLA bionanocomposite properties	39
II.4.3.1. Transparency	39
II.4.3.2. Rheology	40
II.4.3.3. Dynamic mechanical properties	42
II.4.3.4. Crystallisation properties	44
II.4.3.5. Mechanical properties	46
II.4.3.6. Gas barrier properties	48
II.4.3.7. Thermal stability	49
II.4.3.8. Biodegradation	50
II.4.3.9. Flame retardant properties	51
II.4.3.10. Other nanoparticles and properties	51
II.4.4. Combining "toughening agent" and nanoparticles	53
Chapter III. Structure and properties of PLA/NR blends	57
III.1. Summary	59
III.2. Introduction	59
III.3. Experimental section	60
III.3.1. Materials and sample preparation	60
III.3.2. Characterisation	60
III.4. Results and discussion	62
III.4.1. Optimisation of processing	62
III.4.1.1. Morphology of the blends	62
III.4.1.2. Polymer degradation	65

I	II.4.2. Ef	fect of NR concer	tration		
	III.4.2.1	. Morphology			
	III.4.2.2	. Crystallisation b	ehaviour		
	III.4.2.3	. Rheological proj	perties		
	III.4.2.4	. Mechanical prop	oerties		
III.5. Con	clusions				
Chapter	IV.	Physicochemica	l properties	of	PLA/NR/Organoclay
bionanoc	omposite	es			
IV.1. Sum	nmary				
IV.2. Intro	oduction				
IV.3. Exp	erimenta	l section			
Г	V.3.1. Ma	aterials and sampl	e preparation		
Г	V.3.2. Ch	naracterisation			
IV.4. Resu	ults and c	liscussion			
Г	V.4.1. Op	otimisation of pro-	cessing		
Г	V.4.2. M	orphology and loc	ation of the nano	particl	es90
Г	V.4.3. Rh	neological propert	ies		96
Г	V.4.4. Dy	ynamic mechanica	ıl analysis		
Г	V.4.5. Cr	ystallisation beha	viour		
Г	V.4.6. M	echanical properti	es		
Г	V.4.7. Ba	rrier properties			
Г	V.4.8. Th	ermal degradation	1		
Г	V.4.9. Di	sintegration in co	mposting condition	ons	
IV.5. Con	clusions				
Chapter	V.	Deformation	mechanisms	in	PLA/NR/Organoclay
bionanoc	omposite	es as revealed by	synchrotron X-r	ay sca	nttering117
V.1. Sum	mary				
V.2. Intro	duction.				

V.3. Experimental section	120
V.3.1. Materials and sample preparation	120
V.3.2. Characterisation	120
V.3.3. Time resolved wide-angle X-ray scattering (WAXS) and sn	nall-
angle X-ray scattering (SAXS) using synchrotron light	121
V.4. Results and discussion	124
V.4.1. Morphology of the materials	124
V.4.2. Microstructure deformation mechanism as revealed by simultane WAXS, SAXS and stress-strain experiments	eous 125
V.4.3. Nanoclay orientation as revealed by intermediate angle X scattering	-ray 132
V.4.4. Orientation of the polymer chains as revealed by WAXS	133
V.4.5. Comparison with other montmorillonites	134
V.5. Conclusions	136
Chapter VI. Cellulose nanocrystal extraction and modifications	139
VI.1. Summary	141
VI.2. Introduction	141
VI.3. Experimental section	142
VI.3.1. Materials	142
VI.3.2. Extraction of cellulose nanowhiskers	142
VI.3.3. Grafting of n-octadecyl isocyanate	142
VI.3.4. Grafting of PLA chains by <i>in-situ</i> ring opening polymerisation.	143
VI.3.5. Characterisation	143
VI.4. Results and discussion	145
VI.4.1. Characterisation of unmodified cellulose nanowhiskers	145
VI.4.2. Surface modification: grafting of n-octadecyl isocyanate	147
VI.4.2.1. Characterisation of the grafting reaction	148
VI.4.2.2. Structural analysis of C18-g-CNC	151

VI 4.3 Surface modification: grafting of PLA chains	153
	1.50
VI.4.3.1. Characterisation of the grafting reaction	153
VI.4.3.2. Structural analysis of PLA-g-CNC	156
VI.5. Conclusions	157
Chapter VII. Preparation and properties of PLA/NR/Cellulose nanocry	stals
bionanocomposites	
VII.1. Summary	161
VII.2. Introduction	161
VII.3. Experimental section	162
VII.3.1. Materials and sample preparation	
VII.3.2. Characterisation	
VII.4. Results and discussion	164
VII.4.1. Optimisation of processing	
VII.4.2. Morphology of the bionanocomposites	
VII.4.3. Rheological properties	
VII.4.4. Dynamic mechanical analysis	171
VII.4.5. Crystallisation behaviour	
VII.4.6. Mechanical properties	
VII.4.7. Thermal degradation	
VII.4.8. Disintegration in composting conditions	
VII.5. Conclusions	180
Chapter VIII. Conclusions	
Capítulo VIII. Conclusiones	
Future work	193
References	199
List of Publications	229
Resumen	239

## LIST OF SYMBOLS AND ABBREVIATIONS

ACN	Acetylated cellulose nanocrystals
AEM	Ethylene-acrylic rubber
$CNa^+$	Cloisite <sup>®</sup> CNa <sup>+</sup>
C15A	Cloisite <sup>®</sup> C15A
C20A	Cloisite <sup>®</sup> C20A
C30B	Cloisite <sup>®</sup> C30B
CNC	Cellulose nanocrystal
C18-g-CNC	Cellulose nanocrystal grafted with long carbon chains
CNT	Carbon nanotube
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetry
EPM	Ethylene-propylene copolymer
ESEM	Environmental scanning electron microscopy
EVA	Poly(ethylene-co-vinyl acetate)
FESEM	Field emission scanning electron microscopy
IR	Isoprene rubber
LA	Lactide
LTI	Lysine triisocyanate
MCC	Microcrystalline cellulose
MFC	Microfibrillated cellulose
MI	Melt index
MMT	Montmorillonite
MWCNT	Multiwall carbon nanotube
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
PAE	Polyamide elastomer
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
PBSA	Poly(butylene succinate-co-adipate)

PCL	Poly(ɛ-caprolactone)
PE	Polyethylene
PEG	Poly(ethylene glycol)
PES	Poly(ethylene succinate)
PET	Poly(ethylene terephthalate)
PFPE	Perfluoropolyether
РНА	Polyhydroxyalkanoates
РНВ	Polyhydroxybutyrate
PLA	Poly(lactic acid)
PLA-g-CNC	Cellulose nanocrystal grafted with PLA chains
РР	Polypropylene
PPG	Poly(propylene glycol)
PS	Polystyrene
PU	Polyurethane
ROP	Ring opening polymerisation
SAXS	Small angle X-ray scattering
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TFO	Twice functionalised organoclay
TGA	Thermogravimetric analysis
TMC	Trimethylene carbonate
TPE	Thermoplastic elastomer
TPS	Thermoplastic starch
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
WAXS	Wide angle X-ray scattering

В	Slope of the downstream pressure versus time (for permeability
	measurements)
С	Content of the C element
d	basal spacing
Е	Young's modulus
E	Storage modulus (DMA)
viii	

E″	Loss modulus (DMA)
$\mathbf{f}_2$	Herman's orientation function
G′	Storage modulus (rheology)
G΄΄	Loss modulus (rheology)
Ι	Scattering intensity
I <sub>or</sub>	Oriented fraction of intensity
Κ	Viscosity ratio
$K_0$	Apparatus constant for permeability measurements
$M_{\rm v}$	Molecular weight calculated from inherent viscosity
$M_{\rm w}$	Weight average molecular weight
Ν	Content of the N element
P <sub>0</sub>	Upstream pressure (permeability measurement)
$P_{O_2}$	Gas permeability coefficient of O <sub>2</sub>
$P_{CO_2}$	Gas permeability coefficient of CO <sub>2</sub>
q	Scattering vector
t	Sample thickness
Т	Temperature
T <sub>c</sub>	Crystallisation temperature
Tg	Glass transition temperature
T <sub>m</sub>	Melt temperature
T <sub>onset</sub>	Onset degradation temperature
T <sub>dmax</sub>	$T_{max}$ of DTG curves
Tan δ	Loss tangent (E´'/E´)
x	Content of grafted chains
W	Wettability parameter
γ <sub>ij</sub>	Interfacial tension between component i and j
γi	Surface tension of component i
Ÿ	Shear rate
$\Delta H_c$	Enthalpy of crystallisation
$\Delta H_m$	Enthalpy of melting

 $\epsilon_b$  Elongation at break

η	Viscosity
η΄	Real part of the complex viscosity
η΄΄	Imaginary part of the complex viscosity
η*	Complex viscosity
20	X-ray scattering angle
$\theta_i$	Contact angle
λ	X-ray wavelength
μ	Absorption coefficient
ρ	Density
ζ <sub>b</sub>	Tensile strength at break
$arPsi_d$	Volume fraction of the dispersed phase
θ	Azimuthal angle
ω	Frequency

#### **LIST OF FIGURES**

Figure I.1. Plastics recovery in Europe for 2010.	3
Figure II.1. Classification of the different types of biopolymers.	9
Figure II.2. Constitutional unit of PLA.	11
Figure II.3. PLA production process.	12
Figure II.4. PLA transparency. (a) Percent transmission versus wavelength of PLA	
and other commodity plastics and (b) PLA bottle	13
Figure II.5. (a) PLA hydrolysis and molecular weight loss and (b) biodegradation of	
a PLA bottle in real composting conditions.	14
Figure II.6. Production steps of dry coagulated natural rubber.	27
Figure II.7. NR molecules.	27
Figure II.8. Classification of nanofillers depending on their dimensions in the	
nanometric range (from ISO/TS 27687)	29
Figure II.9. Layered silicate structure	30
Figure II.10. Schematic representation of (a) silicate and (b) organosilicate where R	
is the chemical unit	31
Figure II.11. Cellulose structure.	33
Figure II.12. (a) SEM images revealing a network of isolated MFC and fibrils	
aggregates and (b) TEM images of CNC extracted from microcrystalline cellulose	
(left) or from tunicat (right).	34
Figure II.13. (a) Aggregates of starch nanocrystals and (b) organisation of	
nanoplatelets (scale bar: 50 nm).	34
Figure II.14. Representation of the different types of nanocomposites depending on	
the interaction between the layered silicates and the polymer matrix	36
Figure II.15. (a) Thermogravimetric analysis at 185 °C of CNC from suspensions	
without (pH3) and with addition of NaOH (pH9) and (b) melt blended and injected	
moulded samples at 165 °C of PLA/unmodified CNC (left) and PLA/PLA-grafted-	
CNC nanocomposites (right).	39
Figure II.16. (a) Transparency measurement of PLA, PLA/bentonite and	
PLA/microcrystalline cellulose and (b) pictures of the materials.	40

Figure II.17. Frequency dependence of (a) storage modulus $G'$ and (b) complex	
viscosity $\eta^*$ for PLA/C30B 3 wt% nanocomposites at different blending times (6,	
10, 20 and 30 min)	.41
Figure II.18. Temperature dependence of storage modulus G' and tan $\delta$ for pure	
PLA and various nanocomposites at 4 wt% filler content. ODA and SBE are two	
modified montmorillonites, SAP a saponite and MEE a synthetic fluorine mica	.43
Figure II.19. DSC melting thermograms of PLA and PLA/C30B nanocomposites at	
different filler contents.	.45
Figure II.20. Polarised optical microscope images of PLLA, PLLA with 1 wt% of	
CNC and 1 wt% of sylilated CNC after 0, 5 and 10 min at 125 °C crystallisation	
from melt (scale bar: 200 µm).	.46
Figure II.21. Effect of the acetylated CNC (ACN) content on $\varepsilon_b$ , $\zeta_b$ and E for	
PLA/ACN nanocomposites (measurement carried out at 10 mm·min <sup>-1</sup> )	.48
Figure III.1. Morphology and distribution of NR droplet size in the PLA/NR blends	
for different processing temperatures (a) 160 °C, (b) 180 °C and (c) 200 °C	.64
Figure III.2. Thermal degradation of PLA and NR evaluated by TGA in air	
atmosphere for (a) dynamic condition and (b) isothermal condition at 160 °C	.65
Figure III.3. Photos taken by optical polarised microscope. Isothermal	
crystallisation (cooled from 180 °C to 130 °C) of pristine PLA at (a) 0 min,	
(b) 30 min, (c) 1 h, (d) 2 h and processed PLA at (e) 0 min, (f) 10 min, (g) 15 min	
and (h) 1 h	.67
Figure III.4. Torque evolution at 160 °C for PLA and PLA/NR 10 wt% blend	.67
Figure III.5. Photographs of films of about 150 $\mu$ m for (a) PLA and (b) PLA/NR	
blend at 10 wt%	.68
Figure III.6. Morphology and distribution of rubber droplet size in PLA/NR blends	
at different NR concentrations (a) 5 wt%, (b) 10 wt% and (c) 20 wt%.	.69
Figure III.7. DSC heating curves of PLA and PLA/NR blends (second heating	
scan)	.70
Figure III.8. Evolution of complex viscosity during isothermal crystallisation	.72
Figure III.9. Melting curves of crystallised PLA/NR blends.	.73
Figure III.10. Rheological properties of PLA and PLA/NR blends (a) $G'(\omega)$ ,	
(b) $\eta^*(\omega)$ and (c) Cole-Cole diagrams	.74
Figure III.11. Average curves of the mechanical properties of PLA and PLA/NR	
blends	.75

Figure III.12. Fractured surface of stretched materials (a) PLA and (b) PLA/NR
10 wt% blend
Figure III.13. Comparison of PLA/NR 20 wt% blend morphology before and after
compression-moulding77
Figure IV.1. Evaluation of C30B dispersion by XRD measurements as function of
(a) processing temperature at 100 rpm for 15 min, (b) rotor speed at 180 °C for 15
min and (c) blending time at 180 °C and 100 rpm
Figure IV.2. Evolution of torque during blending in the twin screw extruder for
PLA, PLA/NR blend and PLA/NR/C30B 3 wt%
Figure IV.3. Mass spectra of the acetone in which the blend was immersed at
retention times of 6.0, 6.5, 8.2 and 8.5 min
Figure IV.4. SEM images of (a) PLA/NR blend and its composites at 3 wt% of
filler (b) PLA/NR/CNa <sup>+</sup> , (c) PLA/NR/C15A and (d) PLA/NR/C30B
Figure IV.5. TEM image of PLA/NR/CNa <sup>+</sup> 3 wt%
Figure IV.6. Location of C15A at (a) 1 wt%, (b) 3 wt%, (c) 5 wt% (top) and of
C30B at (d) 1 wt%, (e) 3 wt% and (f) 5 wt% (bottom) using TEM94
Figure IV.7. XRD analysis and TEM images (at 3 wt% loading) of (a) C15A
nanocomposites and (b) C30B nanocomposites
Figure IV.8. Influence of (a) nanoclay type at 3 wt%, concentration of (b) C15A,
(c) C30B and (d) composition of the blends over the rheological properties of the
materials
Figure IV.9. NR droplet stabilisation through clay layer interface for
PLA/NR/C15A 3 wt% nanocomposite as seen by TEM99
Figure IV.10. Temperature dependence of $E'$ with (a) nanoclay type at 3 wt%,
concentration of (b) C15A and (c) C30B and (d-e) tan $\delta$ for the nanocomposites at
3 wt% of nanoclays
Figure IV.11. Dynamic crystallisation of PLA/NR/MMT nanocomposites (second
heating scan). Influence of (a) type of clays at 3 wt%, (b) C15A concentration and
(c) C30B concentration
Figure IV.12. (a) Evolution of complex viscosity during isothermal crystallisation
and (b) melting curves of crystallised materials for 3 wt% of clays104
Figure IV.13. XRD of crystallised materials after 45 minutes of isothermal
crystallisation at 110 °C

Figure IV.14. TEM images of the nanocomposites at 3 wt% loading fraction
(a) PLA/NR/C30B and (b) (PLA/C30B)/NR
Figure IV.15. Thermal stability of the bionanocomposites at 3 wt% of clay content
Figure IV.16. Disintegration of the samples at different times of composting
Figure IV.17. Evolution of disintegration of the materials with the composting time113
Figure IV.18. FT-IR spectra of (a) PLA and (b) PLA/NR/C15A as function of the
disintegration time
Figure V.1. Example of scattered intensity for an oriented sample (PLA/NR/C15A
3 wt% at 50 % strain) (a) WAXS 2D pattern: orientation of polymer chains,
(b) orientation of nanoclays and (c) SAXS 2D pattern: microvoid formation and
orientation
Figure V.2. (a) Example of SAXS analysis of 2D patterns (PLA/NR/C15A 3 wt%
at 100 % strain). (b) Integrated intensity as a function of the azimuthal angle $\varphi$ in
order to calculate the Herman's orientation function
Figure V.3. Morphology of (a) PLA/NR blend, (b) PLA/NR/C15A 3 wt%
nanocomposite and (c) location of C15A in PLA/NR/C15A 3wt% by TEM124
Figure V.4. Samples stretched at different elongations (a) PLA, (b) PLA/NR,
(c) PLA/NR/C15A 1 wt% and (d) PLA/NR/C15A 3 wt%
Figure V.5. (a) Mechanical properties of the PLA/NR blend and its
nanocomposites. The pictures present in-situ simultaneous (b) SAXS patterns and
(c) WAXS patterns at selected elongation values. The arrows indicate the stretching
direction
Figure V.6. 1D-SAXS intensity (linear scale) integrated in the equatorial region at
different elongations for (a) PLA and (b) PLA/NR blend128
Figure V.7. 1D-SAXS intensity (linear scale) integrated in the equatorial region at
different elongations for (a) PLA/NR/C15A 1 wt%, (b) PLA/NR/C15A 3 wt%
and (c) PLA/C15A 3 wt%
Figure V.8. Oriented fraction of microvoids in PLA/NR blend and its
nanocomposites
Figure V.9. Variation of total integrated intensity over $q = 0.1$ to 1.2 nm <sup>-1</sup> 131
Figure V.10. (a) X-ray scattering patterns at intermediate angles for selected
elongations and (b) Herman's orientation function variation with the elongation for
PLA/NR/C15A nanocomposites. The arrows indicate the stretching direction132

Figure V.11. Equatorial X-ray intensity (logarithmic scale) at intermediate angles
for PLA/NR/C15A 3 wt% nanocomposite
Figure V.12. Herman's orientation function versus elongation for PLA/NR blend
and its nanocomposites (from WAXS pattern)134
Figure V.13. SAXS patterns of (a) PLA/NR/CNa <sup>+</sup> and (b) PLA/NR/C30B at
3 wt% clay loading at different elongations
Figure V.14. 1D-SAXS intensity (linear scale) integrated in the equatorial region of
(a) PLA/NR/CNa <sup>+</sup> and (b) PLA/NR/C30B at 3 wt% clay loading at different
elongations136
Figure V.15. Scheme of the proposed deformation mechanisms for (a) PLA,
(b) PLA/NR blend and (c) PLA/NR/C15A bionanocomposite137
Figure VI.1. Images of (a) microcrystalline cellulose and (b) nanocrystalline
cellulose obtained through acid hydrolysis with the distribution of nanocrystal
length145
Figure VI.2. TGA analysis coupled with mass spectroscopy of CNC
Figure VI.3. FT-IR spectra of unmodified cellulose nanowhiskers, modified with
long carbon chains and secondary products
Figure VI.4. High resolution $C_{1s}$ XPS spectra of (a) CNC and (b) C18-g-CNC.
Curves inside are the deconvoluted curve fits of the spectra
Figure VI.5. TGA profile coupled with mass spectroscopy of C18-g-CNC151
Figure VI.6. TEM images of (a) unmodified CNC and (b) C18-g-CNC152
Figure VI.7. XRD of unmodified CNC and C18-g-CNC152
Figure VI.8. Contact angle measurement of a water drop onto CNC and
C18-g-CNC153
Figure VI.9. FT-IR spectra of (a) PLA, L-LA and unmodified CNC and (b) CNC
modified with PLA chains and secondary products154
Figure VI.10. Suspension in chloroform of (a) unmodified CNC, (b) unmodified
CNC + PLA and (c) PLA-g-CNC 48 hours after stopping the stirring155
Figure VI.11. TGA analysis of (a) PLA-g-CNC and (b) PLA
Figure VI.12. TEM images of (a) unmodified CNC and (b) PLA-g-CNC156
Figure VI.13. XRD of PLA-g-CNC
Figure VI.14. Contact angle measurement of a water drop onto CNC and
PLA-g-CNC

Figure VII.1 PLA/NR/CNC_E 3 wt% nanocomposites extruded at (a) 160 °C and
(b) 180 °C
Figure VII.2. XRD spectra of pristine CNC and several PLA/NR/CNC
nanocomposites
Figure VII.3. SEM images of PLA/NR blend prepared by (a) extrusion and
(b) casting combined with extrusion
Figure VII.4. Influence of blending procedure over the rheological properties of the
materials
Figure VII.5. SEM images of the PLA/NR blend filled with (a) CNC,
(b) PLA-g-CNC and (c) C18-g-CNC at 3 wt%
Figure VII.6. Morphology of PLA/NR/C18-g-CNC at (a) 1 wt%, (b) 5 wt% and
PLA/NR/PLA-g-CNC at (c) 1 wt%, (d) 5 wt%
Figure VII.7. TEM images of PLA/NR blend filled with (a) 3 wt% CNC,
(b) 5 wt% PLA-g-CNC and (c) 5 wt% C18-g-CNC at two magnifications
Figure VII.8. Influence of the concentration of (a) C18-g-CNC and (b) PLA-g-CNC
over the rheological properties of the composite171
Figure VII.9. Temperature dependence of (a) $E'$ and PLA tan $\delta$ with cellulose
nanowhisker type at 3 wt%, (b) $E'$ and NR tan $\delta$ with C18-g-CNC concentration
and (c) $E'$ and PLA tan $\delta$ with PLA-g-CNC concentration
Figure VII.10. Dynamic crystallisation of PLA/NR/CNC bionanocomposites.
Influence of (a) type of modification at 3 wt%, (b) C18-g-CNC concentration and
(c) PLA-g-CNC concentration
Figure VII.11. DTG curves of the materials at 3 wt% of nanofillers177
Figure VII.12. Disintegration of the samples at different times of composting179
Figure VII.13. Evolution of disintegration of the materials with composting time179
Figure VII.14. FT-IR spectra of (a) PLA/NR and (b) PLA/NR/C18-g-CNC as
function of the disintegration time

## LIST OF TABLES

Table II.1. Comparison of plastic costs.	.12
Table II.2. Mechanical properties of PLA depending on (a) stereochemistry,	
crystallinity and molecular weight and (b) processing	.16
Table II.3. Comparison of PLA mechanical properties with other commodity	
plastics	.17
Table III.1. Average droplet size of NR in the blend as a function of processing	
variables, for a NR concentration of 10 wt%.	.65
Table III.2. Average droplet size of NR in the blend as a function of the NR	
concentration.	.70
Table III.3. DSC data of PLA and PLA/NR blends (second heating scan)	.71
Table III.4. DSC data of PLA and PLA/NR blends after crystallisation	.73
Table III.5. Mechanical properties of PLA and PLA/NR blends.	.75
Table IV.1. Technical characteristics of the layered silicates (data provided by the	
manufacturer)	.82
Table IV.2. Compost composition	.86
Table IV.3. Average droplet size of NR in the PLA/NR/C30B nanocomposite and	
PLA Newtonian viscosity as a function of the processing variables	.87
Table IV.4. (a) Contact angle values for PLA and NR and (b) surface energies and	
interfacial tension between the components - Equilibrium location of the clays in	
the PLA/NR blend.	.92
Table IV.5. DSC data of PLA/NR/MMT nanocomposites (second heating scan)	103
Table IV.6. DSC data of PLA/NR/MMT 3 wt% nanocomposites after	
crystallisation1	104
Table IV.7. Mechanical properties of the materials. 1	106
Table IV.8. Permeability coefficients for O <sub>2</sub> and CO <sub>2</sub> of PLA/NR blend and its	
nanocomposites at 3 wt% of organoclay	109
Table IV.9. Thermal degradation data of the material, reporting the onset	
degradation temperature and the $T_{dmax}$ of DTG curves	111
Table VI.1 (a) Atom ratio and (b) assignment of binding energy (BE) and atomic	
bond contribution (%) after deconvolution of the $C_{1s}$ XPS spectra	150
Table VII.1 DSC data of PLA/NR/CNC nanocomposites (second heating scan)1	175

Table VII.2. Mechanical properties of PLA/NR/CNC nanocomposites	176
Table VII.3. Thermal degradation of the materials.	177

#### ABSTRACT

This doctoral thesis presents the development of new bionanocomposites based on poly(lactic acid) (PLA)/natural rubber (NR) blends with the objective of improving PLA properties in order to broaden its applications. Two types of nanofillers have been selected for this study, namely layered silicates (montmorillonites) and cellulose nanocrystals, and led to the production of PLA bionanocomposites with optimised properties.

The ductility of PLA has been significantly improved by melt blending with 10 wt.-% of NR, which was determined as the optimal rubber concentration. The NR phase was uniformly dispersed in the continuous PLA matrix with a droplet size of about 1  $\mu$ m. In addition, NR acted as a nucleating agent over the PLA crystallisation.

Further improvements of the blend morphology were obtained with the addition of the layered silicates, which behaved as compatibilisers. Nevertheless, different properties were obtained depending on the chemical modification of the nanofillers, which determined their affinity with both polymers and their location in the blend. While the location of the nanofillers at the interface allowed a further increase of the mechanical properties and the elongation at break, their presence in the PLA phase produced stiffer materials with improved barrier properties. A special attention was given to the mechanical properties of the nanocomposites, for which deformation mechanisms were identified by synchrotron X-ray scattering.

Furthermore, it seemed of interest to substitute the inorganic layered silicates by renewable bionanofillers in the bio-based polymer blend. For this purpose, cellulose nanocrystals were extracted from a commercial microcrystalline cellulose and chemically modified in order to increase their compatibility with the polymer matrix. The properties of these new bionanocomposites were assessed as a function of the nanowhisker modifications and concentration.

*Keywords*: polymer blend, melt processing, bionanocomposite, layered silicate, cellulose nanocrystal, surface modification, mechanical properties.

#### **SUMARIO**

La presente Tesis doctoral describe el desarrollo de nuevos bionanocompuestos basados en mezclas de ácido poliláctico (PLA)/caucho natural (NR) con el fin de mejorar las propiedades del PLA para ampliar su uso como plástico de alto consumo. Para este propósito, se emplearon dos tipos de nanocargas, silicatos laminares y nanocristales de celulosa, desarrollándose así bionanocompuestos de PLA con propiedades optimizadas.

La ductilidad del PLA se mejoró significativamente con la adición de un 10 % en peso de NR mediante mezclado en fundido. Esta concentración se definió como la concentración óptima a la cual NR está distribuido homogéneamente en la matriz de PLA, formando gotas de un tamaño medio de 1 µm. Adicionalmente, se observó que la inclusión de NR aumentaba la velocidad de cristalización del PLA, actuando como agente nucleante.

Se obtuvieron mejoras en la morfología de la mezcla con la adición de pequeñas cantidades de silicatos laminares, demostrando un efecto de compatibilización. Las propiedades de los nanocompuestos dependieron de la modificación química de las nanocargas, determinando su afinidad con los dos polímeros y su localización en la mezcla. Mientras la localización de los silicatos en la interfase entre los dos polímeros mejoró las propiedades mecánicas y la ductilidad, su presencia en la fase de PLA dio lugar a materiales más rígidos con buenas propiedades barrera. Se hizo un especial énfasis en el estudio de las propiedades mecánicas mediante medidas de dispersión de rayos-X por radiación sincrotrón.

La sustitución de estas nanocargas inorgánicas por bionanopartículas procedentes de fuentes renovables se consideró de gran interés para este estudio. Por este motivo, se extrajeron nanocristales de celulosa a partir de celulosa microcristalina comercial, que se modificaron superficialmente para obtener una buena compatibilidad con la matriz polimérica. Las propiedades de estos bionanocompuestos fueron estudiadas en función de las modificaciones y concentración de los nanocristales.

*Palabras clave*: mezclas de polímeros, procesado en fundido, bionanocompuestos, silicatos laminares, nanocristales de celulosa, modificación superficial, propiedades mecánicas.

# Chapter I. **INTRODUCTION**

#### I.1. CONTEXT OF THE THESIS

Recently, the possibility of replacing petroleum-derived synthetic polymers by natural, abundant and biodegradable products has gained much interest in both academic and industrial fields.<sup>1, 2</sup> The production of plastics in Europe reached 57 million tons in 2010, mostly divided between polyethylene, polypropylene, poly(vinyl chloride), polystyrene and poly(ethylene terephthalate).<sup>3</sup> These fossil fuel-based plastics were consumed and discarded into the environment, generating 10.4 million tons of plastic wastes ending up in landfills (Figure I.1). Therefore, the development of "environmentally-friendly" materials will result in a huge benefit to the environment and will also contribute to a reduced dependence on fossil fuels. Polymers produced from alternative resources, non-toxic to the environment, biodegradable and with low energy consumption are a crucial issue especially for short-life range applications, as they can be easily degraded by micro-organisms.<sup>4</sup> Moreover, a wide number of biomacromolecules exists in Nature and can be involved in the preparation of these green materials.<sup>5</sup>

Nevertheless, the properties of these biomaterials are often behind those of common thermoplastics and some improvements are needed in order to make them fully operative for their industrial use.



Figure I.1. Plastics recovery in Europe for 2010.<sup>3</sup>

On another hand, polymer nanocomposite materials have aroused a great interest in the area of polymer and material science. A polymer nanocomposite is a hybrid material consisting of a polymer matrix reinforced with fibres, platelets, or spherical particles presenting at least one dimension at the nanometre scale. The ideal design of a nanocomposite involves individual nanofillers homogeneously dispersed in the polymeric matrix. In this case, an ultra-large interfacial area per unit of volume between constituents is obtained, resulting in markedly improved properties for low levels of nanofiller incorporation (< 5 wt.-%) when compared to traditional composites. Especially, significant improvements of mechanical properties, thermal stability, flame retardancy, heat distortion temperatures and gas barrier properties together with weight reduction have been demonstrated.<sup>6-8</sup>

Bionanocomposites can be considered as a subset of polymer nanocomposites where the nanofillers, the matrix or both come from bio-based, renewable resources. Therefore, adding nanofillers into biopolymers presents a practical way to improve the properties of these bioplastics, making them competitive with petroleum-derived materials.<sup>9-11</sup>

One of the most promising biopolymers for its production at an industrial scale is the poly(lactic acid) (PLA). PLA is a biodegradable thermoplastic polyester derived from biomass such as sugar, corn, and beet, which possesses interesting properties combined with biocompatibility and biodegradability properties.<sup>12, 13</sup> Due to its initial production costs, the starting applications of PLA have been focused on high value products such as medical devices.<sup>14</sup> However, its price has been falling as the production increases and new methods for the production of high molecular weight PLA are developed.<sup>15</sup> PLA's potential for consumer products such as packaging is very high due to its transparency, low toxicity and environmentally benign characteristics.<sup>16</sup> Nevertheless, there are some drawbacks, such as its high brittleness, poor crystallisation behaviour and low gas barrier properties that limit its current use.<sup>17</sup>

#### I.2. OBJECTIVES OF THE STUDY

The general objective of this thesis is to improve PLA physical and mechanical properties in order to broaden its applications without compromising its biocompatible

and biodegradable characteristics. For this purpose, different additives have been considered in order to finally develop new PLA bionanocomposites.

Blending two polymers is a practical way to develop new polymeric materials since the combination of the blend components can lead to a material with optimised properties. Consequently, rubber matrices have commonly been used as a second polymer phase to improve the toughness of brittle thermoplastic materials and these thermoplastic/elastomeric blends have received much attention from both academic and industrial areas.<sup>18</sup> Natural rubber (NR) is a renewable resource derived from a milky colloidal suspension or latex found in the sap of some plants.<sup>19</sup> It exhibits a unique combination of toughness and flexibility, that together with its low cost makes it an ideal candidate to improve the brittleness of PLA.

Nevertheless, the addition of NR into the PLA matrix is not expected to overcome the other limitations of PLA. Therefore, the development of bionanocomposites based on PLA/NR blend has been considered and two types of nanofillers, layered silicates and cellulose nanocrystals, have been selected in view of their unique properties.

Layered silicates are widely used as effective reinforcing fillers due to their lamellar structure and high aspect ratio. Smectite clays, such as montmorillonites (MMT), belonging to the structural family called 2:1 phyllosilicates, are the main choice due to their low cost and intercalation chemistry allowing them to be chemically modified and thus, improving their compatibility with polymer matrices. Moreover, it has widely been stated that these inorganic fillers increase the mechanical, thermal and barrier properties of the bioplastics and can effectively generate PLA bionanocomposites with improved properties.<sup>20, 21</sup>

Cellulose is one of most abundant polymer produced by biomass, from which high modulus nanocrystals (CNC) can be extracted.<sup>22, 23</sup> The first report of reinforced polymer matrix using this new type of nanofillers has then motivated academic research.<sup>24</sup> In fact, these nanosized reinforcements present the advantage of being renewable when compared to layered silicates, which is of great interest in this study.

In view of the chosen additives for the PLA matrix, the following specific objectives were defined:

- Optimisation and development of a PLA/NR blend in order to produce a ductile PLA blend.
- Development of PLA/NR/MMT bionanocomposites and study of the influence of the montmorillonites over the properties of the optimised PLA/NR blend.
- Production and modification of cellulose nanocrystals for their incorporation into the polymer blend.
- Development of PLA/NR/CNC bionanocomposites and study of the influence of the cellulose nanocrystals over the PLA/NR blend properties.

#### I.3. OVERVIEW OF THE THESIS

The manuscript has been divided in 8 chapters: from the production of ductile PLA/NR blends to the development of PLA bionanocomposites with optimised properties.

*Chapter II* consists in a literature review focused on the different reported ways of improving PLA properties.

In *Chapter III*, the structure and properties of the PLA/NR blends are studied in detail. The processing conditions were considered in order to optimise the blend morphology and, thus, its properties.

*Chapter IV* is dedicated to the PLA/NR/MMT nanocomposites and is focused on the relation between structure and properties of the nanomaterials. Special attention was given to the influence of the distribution and interaction of the montmorillonites with the polymers over properties such as mechanical, thermal or barrier properties. In view of the results reported, a deeper study of the mechanical properties of nanocomposites based on a particular montmorillonite (C15A) was carried out. This study is the object of *Chapter V*, where the deformation mechanisms of PLA/NR/MMT nanocomposites were revealed by X-ray synchrotron scattering.

*Chapter VI* reports the extraction and surface modifications of the cellulose nanocrystals while *Chapter VII* is dedicated to the PLA/NR/CNC bionanocomposites and to the study of their properties.

Chapter VIII draws the general conclusions of the thesis.
# Chapter II. LITERATURE REVIEW

# **II.1. BIOPOLYMERS**

Generally, the term "biopolymers" is understood as biodegradable polymers, i.e. polymers capable of breaking down cleanly into simple molecules found in the environment, such as carbon dioxide, water or methane, under the enzymatic action of microorganisms, in a defined period of time (European standards EN 14046 and EN 13432). However, polymers derived from natural resources, or "biosourced" polymers, are also considered as biopolymers. Being biosourced does not systematically imply to be biodegradable and vice-versa. Therefore, a clear classification of the different biopolymers is necessary to clarify these different concepts. Bordes *et al.*<sup>11</sup> suggested a classification of biopolymers solely based on biodegradable polymers. Hence, this study includes both types as biopolymers, which are then divided into four categories (Figure II.1):



Figure II.1. Classification of the different types of biopolymers (adapted from Bordes *et al.*<sup>11</sup>).

# • Polymers directly obtained from biomass

Polysaccharides are without a doubt the most abundant renewable macromolecules available on earth. They can be obtained from vegetable sources, as it is the case of cellulose and starch, or from animal sources in the case of chitosan. Vegetable polysaccharides such as cellulose have been known for a long time and used without major modifications in daily products such as paper and cotton. However, recent investigations have found new niches of applications for these biomacromolecules such as thermoplastic starch (TPS)<sup>25, 26</sup> or polysaccharides nanocrystals.<sup>22, 27</sup>

Natural rubber (NR) also enters in this category as this polymer is one of nature's unique materials. NR is derived from latex extracted from rubber plants, cultivated in tropical regions such as Asia or South America. Details about NR properties will be the subject of further discussion along this thesis.

#### • Polymers produced from microbial production

The two main macromolecules that can be synthesised by bacterial production are cellulose and polyhydroxyalkanoates (PHA).<sup>28, 29</sup> However, in spite of their unique properties, these materials present very high production costs that limit their development.

## • Polymers conventionally obtained from petrochemical products

The different mechanisms responsible for the biodegradation of plastic materials can be identified but the most common one and first to occur is the hydrolysis. Thus, polymers containing hydrolysable functional groups in their backbone such as ester, amide or carbonate are usually more susceptible to biodegrade. Some vinyl polymers are also prone to biodegrade through oxidation process.<sup>4</sup> A variety of polymers have been designed and synthesised as biodegradable materials.<sup>30</sup> Among them, poly( $\varepsilon$ caprolactone) obtained from the ring opening polymerisation of  $\varepsilon$ -caprolactone is used for its biodegradable character but also for the preparation of biodegradable polyurethane.<sup>31</sup>

## • Polymers chemically synthesised using monomers obtained from agro-resources

A variety of monomers are produced by nature. Terpene or Rosin, extracted from conifer trees, are examples of such monomers; however the quality of the resulting polymers limits their application and production.<sup>5</sup> On the other hand, monomers derived from sugars have gained a growing interest from both academic and industrial fields. Among them, furan derivatives, such as furfural or hydromethylfuraldehyde, can be produced from a vast array of agricultural and forestry wastes and can be involved in a wide range of polymerisation reactions and procedures.<sup>32</sup>

Finally, lactic acid obtained from the fermentation of carbohydrates and the resulting poly(lactic acid) are without a doubt the most promising biomaterials for industrial applications. Further details of poly(lactic acid) production and properties are reported in the next section.

# II.2. POLY(LACTIC ACID) (PLA)

Poly(lactic acid) is an aliphatic polyester, which constitutional unit is reported in Figure II.2. The building block of PLA, lactic acid, exists in two optically active D(-)-or L(+)- enantiomers. The proportion of both enantiomers in the final polymer strongly influences its ultimate properties, as reported in this review.



Figure II.2. Constitutional unit of PLA.

#### **II.2.1.** Production process

Lactic acid (or 2-hydroxy propionic acid) is a simple hydroxyl acid. This molecule can be produced by carbohydrate bacterial fermentation or by chemical synthesis, the first procedure being the one used in the industry (Figure II.3). Corn, potatoes, sugar cane or beet are the usual sources of simple sugars for fermentation, resulting in almost exclusively L-lactic acid. Direct condensation polymerisation of lactic acid is possible although it is not the main method for industrial production, as the resulting molecular weights are too low.

Once the lactic acid is obtained, the industrial production of PLA proceeds by the formation of lactide (L,L-lactide, D,D-lactide or L,D-lactide also called meso-lactide), an intermediate cyclic dimer formed by the condensation of two lactic acid molecules (Figure II.3). Further ring opening polymerisation (ROP) of lactide leads to the production of high molecular weight thermoplastic PLA, with a typical  $T_g$  varying from 50 °C to 80 °C and a  $T_m$  varying from 130 °C to 180 °C depending on the molecular weight and stereochemistry of the polymer.<sup>13</sup>

Industrial PLA is mostly composed of poly(L-lactic acid) (PLLA) and poly(L,Dlactic acid) (PLDLA), being the L-isomer the main fraction. Although the terminology



would have to differentiate among these isomers, the widespread abbreviation used is PLA.

Figure II.3. PLA production process. [Reprinted with permission from <sup>13</sup>, copyright 2004, John Wiley and Sons]

Dow Cargill (NatureWorks)<sup>33</sup> is nowadays the leading company on PLA market with a production capacity reaching 140000 tons per year. The company also collaborates with other multinationals, such as Danone who recently switched its polystyrene Activia yoghourt packaging for Cargill bioplastic in Germany.<sup>33</sup> Other companies, such as Purac (Netherlands)<sup>34</sup> or Galactic-Total (Belgium)<sup>35</sup>, produce different PLA grades at lower scale. Moreover, the PLA production costs are now competitive when compared to other petroleum-based commodity plastics (Table II.1).

Table II.1. Comparison of plastic costs.<sup>36</sup>

Plastics	PLA	PET	PS	РР
$Cost(\$\cdot kg^{-1})$	2.2 - 3.3	1.5 - 1.6	2.1 - 2.2	2.5 - 2.6

#### **II.2.2.** PLA properties

PLA properties are strongly influenced by the stereochemistry (poly(L-lactic acid) PLLA or poly(L,D-lactic acid) PLDLA) and molecular weight. Next, the general properties of PLA are described emphasising its strengths and weaknesses when compared to petroleum-based plastics.

#### II.2.2.1. PLA strengths

#### • Transparency

Packaging applications such as drinking cups or trays for fruit and vegetables often require high transparency. The transparency of plastic sheets is usually defined as the transmission of visible light in the range of 540-560 nm. From Figure II.4, it is observed that PLA transparency is slightly higher than that of PET or PS and is perfectly adapted for transparent items.





Figure II.4. PLA transparency. (a) Percent transmission versus wavelength of PLA and other commodity plastics<sup>13</sup> and (b) PLA bottle.<sup>37</sup>

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#### Biodegradation

One of the most attractive properties of PLA for its use as packaging material is its degradation in biological environment such as soil or compost.<sup>37</sup> The degradation of PLA takes place in two main stages, which are the hydrolytic and enzymatic degradation. The hydrolysis starts with the diffusion of water into the polymer and leads

to random non-enzymatic chain scissions of the ester group. The cleavage of ester linkages results in the reduction of the molecular weight and in the formation of oligomers and lactic acid that can be assimilated by microorganisms such as fungi and bacteria.<sup>38</sup> A molecular weight of about 10000-20000 g·mol<sup>-1</sup> appears to be the critical upper limit that microbes can metabolise and then convert to carbon dioxide, water and humus. While the first hydrolytic step can occur in the bulk polymer through the diffusion of water into the polymer, the second step caused by microbes only occurs at the surface.<sup>39, 40</sup>

Often packaging materials are soiled with food or biological substances that make them unusable for physical recycling. The biodegradation property of PLA makes it an ideal candidate for composting and could thus reduce the environmental impact of packaging wastes (Figure II.5). A compostable plastic is defined as a plastic that degrades by biological process during composting and is converted to carbon dioxide, water, inorganic compounds and biomass at a rate consistent with other known compostable materials without leaving visually distinguishable or toxic residues. Thus, a compostable material is always biodegradable but the reverse is not always true.<sup>39</sup>



Figure II.5. (a) PLA hydrolysis and molecular weight loss<sup>13</sup> and (b) biodegradation of a PLA bottle in real composting conditions.<sup>39</sup>

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The European norm EN13432 defines four criteria that a packaging material must meet to be defined as compostable, which are: 1) the composition of the material, i.e.

the presence of hazardous substances, 2) the biodegradability, 3) the disintegration, and 4) the compost quality and ecotoxicity after biodegradation. In the context of this thesis, the third criterion will be considered, i.e. the disintegration of the materials.

#### Biocompatibility

PLA has been demonstrated to be biocompatible and to degrade into non-toxic components. Since its approval by the Food and Drug Administration (FDA) for implantation in the human body, PLA has been incorporated into some established applications such as medical implants, drug-delivery system, resorbent sutures or other bio-compatible/bioabsorbable medical systems. PLA degrades in-vivo by simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyse this hydrolysis. The rate of degradation depends on the size and shape of the polymer, the stereochemistry, the presence of low-molecular weight impurities and the catalyst concentration. The duration of degradation can be ranged from 12 months to over 2 years and degradation products of PLA are non-toxic to the living organisms since lactic acid itself occurs in the metabolism.<sup>41-43</sup>

#### • Processability

The main conversion approaches of PLA are based on melt processing. Commercial grades of PLA can typically be processed using a conventional twin-screw extruder and melt viscosities of high molecular weight PLA are in the order of 500 to 1000 Pa s at shear rates of 10-50 s<sup>-1</sup>. In fact, NatureWorks provides various grades of PLA specifically tailored to each processing and application, such as extrusion, thermoforming, injection stretch blow moulding or film, fibre and foam production.<sup>33</sup> Lim et al.<sup>44</sup> reviewed the converting processes in relation to PLA properties. Some PLA properties are desirable, such as its melt behaviour similar to polystyrene or its strainhardening at high strain for blow moulding or fibre spinning. However, its thermal degradation is the main drawback for processing in molten state. PLA thermal degradation can be attributed to hydrolysis, depolymerisation, oxidative random-chain scission, inter- and intramolecular transesterification, resulting in the formation of lactide monomer and oligomers.<sup>13</sup> Residual monomer and traces of water strongly influence the early molecular weight reduction. Therefore, drying PLA pellets before processing is of major importance and recommendations are often given by the suppliers. Another drawback of PLA processing is linked to its brittle behaviour. As an

example, special precautions should be taken for the manipulation of PLA sheets obtained by extrusion before thermoforming to prevent breakage.

## II.2.2.2. PLA weaknesses

• Mechanical properties

As it has just been mentioned, PLA major inconvenient for a wide range of application is its brittle behaviour. PLA properties strongly depend on stereochemistry, crystallinity, molecular weight and processing, these four parameters being linked together. Perego *et al.*<sup>45</sup> studied the effect of molecular weight, stereochemistry and crystallinity over the mechanical properties. It appears that semicrystalline PLLA samples present higher tensile strength and Izod impact value than amorphous PLA. In a similar way, increasing the crystallinity leads to higher tensile strength, Young's modulus and Izod impact value while decreases the elongation at break, as reported in Table II.2.a.

Processing conditions also play an important role on PLA mechanical properties. Especially, biaxial orientation of PLA samples seems to have a favourable impact over the elongation and tensile strength at break, as reported by Bigg *et al.*<sup>46</sup> and Grijpma *et al.*<sup>47</sup> (Table II.2.b). This effect was attributed to the strain-induced crystallisation occurring during orientation.

а.	L-PI	LA	Annealed I (at 105 °C for	L-PLA 90 min)	D,L-	PLA
$M_v (kg \cdot mol^{-1})$	31	66	30	66	47.5	75
$\Delta H (J \cdot g^{-1})$	13	3	59	42	-	-
Young's modulus (GPa)	3.5	3.7	4.1	4.1	3.6	4.0
Tensile strength (MPa)	55	59	54	66	40	44
Elongation at break (%)	5.5	7.0	3.3	4.0	7.5	4.8
Impact strength $(J \cdot m^{-1})$	22	26	55	66	18	17

Table II.2. Mechanical properties of PLA depending on (a) stereochemistry, crystallinity and molecular weight and (b) processing.<sup>45, 46, 48</sup>

b.	Processing conditions for (L/D,L)-PLA 90/10			
	Injection moulded amorphous	Injection moulded crystallised	Extruded, biaxially oriented, strain crystallised	
Young's modulus (GPa)	1.0	1.3	3.4	
Tensile strength (MPa)	53.4	58.6	80.9	
Elongation at break (%)	4.6	5.1	41.2	

Thus, in spite of its high strength and modulus, PLA displays an inherent brittleness when compared to other petroleum-based thermoplastics, such as PET or PP (Table II.3). However, its properties are similar to PS. Therefore, modifications of PLA are required in order to broaden its applications, in a similar way in which high impact polystyrene (HIPS) has been developed.

Table II.3. Comparison of PLA mechanical properties with other commodity plastics.<sup>36</sup>

	PLA	PET	РР	PS
Young's modulus (GPa)	3.4	2.8	0.9	2.9
Tensile strength (MPa)	53	54	31	45
Elongation at break (%)	6	130	120	7
Impact strength $(J \cdot m^{-1})$	13	59	27	27

## Crystallisation behaviour

Crystallinity can induce significant improvements on the stiffness, heat deflection temperature or barrier properties of PLA, thus it is an important parameter to control in order to tailor its ultimate properties. As previously observed in Table II.2.a, PLA crystallisation not only depends on its molecular weight but also on its stereochemistry. Moreover, as PLA undergoes molecular weight reduction during processing, the study of crystallisation kinetics of virgin PLA can lead to erroneous conclusions about PLA post-processing crystallisation, as reported by Pantani *et al.*<sup>49</sup>

PLLA is a semicrystalline polymer that can crystallise in  $\alpha$ -,  $\beta$ - and  $\gamma$ -forms. The  $\alpha$ form is the most common one and is obtained under normal conditions such as melt, cold and solution crystallisation. Crystal structure of  $\alpha$ -form is characterised by two antiparallel chains in a left-handed 10<sub>3</sub> helix conformation packed in an orthorhombic unit cell and has a limiting disordered modification defined as the  $\alpha'$ -form.  $\beta$ -form is usually obtained upon hot-drawing the melt-spun or solution-spun PLLA fibres to a high-draw ratio while  $\gamma$ -form is observed via epitaxial crystallisation.<sup>50-51</sup>

100 % PLLA displays high crystallinity but can also crystallise in presence of Dlactide, having the same crystallisation and polymorphism behaviour. However, the crystallinity degree and crystallisation rate strongly depend on the D-content. In general, the crystallisation half-time increases about 40 % for every 1 wt.-% meso-lactide in the polymerisation mixture and the presence of more than 7 % of D-lactide results in amorphous material. Thermally crystallisable PDLLA can be crystallised over a temperature range from 75 °C to melt temperature, as its typical  $T_g$  value is between 50 °C and 80 °C and its  $T_m$  from 130 °C and 180 °C.<sup>52</sup>

Moreover, it has been reported in the literature that PLA presents completely different crystallisation behaviour when cooled from melt (melt crystallisation) or heated from solid state (cold crystallisation).<sup>53</sup> Materials show much higher crystallisation rate during heating than during cooling, which is ascribed to the generation of nuclei at low temperature that grow on increasing the temperature.<sup>49</sup> Another significant fact about PLA crystallisation is the presence of two melting peaks that has often been reported in the literature and has been ascribed to recrystallisation, i.e. to the change of small and imperfect crystals into more stable crystals through the melting and recrystallisation process.<sup>54</sup>

To conclude, PLA is a slowly-crystallising material similar to PET, which can produce amorphous or up to 40 % crystalline material. Crystallisation may or may not be desirable depending on the end-user requirements of PLA articles. However, if crystallinity is required, the incorporation of a nucleating agent will be necessary.

• Gas barrier properties

Gas barrier properties of PLA are of major importance when considering this plastic as an alternative to non-biodegradable materials used in the food industry. Gases commonly studied for PLA are those susceptible to react or damage the food, such as  $O_2$ ,  $CO_2$  or  $H_2O$ . Here again, controlling PLA crystallinity is of major importance as crystals can generate a more tortuous path to gas molecules. Gas barrier properties of PLA have been studied by various research groups and appeared to depend on temperature, humidity and sample preparation.<sup>55, 56</sup> In general, PLA displays CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O permeability coefficients lower than PS, but higher than PET. Actually, PLA bottles are predominantly used for beverages not sensitive to oxygen such as flat water or pasteurised milk. Moreover, PLA barrier properties to organic compounds such as ethyl acetate or D-limonene were found to be very good and are comparable to those of PET.<sup>13</sup>

This short review demonstrates that some of PLA properties such as its biocompatibility, biodegradability, mechanical strength and modulus are highly desirable and should be maintained. However, some improvements are required regarding its gas barrier properties, slow crystallisation rate and high brittleness. Special interest have been shown in developing new methods to toughen PLA and will be the object of the following section.

## II.3. IMPROVEMENT OF THE MECHANICAL PROPERTIES OF PLA

Different methods have been proposed in order to modify PLA mechanical properties and have critically been reviewed by Liu *et al.*<sup>36</sup> and Anderson *et al.*<sup>48</sup> Among them, plasticisation, copolymerisation and blending with other polymers have been subject of intense academic and industrial research.

#### II.3.1. Addition of plasticisers

Plasticisers are used to enhance the processability, flexibility and ductility of polymers. They usually are small molecules, such as monomers or oligomers, that are miscible with the polymer and induce a decrease of  $T_g$ . Plasticisers have demonstrated to be very efficient in improving PLA flexibility and toughness, however various issues still remain. Monomeric molecules are often volatile at PLA processing temperature, as it is the case of lactic acid. The addition of 20 wt.-% of LA to PLA induced an increase of up to 530 % of the elongation at break and a strong decrease of the  $T_g$ , however this solution is not viable due to the low boiling point of LA.<sup>57</sup> Citrate esters have also been widely used as plasticisers for PLA as they are non-toxic and are industrially used for food film contact.<sup>58-61</sup> Nevertheless, the reduction of PLA  $T_g$  induced cold crystallisation and a reduction of PLA amorphous domains, leading to phase separation

and migration of the plasticisers.<sup>60</sup> In this case, PLA could even regain its inherent brittleness. Recently, Hassouna *et al.*<sup>61</sup> proposed an interesting solution to plasticiser leaching by grafting hydroxyl-functionalised citrate plasticiser into anhydride-grafted PLA chains through reactive extrusion. A decrease of  $T_g$  and an improvement of ductility were obtained while no major leaching phenomena were observed after six months of aging.

Increasing plasticiser molecular weight might be another solution to reduce plasticisers leaching. Ljungberg *et al.*<sup>60</sup> prepared oligoesters and oligoesteramides based on tributyl citrate and diethyl bishydroxymethyl malonate as plasticisers. They reported that their compatibility with PLA depended on the molecular weight and on the presence of polar amide groups that can interact with PLA chains, enhancing the stability of the blends. Moreover, Martino *et al.*<sup>62</sup> compared the efficiency of one monomeric and two polymeric commercial adipates. Good compatibility between the polymeric plasticisers and PLA was observed, while lack of homogeneity as well as plasticiser release during processing were observed for the monomeric adipate. For a 20 wt.-% of polymeric adipates, the  $T_g$  was reduced around 25-30 °C while the elongation at break increased of up to 480 %, the Young's modulus decreased from 2 GPa to 0.2 GPa and the tensile strength from 47 MPa to 25 MPa.

Poly(ethylene glycol) (PEG) is another widely used plasticiser for PLA due to its non-toxic properties.<sup>63-66</sup> Low molecular weight PEGs display a better miscibility with PLA and lead to more efficient reduction of the  $T_g$ . Baiardo *et al.*<sup>65</sup> reported miscibility for PEG400 concentrations up to 30 wt.-% while this value dropped to 15 wt.-% for PEG10000. For a 10 wt.-% of PEG 400, the  $T_g$  was reduced around 30-35 °C while the elongation at break increased up to 140 % and the Young's modulus decreased from 3.2 GPa to 1.2 GPa. However, the addition of PEGs also shifts PLA crystallisation temperature towards lower values, plus aging could cause PEG crystallisation.<sup>64, 66</sup> Both phenomena could lead to materials with regained brittleness. Poly(propylene glycol) (PPG) is an alternative to PEG as it is an amorphous polymer.<sup>67, 68</sup> Kulinski *et al.*<sup>67</sup> compared the effect of both plasticisers and concluded that PPG induced less crystallinity of the PLA matrix than PEG. Moreover, Piorkowska *et al.*<sup>68</sup> observed that the addition of 10 wt.-% of PPG with a molecular weight of 1000 g·mol<sup>-1</sup> formed small droplets that facilitated plastic deformation, of up to 100 % elongation at break, in spite of a relatively high  $T_g$  of 47 °C. Thus, plasticisers appear to be a practical way to produce ductile PLA. However, the right optimal balance between plasticiser content, miscibility,  $T_g$  reduction and PLA induced crystallisation needs to be found. Moreover, one of the major drawbacks of this method is the reduction of PLA  $T_g$  which can reach ambient temperature, leading to a lost of its physical stability and limiting its possible applications.

An extensive review of the effects of different plasticisers over PLA mechanical properties can be found in Liu *et al.* review.<sup>36</sup>

#### **II.3.2.** Copolymerisation

Copolymerisation has been studied in order to optimise the tensile and impact performance of PLA. Ring opening polymerisation (ROP) with other cyclic monomers has been the preferred synthesis method as it allows a better control of polymer reaction. Poly(*ɛ*-caprolactone) is a very ductile biodegradable polyester, polymerised via ROP. Thus, it has been the most used polymer to be copolymerised with PLA.<sup>69-73</sup> Gripima et al.<sup>69, 70</sup> reported the copolymerisation with PCL and also with poly(trimethylene carbonate) (TMC), which is another ductile polyester, and studied the mechanical properties of PDLA blends, block copolymers and block copolymer blends with poly(TMC) and poly(TMC/PCL).<sup>70</sup> The elongation at break was found to increase for the copolymers compared to the simple blends. As an example, PLA/TMC 20 wt.-% blend displayed an elongation at break of 130 % while this value increased of up to 280 % for a block copolymer containing 21 wt.-% of TMC.<sup>70</sup> Hiljanen-Vainio et al.<sup>71</sup> also prepared poly(CL-co-L-LA) and poly(CL-co-D,L-LA) by ROP carried out from a blend of LA and  $\epsilon$ -CL. Copolymers containing more than 40 wt.-% of CL presented an elongation at break higher than 100 % with a strong decrease of tensile modulus (3 MPa for poly(CL40/D,L-LA60). More recently, PLA-PCL copolymers have been prepared by chain extending reaction between PLA and PCL oligomers through the reaction with hexamethylene diisocyanate (HDI).<sup>72, 73</sup> Using this method, Zhang et al.<sup>72</sup> reported an increase of the elongation at break from 5 % for PLA/PCL 80/20 blend to 60 % after compounding with HDI.

Other copolymers with interesting mechanical properties can be mentioned here. Haynes *et al.*<sup>74</sup> copolymerised PLA with perfluoropolyether and observed an increase of the elongation at break of up to 300 % with 5 % of PFPE. Another alternative was described by Pitet *et al.*<sup>75</sup> who synthesised ABA triblock copolymers from 1,5-

cyclooctadiene (COD) and D,L-lactide. The triblocks were considerably tougher than PDLA, especially for polyCOD low midblock contents. An elongation at break of 180 % was obtained for a triblock containing 0.76 volume fraction of PLA.

PLA copolymers have also been used as effective compatibilisers for PLA blends and some of these studies are reported below.<sup>76,77</sup>

Although interesting results are obtained by copolymerisation of PLA, direct blending with other polymers appears to be a less expensive and more practical strategy to overcome PLA drawbacks.

#### II.3.3. Blending with other polymers

Blending PLA with other polymers in order to broaden its applications is a method that has been the object of intense research. Among the chosen polymers, biodegradable and biocompatible materials are the most attractive alternatives. Nevertheless, some studies have focused on blending with petroleum-based non-biodegradable polymers. As most polymer blends are immiscible, a very important aspect of PLA blends is related to their morphology which strongly determines the ultimate mechanical properties obtained. Here, the chosen toughening polymers are divided in three categories: biodegradable polymers, petroleum-based non-biodegradable polymers and elastomers.

#### II.3.3.1. Blending with biodegradable polymers

As for PLA copolymerisation, PCL has been a first choice for PLA blending, due to the high flexibility and ductility of this polymer which presents a  $T_g$  of about - 60 °C.<sup>78-<sup>84</sup> PLA and PCL were demonstrated to be immiscible, and PCL formed droplets in the PLA matrix at a concentration of 25 wt.-%.<sup>79, 84</sup> Wang *et al.*<sup>78</sup> studied the mechanical properties PLA/PCL simple blend without observing any significant improvement. Therefore, they proposed the addition of triphenyl phosphite which could act as a coupling agent through transesterification during reactive blending. An interesting increase of the elongation at break from 28 % up to 127 % was observed when adding 2 wt.-% of triphenyl phosphite to a PLA/PCL 80/20 blend. However, this result could also be attributed to the reduction of PCL molecular weight during the transesterification</sup> reaction acting then as a plasticiser. Generally, only minor improvements of mechanical properties were obtained for the simple addition of less than 40 % of PCL.<sup>80, 84</sup>

Different compatibilisation methods have therefore been used. Semba *et al.*<sup>81</sup> added dicumyl peroxide (DCP) as a crosslinking agent. A reduction of the droplet size was observed with the addition of different amounts of DCP for a PCL content of 30 wt.-%. The best results of elongation at break (130 %) were obtained with the addition of 0.1 and 0.2 phr of DCP while the addition of 0.3 phr of DCP showed an impact strength value during Izod impact test of 2.5 times higher than pristine PLA.

Other reactive compatibilisers have been used for PLA/PCL systems, such as isocyanate that could react with hydroxyl or carboxyl groups.<sup>82, 83</sup> Harada *et al.*<sup>83</sup> studied the effect of various reactive processing agents and concluded that lysine triisocyanate (LTI) was the most effective one. An increase of the impact strength from 2 kJ·m<sup>-2</sup> up to 15.8 kJ·m<sup>-2</sup> was observed when adding 0.3 phr of lysine triisocyanate to a PLA/PCL 80/20 blend. The elongation at break also increased from 22 % to 288 % while maximum tensile strength decreased from 55.4 to 47.2 MPa.

Poly(butylene succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT) or poly(ethylene succinate) (PES) are flexible biodegradable polyesters that have also been considered for blending with PLA.<sup>85-87</sup> PBAT/PLA blends were described by Jiang *et al.*<sup>85</sup> The two polymers are immiscible and the PBAT phase formed small droplets in the PLA matrix. Drastic increase of elongation at break was observed (200 % with only 5 wt.-% of PBAT) due to interfacial debonding mechanisms as the interfacial adhesion between the two polymers was low. The impact toughness was only slightly increased, suggesting the need of a better compatibilisation agent. Meanwhile, Shibata *et al.*<sup>86</sup> reported good mechanical properties for PLA/PBS blends with an elongation at break increasing up to 110 % for a PBS content of 10 wt.-%. PLA/PES blends were studied by Lu *et al.*<sup>87</sup>, reporting the improvement of mechanical properties at high PES contents, 40 wt.-% of PES leading to an elongation at break of up to 140 %.

Compatibilising reactive agents such as DCP and isocyanate were also used for this type of blends, resulting in an improved interfacial adhesion between the two polymers.<sup>88, 89</sup> Harada *et al.*<sup>88</sup> used LTI as a reactive compatibilising agent for PLA/PBS blends in a similar way than for PLA/PCL blends. The spherical particles of PBS domains were reduced from 2.60 µm for PLA/PBS 90/10 to 1.29 µm after the addition

of 0.5 wt.-% of LTI. Moreover, the impact strength increased for the same blends from 18 kJ·m<sup>-2</sup> to 50-70 kJ·m<sup>-2</sup>. Meanwhile, Wang *et al.*<sup>89</sup> mixed PLA and PBS in the presence of DCP. Simple PLA/PBS 80/20 blend already showed a strong increase of the elongation at break (up to 250 %). Nevertheless, no improvement of the impact strength was observed. The addition of 0.1 phr of DCP allowed a further increase of the impact strength of up to 30 kJ·m<sup>-2</sup> when compared to the simple PLA/PBS blend (impact strength of  $3.7 \text{ kJ·m}^{-2}$ ) while the elongation at break remained unchanged. Therefore, the interfacial adhesion appeared to be a crucial issue regarding impact strength improvement of the blends.

PLA/thermoplastic starch (TPS) blends have also been the subject of intense research.<sup>63, 90-92</sup> When starch is heated above 80-90 °C in presence of a plasticiser such as water or glycerol, a gelatinisation process occurs and leads to the disappearance of the starch crystalline structure. Once starch is gelatinised and plasticised, a thermoplastic starch able to be processed in an extruder is obtained. The mechanical properties of TPS strongly depend on the plasticiser content. Huneault *et al.*<sup>90</sup> used an extrusion process to obtain water free glycerol plasticised TPS which was then blended with a PLA matrix. However, the compatibility between both polymers was very poor and the authors grafted maleic anhydride onto PLA to improve the morphology of the blend. Improvements of mechanical properties were then obtained and an elongation at break of 200 % was attained for 20 wt.-% of TPS containing 36 wt.-% of glycerol. TPS phase appeared to be too rigid for lower contents of glycerol and no improvement of the ductility of the final PLA/TPS blend was observed. Sarazin et al.<sup>91</sup> also studied a binary PLA/glycerol plasticised TPS blend and a ternary PLA/PCL/TPS blend observing some improvements on the mechanical properties but at high TPS and PCL contents (more than 50 wt.-%). Ren et al.92 prepared TPS/PBAT/PLA ternary blends using a compatibiliser with anhydride functional groups to improve the adhesion between TPS and the two polyesters. Again, improvements of mechanical properties were observed at low PLA contents.

To conclude, PLA blending with other biodegradable polymers leads to interesting mechanical properties. Nevertheless, the use of non-biodegradable or biocompatible compatibilisers is often required in order to optimise these properties.

#### II.3.3.2. Blending with non-biodegradable petroleum based polymers

Blending PLA with non-biodegradable petroleum based polymers does not seem to be the best option in order to preserve the biodegradable and biocompatible character of PLA. However, this approach could have the advantage of enabling the production of low cost toughen PLA. Thus, the addition of petroleum-based polymers such as linear low density polyethylene (LLDPE), thermoplastic polyolefin elastomer (TPO) or poly(ethylene-co-vinyl acetate) (EVA) have been reported in the literature.<sup>76, 77, 93, 94</sup> Anderson et al.<sup>76</sup> reported the mechanical properties of PLDA/LLDPE and PLLA/LLDPE blends compatibilised with a PLLA-PE block copolymer. A super tough material was obtained for a PLA/LLDPE 80/20 blend with 5 wt.-% of the copolymer (Izod impact resistance of 460  $J \cdot m^{-1}$  compared to 12  $J \cdot m^{-1}$  for pure PLA and to 36  $J \cdot m^{-1}$ for the simple blend). Copolymers were also used in Ho et al. study.<sup>77</sup> They blended PLA with a TPO, in particular poly(ethylene-octene), and synthesised TPO-PLA copolymers to compatibilise the blend. The best results of the elongation at break were obtained for 2.5 wt.-% of a copolymer with long PLA segments in PLA/TPO 80/20 blends. The elongation increased from 15 % for the simple blend of up to 182 % after the addition of the copolymer. Moreover, the samples containing copolymers did not break during impact tests.

Another interesting study was reported by Ma *et al.*<sup>94</sup> where PLA was toughen using an EVA copolymer. EVA properties can be tailored from a thermoplastic to a rubber material by increasing the vinyl acetate content. Moreover, the major advantage of EVA is that its compatibility with PLA can also be tailored as poly(vinyl acetate) has been shown to be miscible with PLA.<sup>95</sup> Thus, the toughness of the PLA/EVA 80/20 blend increased with VA content up to 50 %, which was then the optimal VA content for EVA. The addition of 5 wt.-% EVA50 into PLA displayed an elongation at break of 300 % and super tough materials were obtained for EVA50 content of 15 % or more.

## II.3.3.3. Blending with elastomers

Rubber matrices have commonly been used as a second phase polymer to improve the toughness of brittle thermoplastic materials.<sup>18</sup> However, physical and mechanical properties of PLA/rubber blends have received little attention until now. Two biodegradable elastomers have been incorporated into PLA matrix, in particular a polyamide elastomer (PAE) and a poly(ether) urethane elastomer (PU).<sup>96, 97</sup> Li *et al.*<sup>96</sup> reported a significant increase of the elongation at break and the impact toughness in PLA/PU blends. The addition of 10 wt.-% of PU led to an increase of the elongation at break of up to 225 % meanwhile the tensile strength remained high (47 MPa). Also, the impact strength gradually increased with PU contents (315 J·m<sup>-1</sup> for 30 wt.-% of PU). The mechanisms of deformation were investigated by analysing the morphology of different necking regions of the tensile tested samples. Shear yielding of the PLA matrix facilitated by the debonding of the PU droplets was identified as the main deformation mechanism. Zhang *et al.*<sup>97</sup> also described the increase of the elongation at break of up to 195 % with the addition of 10 wt.-% of PAE. Here again, the authors explained that the PAE domains acted as stress concentrators and led to energy-dissipation process preventing PLA matrix from breaking at high deformation. Interestingly, they observed a shape memory ability of the stretched blends when heating above the PLA *T<sub>g</sub>*.

Ishida *et al.*<sup>98</sup> reported PLA melt blending with different types of common rubbers, such as ethylene-propylene copolymer (EPM), ethylene-acrylic rubber (AEM), acrylonitrile-butadiene rubber (NBR) and isoprene rubber (IR) at concentrations of 10 and 20 wt.-%. Izod impact testing showed that toughening was only achieved for NBR as this blend presented the best morphology and lowest interfacial tension. The tensile behaviour demonstrated that the tensile modulus and strength decreased in a similar way for all rubbers. Nevertheless, a slight increase of elongation at break (up to 20 %) was observed for IR and NBR. The authors attributed this effect to the absence of rubber crosslinks for these two rubbers compared to EPM and AEM which were thermoreversibly crosslinked. They believed that rubber chain mobility helped the release of tensile strength.

The only study regarding PLA/NR blend dates from 2011 and has been carried out simultaneously and independently of this work.<sup>99</sup> Comments on this article will be reported in the result section.

## II.3.4. Blending with natural rubber (NR)

In view of the reported ways of toughening PLA, blending with other flexible polymers appears to be the most effective and practical solution in order to retain other PLA mechanical properties, such as high modulus and physical stability at room temperature. Moreover, the addition of another biopolymer seems to be the best option. As mentioned above, a limited number of studies have been reported regarding PLA/elastomer blends. The only biosourced naturally occurring elastomer is natural rubber which is then a logical choice for toughening PLA.

Natural rubber (NR) was the first elastomer to be industrially exploited and is obtained from the sap ("latex") of several rubber-yielding plants by coagulation. The rubber latex occurs in tiny vessels embedded in the inner cortex of the bark of the tree. Incisions into the bark cause the latex to exude as a result of osmotic pressure. The exudate is collected in cups and then subsequently coagulated to obtain a dry rubber. Nowadays the commercial market is totally dominated by one plant, *Hevea Brasiliensis*, and Far East producers (Malaysia, Indonesia, Thailand and Sri Lanka) account for about 80 % of the NR market.<sup>19</sup> Figure II.6 shows a picture sequence representing the steps for obtaining dry coagulated NR.



Figure II.6. Production steps of dry coagulated natural rubber.<sup>100</sup>

NR molecules consist mainly of *cis*-1,4-polyisoprene with practically no evidence for any *trans* materials in the natural product, in contrast to the synthetic polyisoprene (Figure II.7).



Figure II.7. NR molecules.

The molecular weight of the natural polymer is very high but varies between lattices from different tree clones. Nonetheless, typical values of average molecular weight can range from  $3.4 \times 10^6$  to  $10.2 \times 10^6$  g·mol<sup>-1</sup>. The very flexible backbone of NR leads to a very low glass transition temperature ( $T_g$ ) of about -70 °C. Besides, due to its highly regular structure, NR is capable of crystallising while stretching. Commercial raw natural rubber has also a small, but important number of non-rubber constituents, which can account for 5-8 % of the total composition. The most important are the naturaloccurring proteins, phospholipids, sugars, and fatty acids. These non-rubber constituents can influence the methods of coagulation, the vulcanisation and ageing characteristics of rubber compounds, and hence the physical properties of NR.<sup>19</sup>

As a natural product, NR is subjected to biological mineralisation cycles, and reports on its biodegradation have been published.<sup>101, 102</sup> However, the biochemical and molecular basis of rubber disintegration is poorly understood. It is assumed that the degradation of the polymer backbone is initiated by an oxidative cleavage of the double bond. Low-molecular weight oligomers with aldehyde and ketone groups at their respective ends have been identified as degradation products, confirming the assumption of oxidative cleavage. Moreover, rubber-degrading bacteria have been isolated but the rubber biodegradation, as well as the growth of bacteria using rubber as a sole carbon source, are slow processes.<sup>101, 102</sup> The addition of additives for the vulcanisation and the resulting cross-linking bonds delay even more NR biodegradation. Nevertheless, in the context of this study, NR is used as a non-vulcanised raw material and it is expected that, in such state, NR will undergo biodegradation.

NR has found applications in wide range of areas, such as tires, automobiles, shoes, etc. because of its elastomeric properties, but also in medical applications due to its biocompatibility. Treated correctly, NR has been used for production of surgical gloves, condoms, but also for medical equipments or as a drug delivery system.<sup>103-106</sup>

Therefore, the unique elastomeric properties of natural rubber as well as its biocompatibility and possible biodegradation make it the ideal candidate to toughen the PLA matrix. The improvements of other PLA properties could be obtained from a different class of additives such as nanofillers.

# **II.4. PLA BIONANOCOMPOSITES**

This short review on PLA nanocomposites aims at understanding how the addition of small amounts of nanofillers can result in improved PLA properties. For this purpose, a classification of nanofillers employed in biopolymers is completed and the different preparation methods as well as the resulting properties of PLA nanocomposites are described, focusing on bionanoparticles and layered silicates.

#### **II.4.1.** Nanoparticle classifications

The most common classification of nanofillers is based on the number of the filler external dimensions found in the nanometre range (Figure II.8). Spherical nanoparticles refer to fillers where all the three external dimensions are on the nanoscale range, such as silica nanoparticles. When two dimensions are within the nanometre scale, the fillers are described as rod-like particles, such as carbon nanotubes or cellulose nanocrystals. Finally, platelet-like fillers present one dimension of nanometre range, including graphene sheets and layered silicates.



Figure II.8. Classification of nanofillers depending on their dimensions in the nanometric range (from ISO/TS 27687).

Here, the classification is done based on their use and applications in biopolymers such as PLA. Three main categories are defined: traditional nano-reinforcements, functional nanofillers and bionanoparticles.

#### Traditional nano-reinforcement

Since the first report of the successful dispersion of layered silicates in nylon by Toyota research group in Japan, nanofillers have widely been inserted into polymeric matrix leading to significant improvements of mechanical properties, thermal stability, flame retardants, heat distortion temperatures and gas barrier.<sup>6, 107</sup> Therefore, nanofillers have also been used with the same objective in biopolymers. For this purpose, layered silicates have been the most utilised nanoparticles and several reviews are focused on the development of such materials.<sup>10, 11, 21</sup> Special attention has been given to possible packaging applications for these materials as they present improved properties as well as improved biodegradation.<sup>10, 108</sup>

Smectite clays are the most common used type of layered silicates for the preparation of nanocomposites and belong to the family of 2:1 phyllosilicates. Their crystals structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide (see Figure II.9). Layered sheet is about 1 nm thick and the length varies from 30 nm to several microns.<sup>20</sup>



Figure II.9. Layered silicate structure.<sup>20</sup> [Reprinted with permission from <sup>20</sup>, copyright 2003, Elsevier]

These layers organise themselves to form stacks with a regular Van der Waals gap called interlayer space. Isomorphic substitution within the layers generates negatives charges that are counterbalanced by alkali and alkaline earth cations located inside the galleries. These cations can be exchanged by ammonium or phosphonium cations with long alkyl chain or other substituted groups, facilitating the dispersion and compatibilisation of the resulting so-called organoclays with polymeric matrices (Figure II.10).



Figure II.10. Schematic representation of (a) silicate and (b) organosilicate where R is the chemical unit (adapted from Ray *et al.*<sup>20</sup>).

Montmorillonites, hectorites and saponites are the most used layered silicates.<sup>20</sup> Their chemical structures are:

Montmorillonites:  $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ Hectorites:  $M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$ Saponites:  $M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$ 

# • Functional nanofillers

Biocompatibility, low toxicity and biodegradability make biopolymers suitable for a wide range of applications such as medicine, coating, automotive, packaging applications, etc. Thus, the addition of specific nanoparticles could provide them of multifunctional properties. Armentano *et al.*<sup>109</sup> critically reviewed how the combination of biopolymers and nanostructures could lead to the production of new materials for

tissue engineering applications. As an example, biohybrids involving ceramic nanoparticles could improve fracture hardness and mechanical properties necessary for orthopaedic or bone repair applications; as it is the case of biocompatible hydroxyapatite nanoparticles.<sup>110</sup> In the same way, metal nanoparticles present interesting properties such as the antimicrobial activity of silver nanoparticles.<sup>111</sup> Also, the addition of carbon nanoparticles could provide the materials of interesting electrical properties.<sup>112</sup>

Moreover, traditional nanofillers such as layered silicates can be tailored to display functional properties, such as enhanced rate of biodegradation under solar irradiation thanks to the insertion of layered titanate with photocatalytic reactivity.<sup>113</sup> Also, Darder *et al.*<sup>114, 115</sup> developed a series of new class of hybrid materials based on clays, such as Na<sup>+</sup>-montmorillonite/chitosan bionanocomposites exhibiting anion-exchange ability suitable to build potentiometric sensors<sup>114</sup> or the so called *"caramel/clay nanocomposite"* as electroactive components for electrochemical devices.<sup>115</sup>

• Bionanoparticles

With regard to the nanocomposite biodegradability, the use of biodegradable nanoparticles extracted from renewable resources has been subject to intense research in the last few years and appears to be the more ecological alternative.<sup>116</sup>

Polysaccharides such as cellulose and starch are good candidates for renewable nanofillers due to their partly crystalline structures (Figure II.11).



Figure II.11. Cellulose structure.<sup>117</sup>

Two types of nanosized cellulose nanoparticles are usually used as reinforcement in biopolymers, which are microfibrillated cellulose (MFC) cellulose or nanocrystals/nanowhiskers (CNC). The preparation of these nanoparticles starts by milling the cellulose fibres and removing the lignin and hemicelluloses by bleaching treatments. Then, bleached fibres are subjected to either acid hydrolysis, to produce cellulose nanowhiskers, or to disintegration by mechanical shearing at high pressure, to obtain the MFC. During acid hydrolysis, the disordered regions of cellulose are preferentially hydrolysed, whereas crystalline regions that have a higher resistance to acid attack remain intact. CNC presents typical dimensions of 5 to 10 nm in diameter and 100 to 500 nm in length.<sup>22, 23</sup> On the contrary, MFC are highly elongated and flexible nanoparticles with lateral dimensions from 10 - 100 nm and length in the micrometer range.<sup>116</sup> Both CNC and MFC can be extracted from different sources (Figure II.12) and acid hydrolysis conditions from microcrystalline cellulose have been studied and optimised by Bondeson et al.<sup>118</sup>



Figure II.12. (a) SEM images revealing a network of isolated MFC and fibrils aggregates and (b) TEM images of CNC extracted from microcrystalline cellulose (left) or from tunicat (right).<sup>116</sup> [Reprinted with permission from <sup>116</sup>, copyright 2012, Elsevier]

By analogy to cellulose nanocrystals, the first starch nanocrystals were prepared by Dufresne *et al.*<sup>119</sup> Their production, consisting as well in acid hydrolysis, was optimised by the same research group.<sup>120</sup> Starch nanocrystals display a platelet-like morphology (Figure II.13) and a crystallinity of about 45 %.



Figure II.13. (a) Aggregates of starch nanocrystals and (b) organisation of nanoplatelets (scale bar: 50 nm). [Reprinted with permission from <sup>120</sup>, copyright 2004, ACS]

Bionanoparticles have been demonstrated to be effective fillers for polymeric matrix. However, some of their properties, such as low thermal stability or gelatinisation process that undergo starch nanocrystals, often limit their applications in polymer matrices.

#### II.4.2. Methods of preparation of PLA nanocomposites

The preparation method of PLA nanocomposites is of major importance as it further determines the dispersion of the nanofillers and the morphology of PLA nanocomposites. Three main methods are usually employed for the preparation of nanocomposites in general, which are solution mixing, *in-situ* polymerisation and melt mixing.<sup>121</sup>

Solution mixing can be used for polymers that effectively dissolve in common solvents. The soluble polymer and the nanofillers are then mixed in the solvent system and the solvent is evaporated in a controlled way with or without vacuum conditions. Modification of the nanofillers is often required to facilitate its dispersion in the solvent and to obtain homogenous nanocomposites.

In the case of *in-situ* polymerisation, the particles are dispersed in a monomer or monomer solution, which is then polymerised, leading to the production of nanocomposites.

Melt processing is used for thermoplastic polymers, which are melted and mixed with nanofillers under intense shear. Extruders and internal mixers are the most common machines used for melt processing. This is the most promising technique as it is solvent free and compatible with the current industrial processes.

Moreover, the preparation methods depend of the type of nanoparticles used. Here, the particular cases of layered silicates and bionanoparticles for PLA nanocomposites are described.

#### II.4.2.1. PLA layered silicate nanocomposites

When blending layered silicates with polymers, the polymer chains can penetrate into the layered structure of the clays. Microcomposites, intercalated or exfoliated nanocomposites can be obtained depending of their degree of insertion within the interlayer space (Figure II.14). Moreover, due to their regular structure, layered silicates give signals in XRD corresponding to the interlayer space, which enable determining the morphology of nanocomposites.



Figure II.14. Representation of the different types of nanocomposites depending on the interaction between the layered silicates and the polymer matrix.<sup>6</sup> [Reprinted with permission from <sup>6</sup>, copyright 2000, Elsevier]

PLA/clay nanocomposites have widely been studied, especially by Ray and coworkers<sup>20, 21, 122-126</sup> and Dubois and co-workers.<sup>40, 127-130</sup> However, the first report of exfoliated clays in PLA was reported by Krikorian *et al.*<sup>131</sup> which prepared the exfoliated nanocomposite by solvent intercalation with a commercial organomodified clay from Cloisite, abbreviated C30B. This organoclay has been particularly studied for PLA nanocomposites as the interlayer alkylammonium cation possesses hydroxyl groups that can interact with the ester group of PLA chain, leading to a better intercalation and compatibility. In this study, the authors dispersed the montmorillonites in dichloromethane which swollen the layered silicates and facilitated the insertion of polymer chains. Although several organomodified clays with different types of modification were tested, influencing strongly the final structure of the nanocomposite, only C30B led to the exfoliated morphology.

The same organoclays were used for the preparation of PLA nanocomposites by melt blending.<sup>40, 130</sup> Intercalated morphology was the most common structure observed when using organoclays while microcomposites were obtained for unmodified

montmorillonites. Intense shear mixing was needed in order to observe an exfoliated structure, even for the organoclays having the best compatibility with PLA. Pluta *et al.*<sup>132</sup> studied the compounding conditions of PLA/C30B nanocomposites. The nanocomposites showed a diffraction maximum at lower angle than C30B, evidencing the intercalated structure. Moreover, the authors observed that the diffraction maximum peak decreased when increasing the blending time. Exfoliation was achieved for a blending time of 30 min. Nevertheless, this study attests the difficulty of obtaining exfoliated nanocomposites by melt blending.

*In-situ* polymerisation has also been described by the same authors.<sup>128</sup> The clays were allowed to swell in the monomer melt before polymerisation. Again, C30B led to a better nanocomposite structure. In this case, exfoliation was achieved as the PLA chains could grow from the hydroxyl groups covering the organoclay surface.

In a general way, it has to be noted that melt blending is the most common method of preparation and is industrially scalable. Moreover, all these nanocomposites exhibited improved properties, even if the organoclays were not completely exfoliated.

#### II.4.2.2. PLA bionanoparticle nanocomposites

Bionanoparticles such as cellulose or starch nanowhiskers are highly hydrophilic, and their incorporation into polymeric matrix has initially been limited to hydrosoluble polymers or to emulsion polymers such as natural rubber latex.<sup>24, 133</sup> Therefore, solution mixing for the preparation of PLA nanocomposites often requires surface modification of the bionanoparticles in order to obtain a stable suspension in organic solvents and a better compatibility with the PLA matrix. Another drawback of bionanoparticles, and especially cellulose nanoparticles, is their strong aggregation when drying. Cellulose nanowhiskers form a thin film while cellulose microfibrillated form a highly toughness nanopaper, due to strong hydrogen bonds.<sup>134</sup> Freeze-drying is the best option to dry cellulose nanowhiskers but redispersion in polymeric matrices remains a major issue. An alternative option when working by solution mixing is to solvent exchange the bionanoparticles from their original aqueous suspension to the required solvent.<sup>135</sup> Moreover, bionanoparticles present a low thermal stability and could be subjected to degradation during melt mixing. Based on this information, different strategies have been used to produce PLA bionanoparticles composites.

Heux *et al.*<sup>136</sup> first reported the preparation of stable nanocrystals solution in a nonpolar solvent using a phosphoric ester as surfactant. Cellulose nanowhiskers were mixed in an aqueous suspension with the surfactant, freeze-dried and redispersed in an organic solvent, resulting in a suspension showing birefringence in toluene. Similar procedure has then been applied in order to prepare PLA-cellulose nanocomposites.<sup>135, 137, 138</sup> Petersson *et al.*<sup>135</sup> observed birefringence for the CNC suspension in chloroform and good dispersion in the nanocomposites prepared by solution casting, although the surfactant was believed to encapsulate several nanowhiskers limiting their interaction with the PLA. The use of surfactants also seemed to improve the whisker dispersion during melt blending.<sup>137, 138</sup>

Surface functionalisation of bionanoparticles has also been employed in order to ease the nanoparticle dispersion in PLA. Pei *et al.*<sup>139</sup> prepared silylated nanowhiskers while Lin *et al.*<sup>140</sup> and Tome *et al.*<sup>141</sup> reported the surface acetylation by reaction of acetic anhydride with the hydroxyl group of cellulose. Likewise, Lee *et al.*<sup>142</sup> described the functionalisation of bacterial cellulose by several organic acids via esterification reaction. The authors proposed an original method to process the nanocomposites: composite microspheres were obtained from a dispersion of modified bacterial cellulose/PLA in dioxane by adding it drop by drop in liquid nitrogen. The precipitate was then collected and freeze-dried, resulting in porous composite microspheres that could be subsequently processed in an extruder. All these methods led to an improvement of nanoparticle dispersion in PLA.

Recently, polymer grafting onto bionanoparticles have been reported. Poly( $\varepsilon$ -caprolactone)-grafted-starch nanocrystals and poly( $\varepsilon$ -caprolactone)-grafted-cellulose nanowhiskers have been prepared by micro-wave assisted ROP by Chang and co-workers<sup>143, 144</sup> and inserted in a PLA matrix. Interesting results were observed with cellulose, with a simultaneous reinforcement of the strength and an improved elongation due to the combining effect of the nanowhiskers and PCL chains. In a similar way, Goffin *et al.*<sup>145</sup> described the preparation of polylactide-grafted-cellulose nanowhiskers and a good dispersion was reported.

In a general way, it should be emphasised that most PLA/bioparticle nanocomposites are still prepared by solution casting as thermal degradation of fillers remains an important issue during melt blending. Roman *et al.*<sup>146</sup> demonstrated that the introduction

of sulphate groups at the crystal surface during sulphuric acid hydrolysis caused a significant decrease in the degradation temperature. Neutralising whisker suspension with a NaOH solution after acid hydrolysis helps reducing the degradation, as it can be observed from Figure II.15.a. Also, the modification of the nanoparticle surface could limit the degradation (Figure II.15.b).



Figure II.15. (a) Thermogravimetric analysis at 185 °C of CNC from suspensions without (pH3) and with addition of NaOH (pH9)<sup>138</sup> and (b) melt blended and injected moulded samples at 165 °C of PLA/unmodified CNC (left) and PLA/PLA-grafted-CNC nanocomposites (right).<sup>145</sup>

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#### **II.4.3. PLA bionanocomposite properties**

#### II.4.3.1. Transparency

Due to the physical characteristics of nanofillers, transparent matrices, such as PLA, should retain their transparency with no reduction of the amount of light transmitted when a low percentage of well-dispersed nanoreinforcement is added. Thus, the transparency of nanocomposites is also an indication of dispersion of the nanofillers. Pluta *et al.*<sup>127</sup> observed that some opacity was obtained for a microcomposite based on unmodified clays, since the particle size was comparable to the light wavelength. Meanwhile, organoclay nanocomposites displayed a transparency comparable to PLA. However, Sanchez-Garcia *et al.*<sup>147</sup> reported a brownish colour for the clay nanocomposites and a gradual increase of yellowness index with increasing the filler

content. A reduction of 32 % of visible light transmitted (at 650 nm) was also observed when 5 wt.-% of clays were added. Peterson *et al.*<sup>148</sup> compared the optical properties of bentonite and swollen microcrystalline cellulose nanocomposites, observing a poor light transmission, and concluded that exfoliation was not achieved (Figure II.16).



Figure II.16. (a) Transparency measurement of PLA, PLA/bentonite and PLA/microcrystalline cellulose and (b) pictures of the materials.<sup>148</sup> [Reprinted with permission from <sup>148</sup>, copyright 2006, Elsevier]

On the other hand, good transparency was obtained with well-dispersed, modified cellulose nanocrystals in the PLA matrix, as observed by Fortunati *et al.*<sup>138</sup> and Sanchez-Garcia *et al.*<sup>149</sup>

## II.4.3.2. Rheology

Melt behaviour of polymer nanocomposites is sensitive to structure, particle shape and surface characteristics of the fillers. Thus, rheological measurements offer a realistic picture to evaluate the filler dispersion into a polymeric matrix. In the case of layered silicates, rheological measurements have been used to evaluate the degree of exfoliation and an increase in the shear viscosity, storage and loss modulus was reported when increasing the clay concentration.<sup>150</sup> Dynamic strain sweep experiments also demonstrated that the linear viscoelastic zone shortened with the presence of organoclays due to an increase of the melt strength.<sup>132</sup> Moreover, a transition from liquid-like to solid-like behaviour with appearance of a plateau in the storage modulus was observed at low frequency during the frequency sweep measurement, driving also by the increasing clay concentration.<sup>150</sup>

Pluta *et al.*<sup>132</sup> demonstrated the influence of clay dispersion by preparing PLA/C30B nanocomposites by melt blending at different extrusion times and observed a better exfoliation at longer extrusion times. The modulus and viscosity of the systems clearly increased with dispersion time at low frequency, showing a shear thinning effect (Figure II.17). Meanwhile, the effect of clay concentration was studied by Gu *et al.*<sup>151</sup> showing that the presence of organoclays led to the solid-like behaviour, being more noticeable at high concentration. This behaviour was attributed to the formation of a percolating network due to particle-particle as well as particle-matrix interactions.



Figure II.17. Frequency dependence of (a) storage modulus G' and (b) complex viscosity  $\eta^*$  for PLA/C30B 3 wt.-% nanocomposites at different blending times (6, 10, 20 and 30 min).<sup>132</sup> [Reprinted with permission from <sup>132</sup>, copyright 2006, John Wiley and Sons]

No reports were found about the effect of bionanoparticles on PLA rheological properties. Nevertheless, Goffin *et al.*<sup>152</sup> studied PCL/CNC bionanocomposite viscoelastic properties, observing no effect of the pristine CNC while PCL-grafted-CNC induced solid like behaviour at 8 wt.-%. They ascribed this difference to the formation of a physical network based on the entanglement of surface grafted PCL chains and PCL matrix chains. This hypothesis was confirmed by grafting shorter PCL chains onto CNC surface and reducing the ROP reaction time, since these changes had no effect over PCL rheological behaviour.

#### II.4.3.3. Dynamic mechanical properties

Dynamic mechanical analysis of PLA shows a typical behaviour with three different regions. In the glassy state, the tensile storage modulus E' only slightly decreases with temperature, and then drops considerably in the range 50–80 °C, due to the glass–rubber transition of the polymer.

The increment of DMA properties strongly depends on the structure of the nanocomposites. When comparing the effect of different types of organoclays with different modified surfactants, Ray *et al.*<sup>126</sup> observed an enhancement of the elastic modulus G' below the PLA  $T_g$  for all nanocomposites. The best results at room temperature were obtained for the montmorillonites demonstrating the best intercalation morphology (montmorillonites modified with an octadecylammonium cation for ODA and with an octadecyltrimethyl ammonium cation for SBE in Figure II.18). Furthermore, the enhancement became clearer above the  $T_g$  as the silicate particles restricted the movement of the polymer chains when the material softened, resulting in a strong enhancement of the modulus, up to 110 %. However, the presence of fillers did not lead to a significant shift or broadening of the *tan*  $\delta$  curves for all nanocomposites compared to that of pure PLA.


Figure II.18. Temperature dependence of storage modulus G' and  $tan \delta$  for pure PLA and various nanocomposites at 4 wt.-% filler content. ODA and SBE are two modified montmorillonites, SAP a saponite and MEE a synthetic fluorine mica.<sup>126</sup> [Reprinted with permission from <sup>126</sup>, copyright 2003, Elsevier]

Opposite conclusions were drawn by Krikorian *et al.*<sup>131</sup> who found that improvements of storage modulus tended to zero in the plateau region above 120 °C. They concluded that after a specific temperature, the effect of clays on storage modulus become negligible. Higher G' was also achieved for the clays (C30B) presenting the best exfoliation stage.

Dynamic mechanical properties of PLA/bionanoparticle composites were reported by several research groups. Peterson *et al.*<sup>135</sup> reported that unmodified whiskers were able to improve the storage modulus of pure PLA at high temperatures while no changes were observed in the elastic region. As for layered silicates, the reinforcing effect of the whiskers increased at high temperatures due to their ability to restrict the motions of the PLA chains. When the whiskers were modified with a surfactant, an increase of the storage modulus in the elastic region also occurred when compared to the PLA-surfactant blend. Other research groups also observed an increment of the storage modulus, concluding that the modification of the CNC surface led to a larger improvement of the modulus, although no significant changes were observed regarding

tan  $\delta$ .<sup>141, 142</sup> Nevertheless, Lin *et al.*<sup>140</sup> reported two relaxation temperatures located at about 50 °C and 65 °C in the *tan*  $\delta$ -temperature curves. The first temperature was assigned to the true relaxation temperature of the amorphous PLA component, whereas the second temperature was assigned to the relaxation temperature of amorphous PLA component adjacent to the crystalline PLA domains. The first relaxation peak initially increased up to 6 wt.-% of acetylated CNC and then gradually decreased with the increase of the CNC loading-level. The increase of the relaxation temperature of nanocomposites indicated that the addition of a certain amount of CNC nanoparticles could inhibit the motion of the PLA segments in the amorphous region.

#### II.4.3.4. Crystallisation properties

As described in the first part of this literature review, increasing the PLA crystallisation rate is of major importance for some industrial applications. The addition of nanoparticles into PLA matrix could act as nucleating agents and, hence, the effect of layered silicates on the PLA crystallisation has widely been studied. Ray et al.<sup>126</sup> reported the crystallisation behaviour of PLA nanocomposites using different types of layered silicates at 4 wt.-% and observed an enhancement of PLA crystallisation in all cases. Moreover, layered silicates generated the formation of smaller spherulites and increased the nuclei density. In the same way, Nam et al.<sup>153</sup> showed that the overall crystallisation rate increased for PLA/clay nanocomposites; however, the order of the spherulites was much higher for pure PLA, confirming that clays can act as nucleation agents. The same nucleating effect was observed by Di et al.<sup>154</sup> at low concentration of organoclays. However, an antagonist effect was reported at higher concentrations where the organoclays were described to act as physical hindrance to the PLA chain mobility, due to the strong affinity of the exfoliated clay with the polymer matrix (Figure II.19). In general, PLA crystallisation form does not seem to be affected by the addition of organoclays.<sup>130</sup>



Figure II.19. DSC melting thermograms of PLA and PLA/C30B nanocomposites at different filler contents.<sup>154</sup> [Reprinted with permission from <sup>154</sup>, copyright 2005, John Wiley and Sons]

Bionanoparticles were also described as nucleating agents for the PLA matrix. The addition of 10 wt.-% of MFC was reported to reduce by half the annealing time necessary to fully crystallise neat PLA.<sup>155</sup> Interestingly, this study also demonstrated that partially crystalline PLA/MFC composites displayed the same mechanical properties than fully crystalline neat PLA, reducing the crystallisation time by 1/7.

Moreover, the modification of CNC and the resulting improved dispersion appear to have an important influence over their nucleation effect as reported by several research groups.<sup>138-140</sup> The nucleating agent behaviour of unmodified and surface silylated cellulose nanocrystals in a PLLA matrix were observed by polarised optical microscopy by Pei *et al.*<sup>139</sup> The nuclei density increased significantly with the addition of silylated CNC, due to the improved dispersion of cellulose nanocrystals in the PLLA matrix. As a result, more crystals were able to nucleate and grow on the increased surface area of the interface due to the increasing number of nucleating particles (Figure II.20). The influence of PLA grafting onto CNC surface over PLA crystallisation was studied by Goffin *et al.*<sup>145</sup> The reduction of the half-time crystallisation together with the increase of crystallisation degree suggested that PLA-grafted-CNC also acted as nucleating agents. However, in this case, the effect of shorter PLA chains grafted or not into the PLA matrix could also influence its crystallisation.



Figure II.20. Polarised optical microscope images of PLLA, PLLA with 1 wt.-% of CNC and 1 wt.-% of sylilated CNC after 0, 5 and 10 min at 125 °C crystallisation from melt (scale bar: 200 μm).<sup>139</sup> [Reprinted with permission from <sup>139</sup>, copyright 2010, Elsevier]

#### **II.4.3.5.** Mechanical properties

Due to the high interfacial area of nanoparticles, mechanical enhancement is observed for very low loading fractions (up to 10 wt.-%). Moreover, a further increase of the nanofiller content could lead to property deteriorations due to the likely formation of agglomerates. Mechanical properties of PLA nanocomposites are mainly evaluated by tensile properties.

The dispersion of the clays is of major importance regarding the tensile properties. Rhim *et al.*<sup>156</sup> observed a decrease in the tensile strength and the elongation when adding 5 wt.-% of unmodified clay and organoclays (C20A and C30B) to the PLA matrix, attributing this reduction to a poor dispersion of the clays. Overall, an enhancement of the tensile modulus of PLA-organoclay nanocomposites is observed, due to the addition of rigid inorganic fillers with high modulus and to the high surface area of clays exposed to the polymer. The variation of tensile strength depends strongly on polymer-filler compatibility. So, low interactions result in the appearance of cavities between the matrix and nanoparticles while stretching, leading to premature yielding. Likewise, a reduction of elongation at break is usually observed.<sup>157</sup>

Nevertheless, some authors reported an interesting toughening effect of layered silicates. Lewitus *et al.*<sup>158</sup> observed an increase of tensile modulus and elongation at break by 37 % and 48 % respectively with the addition of 5 wt.-% of organoclay using a masterbatch processing method. However, no changes were observed for tensile strength compared to neat PLA. They concluded that the toughening effect was due to interactions at molecular level and to a high degree of exfoliation. In a similar way, Li *et al.*<sup>159</sup> observed an increase of the elongation at break of up to 200 % with the addition of 1 wt.-% of organically modified rectorite to the PLA matrix. Further increase of the clay content led to a decrease of this value, while the modulus gradually increased with clay content and tensile strength decreased. The mechanisms responsible for the toughening effect of the clays were analysed through the observation of the samples after tensile tests using scanning electron microscopy. They concluded that debonding of the clay from the PLA matrix facilitated the plastic deformation of PLA.

Tensile properties of PLA/bioparticles nanocomposites present similar characteristics to layered silicate nanocomposites. The improvement of the Young's modulus is attributed to the high modulus of the rigid nanocrystals while tensile strength changes depended on filler surface modifications. Figure II.21 reports the results obtained by Lin *et al.*<sup>140</sup> with the addition of acetylated CNC (noted ACN). All the PLA/ACN nanocomposites exhibited dramatically increased Young's modulus meanwhile the evolution of the elongation at break was just the opposite, due to the presence of rigid nanocrystals. The tensile strength at break reached a maximum for 6 wt.-% loading. It is believed that when an excess of nanofiller was added, a rigid network formed among the nanocrystals in the composites as well as self-aggregation, resulting in a decrease in the strength and elongation.



Figure II.21. Effect of the acetylated CNC (ACN) content on  $\varepsilon_b$ ,  $\zeta_b$  and *E* for PLA/ACN nanocomposites (measurement carried out at 10 mm·min<sup>-1</sup>).<sup>140</sup> [Reprinted with permission from<sup>140</sup>, copyright 2011, Elsevier]

#### II.4.3.6. Gas barrier properties

Polymer-layered silicate nanocomposites are expected to have excellent barrier properties to gases as the addition of the nanoparticles to the polymer creates a tortuous pathway and hinders the migration of the molecules through the material.<sup>21</sup> Sheet-like morphology is particularly efficient due to the large length-to-width ratio. However, only few results have been reported on PLA/clay systems.<sup>123, 126, 160, 161</sup> Ray et al.<sup>126</sup> compared the effect of four types of organoclays, i.e. montmorillonites, saponite and mica with different interlayer cations. They determined the aspect ratio of the layered silicates in the nanocomposites from TEM images and calculated the theoretical value of the gas barrier relative coefficient (P<sub>nanocomposites</sub>/P<sub>PLA</sub>) for the O<sub>2</sub> permeability from Nielsen model.<sup>162</sup> The experimental values matched quite well the theoretical ones, except for the saponite modified with a hydroxylated cation for which the experimental value was lower than the theoretical one. The difference was attributed to the good interaction of this layered silicate with PLA matrix. Exfoliated nanostructure gave the strongest gas permeability decrease. More recently, Picard et al.<sup>161</sup> reported an interesting study where the effect of organoclays was combined with their crystallisation nucleating effect. Therefore, the observed decrease in permeability was attributed to the contributions of the clay presence and polymer crystalline phase.

Moreover, it has been reported that orienting and parallel ordering of the layered silicates induced by extrusion blow moulding can further decrease the O<sub>2</sub> transmission.<sup>163</sup> In general, PLA/organoclay nanocomposites prepared by traditional methods showed a maximum of 60 % reduction of the oxygen permeability coefficient for a clay content of about 5-10 wt.-%. Higher contents led to the formation of aggregates that hindered further improvements. Meanwhile, the layer-by-layer approach seemed to give much better results, as recently published by Svagan *et al.*<sup>164</sup> Very thin laminar multilayer structures of chitosan and montmorillonites were assembled as a result of the electrostatic forces on the PLA film. When the PLA films were coated with 70 MMT/chitosan bilayers, their oxygen permeability coefficient was reduced up to 97 %. This is the best result ever reported for PLA/clay nanocomposites.

Gas barrier properties of PLA/cellulose nanoparticles have also been described in the literature, especially by Sanchez-Garcia *et al.*<sup>149, 165</sup> Interestingly, they compared the effect of the same content of cellulose microfibres and cellulose nanocrystals. The addition of 5 wt.-% of MFC had no effect over gas barrier properties while 5 wt.-% of CNC led to a decrease of 90 % in oxygen permeability. Finally, the layer-by-layer method also appeared to be a viable option for cellulose nanoparticles, as reported by Fukuzumi *et al.*<sup>166</sup> The oxygen permeability of PLA film drastically decreased by forming a thin layer of oxidised cellulose nanofibres.

# II.4.3.7. Thermal stability

The thermal stability and degradation profiles of materials are usually assessed by thermogravimetric analysis (TGA). TGA tracing of the PLA matrix under inert atmosphere exhibits a typical single weight-loss step, with a maximum decomposition rate at about 370 °C. In general, layer silicates have been reported to increase the thermal degradation temperature of PLA. The silicate layers act as a barrier for incoming gases as well as for gaseous by-products formed during degradation, improving the thermal stability of the materials.<sup>21</sup> The extent of this increase usually depends on the exfoliation degree of the organoclays.<sup>129</sup>

It is more complicated to make general statements about the thermal degradation of PLA/bioparticle nanocomposites. The effect over the degradation temperature strongly depends on the properties of the filler, which in turn depend on the extraction source

and hydrolysis conditions. No real influence was observed regarding the addition of cellulose nanowhisker.<sup>138, 149</sup> Nevertheless, the outstanding performances of bacterial cellulose fibres associated to their high crystallinity and purity generate higher thermal stability of the resulting nanocomposites, as reported by Lee *et al.*<sup>142</sup> They observed an increase of the nanocomposite degradation temperature of 20 °C after the addition of 5 wt.-% of bacterial cellulose. Likewise, Tomé *et al.*<sup>141</sup> reported a slight increase of 6 °C of the nanocomposite thermal degradation temperature with the addition of 6 wt.-% of bacterial cellulose nanofibres and of 15 °C with acetylated nanofibres.

#### II.4.3.8. Biodegradation

The effect of organoclay addition over PLA biodegradation in compost has been reported over the past few years; however, no clear conclusion can be drawn from the results reported so far. Some authors observed an improvement of the biodegradability, especially when the interlayer cation of the silicates possessed terminal hydroxylated groups which could start heterogeneous hydrolysis of PLA.<sup>38, 108</sup> Ray *et al.*<sup>108</sup> demonstrated this effect by comparing nanocomposites using two types of clays, with and without hydroxyl groups, and different dispersion degrees. It appeared that exfoliated organoclays with hydroxyl-groups gave the highest degradation rate as the PLA matrix was in contact with the clay edge and surface. Moreover, Paul *et al.*<sup>40</sup> studied the hydrolytic degradation of PLA nanocomposites in a phosphate buffer solution and observed that the more hydrophilic the clay, the more pronounced was the degradation. Additionally, Fukushima *et al.*<sup>38</sup> confirmed that the dispersion and the hydrolytic degradation rate.

Meanwhile, other researchers have observed a delayed biodegradability due to a counterbalanced effect caused by the improved barrier properties of the materials, which could hinder the microorganism diffusion through the bulk.<sup>167</sup> Fukushima *et al.*<sup>168</sup> also observed a reduction of the degradation rate of PLA when adding silicates and attributed this effect to the chain mobility reduction due to polymer-silicate interactions. Furthermore, some authors have reported an antimicrobial activity of the organoclays due to their quaternary ammonium group.<sup>156, 169</sup>

No reports were found on the influence of bionanoparticles over PLA biodegradation. However, Mathew *et al.*<sup>170</sup> described the biodegradation in compost of PLA composites reinforced with microcrystalline cellulose, wood flour and wood pulp. Surprisingly, a slower disintegration rate was observed for the composites and was attributed to resistance to water uptake and diffusion through the composites compared to pure PLA.

#### II.4.3.9. Flame retardant properties

In general, the nanocomposite flame retardancy mechanism involves the formation of char, which builds up on the surface during burning. The underlying material is then insulated and the mass loss rate of decomposition products is slowed down. Such mechanism has been described for layered silicate nanocomposites.<sup>20</sup> During combustion, clays form a clay-rich barrier that results in a decrease of the burning rate. However, no self-extinguishment has been observed. Therefore, combining layered silicates with other flame retardant appears to be an attractive solution to improve the PLA combustion and expand its application in electronic systems.

As an example, Li *et al.*<sup>171</sup> combined a traditional intumescent flame retardant filler and montmorillonites and demonstrated a synergetic effect of both components. The addition of MMT increased PLA melt stability and suppressed effectively the melt dripping. A similar melt dripping reduction with the addition of layered silicates to PLA was observed by Cheng *et al.*<sup>172</sup>

No reports regarding PLA/biofiller nanocomposite flame retardant properties were found.

#### II.4.3.10. Other nanoparticles and properties

In this short review, the properties of PLA bionanocomposites based on layered silicates and bionanoparticles were reported. Nevertheless, other nanoparticles such as carbon-based nanoparticles confer very interesting properties to the PLA matrix. As for layered silicates and bionanoparticles, modification of carbon nanoparticles is often required in order to observe any significant improvement of the properties. Thus, hydroxyl-functionalised multi-walled carbon nanotubes, (MWCNT), carboxylic MWCNT or PLA-grafted-MWCNT have been reported.<sup>173-176</sup> A drastic increase of the

initial degradation temperature was obtained, up to 77 °C for 1 wt.-% of hydroxyl-MWCNT in an acrylic acid grafted PLA, as well as a strong increase of the Young's modulus and tensile strength.<sup>173</sup> Crystallisation rate also seemed to be globally accelerated with the addition of unmodified and modified MWCNT which can act as nucleating agents.<sup>175, 177</sup> Barreau *et al.*<sup>177</sup> reported that CNT increased the number of nucleation sites during isothermal crystallisation and reduced the average spherulite size. PLA crystallisation form remained unchanged with the addition of CNT. On the other hand, Xu *et al.*<sup>176</sup> demonstrated that functionalised MWCNT retarded crystallisation above the percolation threshold due to physical hindrance.

Additionally, several authors evaluated the electrical properties of these nanocomposites. Yoon *et al.*<sup>175</sup> demonstrated that the surface resistivity significantly decreased for 0.5 wt.-% MWCNT content due to the formation of a percolation path. The resistivity with PLA-grafted-MWCNT seemed to depend on the length of the PLA-graft and was found to increase with molecular weight up to 200 g·mol<sup>-1</sup> and then remained constant.<sup>112</sup> The authors explained that PLA-grafted chains impeded the formation of electrical conduction paths of MWCNT. Shih *et al.*<sup>178</sup> also demonstrated that the addition of 3 wt.-% of modified MWCNT with long chain alkyl reduced the surface resistivity from  $10^{16} \,\Omega \cdot \text{cm}^{-2}$  for pure PLA to  $10^4 \,\Omega \cdot \text{cm}^{-2}$ . These nanocomposites could then support electrostatic discharges and find applications as anti-static coating.

However, the addition of carbon nanotubes has been reported to influence negatively the biodegradation of PLA and enzymatic hydrolysis.<sup>179, 180</sup> Chrissafis *et al.*<sup>179</sup> reported a strong decrease of mass loss during enzymatic hydrolysis when added low filler contents (from 0.5 wt.-% to 2.5 wt.-% of oxidised multiwalled carbon nanotubes). They attributed these changes to the higher crystallinity of the nanocomposites due to the nucleating effect of MWCNT when compared to pure PLA. Moreover, a lower surface availability of PLA is expected in the nanocomposites. The biodegradation in soil of PLA/CNT composites was studied by Wu *et al.*<sup>180</sup> For amorphous and crystalline samples, lower levels of degradation were observed after the addition of 2 wt.-% of CNT. Thus, CNT could act as an inhibitor and also as a physical barrier, decreasing the biodegradation rate of the nanocomposites.

Several research groups also investigated the effect of the addition of expanded graphite over PLA properties. Nano-graphite platelet improved mechanical, thermal and

electrical properties up to 4 wt.-% loading.<sup>181-183</sup> Above this concentration, the presence of carbon aggregates degraded the structural properties of the materials.<sup>183</sup> Murariu *et al.*<sup>181</sup> also showed that expanded graphite accelerated the crystallisation process of PLA under isothermal conditions. The percolation threshold for electrical conduction for PLA/exfoliated graphite nanocomposites was observed for concentrations between 3 and 5 wt.-%.<sup>182</sup>

#### II.4.4. Combining "toughening agent" and nanoparticles

In view of the excellent results obtained with PLA bionanocomposites, some authors tried to combine the effect of toughening additives with nanoparticles with the objective of preparing toughen PLA materials with improved properties. As an example, Thellen et al.<sup>184</sup> combined a plasticiser (citrate ester) and montmorillonites to produce PLA blown films. However, the plasticiser acted more as a processing aid than a toughening agent as the elongation at break of the materials remained below 10 %. Interestingly, a 48 % improvement of oxygen barrier was reported for the film containing 5 wt.-% of clays, probably due to orientation of the clays during the blowing process. Later, Martino et al.<sup>185</sup> combined the effect of 15 wt.-% of polymeric adipates and 3 wt.-% of organoclays (C30B). When the organoclays were previously mixed with low molecular weight liquid polyadipates, swelling occurred and eased the further intercalation of PLA chains into C30B galleries. The addition of 15 wt.-% of polyadipate led to an increase of the elongation at break of up to 300 %. A loss of ductility was observed with the addition of 3 wt.-% of C30B but the elongation at break still remained above 200 %. A slight increase of modulus was observed while the oxygen transmission rate was reduced of about 25 %.

Plasticised PLA/montmorillonites with poly(ethylene glycol) has been reported by several authors.<sup>129, 130, 186-188</sup> Pluta *et al.*<sup>129</sup> studied the effect of the addition of four types of organoclays on PLA plasticised with 20 wt.-% of PEG 1000. It appeared that both PLA and PEG were able to intercalate in the clay galleries, depending on the clay modifications. Intercalated nanocomposites were obtained even for unmodified montmorillonites due to the interlayer migration of PEG. Two other studies of the same authors reported in detail the properties of the systems.<sup>130, 187</sup> Plasticisation reduced the PLA  $T_g$  by 26 °C for unfilled sample and by about 21 °C after the addition of the nanoclays. The dynamic mechanical properties were also analysed and two peaks were

observed in the loss modulus attributed to PLA and PEG rich phase. Moreover, PEG acted as a reinforcement below its glass temperature and the storage modulus also gradually increased with the filler content. However, the blends appeared to be unstable over time as PEG diffusion towards the surface was observed.<sup>130, 187</sup> No tensile or impact mechanical properties were reported in these studies. Nevertheless, Tanoue *et al.*<sup>188</sup> observed that the addition of PEG to the PLA/MMT blend resulted in more agglomerated structures and the elongation at break of the materials remained below 5 %. Copolymers have also been used for such system, as reported by Paul *et al.*<sup>186</sup> They synthesised P(L,L-LA-b-EG-b-L,L-LA) triblock copolymer by *in-situ* polymerisation in presence of C30B. They reported intensive exfoliation of the clays and the  $T_g$  of the nanocomposites decreased from 60 °C to 12 °C for a PEG content of 16.2 wt.-%. This method could be a good solution to avoid PEG migration.

Finally, blending PLA with other polymers and nanoparticles has also attracted the interest of researchers as it has been demonstrated that immiscible polymer blends could be stabilised and compatibilised by nanoparticles.<sup>189</sup> Cheng *et al.*<sup>190</sup> reported the properties of PLLA/PBS 75/25 nanocomposites. A twice functionalised organoclay (TFO) containing epoxy groups prepared from a commercial organoclay (C25A) was used in this study. At low contents, TFO was exfoliated and located in the PLA phase. When the concentration was increased to 5 and 10 wt.-%, intercalated/exfoliated clays were observed in both PLA and PBS phase. PBS domains gradually decreased with the addition of TFO. The addition of 10 wt.-% of TFO into the PLA/PBS blend led to better mechanical properties, as the Young's modulus increased from 1100 to 2000 MPa and the elongation at break from 70 % to 120 % when compared to the simple blend. Simultaneous increase of modulus and elongation at break was attributed to the chemical bonds formed between TFO and both polymers. Chen *et al.*<sup>191</sup> also reported the incorporation of TFO in PLA/PBSA, however in this case, the elongation at break decreased from 150 % to 45 % with the addition of 5 wt.-% of clays to the blend.

Ojijo *et al.*<sup>192</sup> studied the morphology and properties of poly(lactic acid)/poly(butylene succinate-co-adipate)/MMT composites (PLA/PBSA/MMT 70/30/6) using four types of organoclays. It appeared that the morphology of the blend was strongly influenced by the clay addition, the PBSA domain size being strongly reduced, depending on the clay interlayer spacing and interaction with both polymers. The smallest domain size was reported for the commercial Cloisite C20A. Nevertheless,

the mechanical properties showed that no improvement of elongation at break was achieved for these blends, probably due to the crystallinity of the blends.

PLA/PCL/MMT nanocomposites were described by Hasook *et al.*<sup>193</sup>. They reported an increase of Young's modulus and tensile strength with respect to neat PLA for PLA/PCL/MMT 90/5/5. However, the elongation at break always remained below 4 %. Sabet *et al.*<sup>194</sup> premixed an organoclay with maleated polypropylene to improve its compatibility with both polymers. The clay content was 3 wt.-% in a PLA/PCL 80/20 blend, obtaining a better exfoliation when using the maleated polypropylene (in a ratio of 3:1 with the clay). A reduction of PCL dispersed domain and a decrease of  $O_2$ permeability were observed with the addition of the clays. Nevertheless, the mechanical properties were not evaluated.

Arroyo *et al.*<sup>195</sup> also reported the preparation of PLA/TPS/MMT blends using unmodified clay. However, the addition of 2 and 5 wt.-% of clays seemed to have a negative influence over an already compatibilised PLA/TPS 73/27 blend through the use of maleic anhydride grafted PLA. The location of the clays in the TPS flexible phase or at the interface between the two polymers led to a reduction of the fracture toughness and elongation at break.

# Chapter III. STRUCTURE AND PROPERTIES OF PLA/NR BLENDS \*

\* Part of the work described in this chapter has been published in *Materials Chemistry and Physics* **2011**, 129, 823-831. Reprinted from <sup>196</sup>, with permission from Elsevier.

# III.1. SUMMARY

New formulations based on poly(lactic acid)/natural rubber (PLA/NR) blends have been developed. The processing window, temperature, time, and rotor speed, and the rubber content have been optimised in order to obtain a blend with useful properties. The rubber phase was uniformly dispersed in a continuous PLA matrix with a droplet size range from 1.1 to 2.0  $\mu$ m. The ductility of PLA has significantly been improved by blending with NR. The elongation at break improved from 5 % for neat PLA to 200 % by adding 10 wt.-% NR. In addition, the incorporation of NR not only increased the crystallisation rate but also enhanced the crystallisation ability of PLA. These materials are, therefore, very promising for industrial applications.

# **III.2.** INTRODUCTION

Rubbers have commonly been used as a second phase in thermoplastic polymers to improve their mechanical brittleness.<sup>18</sup> In fact, well dispersed rubber particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately result in materials with improved toughness. In order to impart toughness to polymers, the rubber must meet several criteria: it must be distributed as small domains in the polymer matrix, it must have good interfacial adhesion with the polymer, its glass transition temperature must be at least 20 °C lower than the use temperature, its molecular weight must not be low, it should not be miscible with the polymer matrix, and it must be thermally stable at the polymer processing temperatures.<sup>197-199</sup> Especially. NR has been used in various thermoplastic elastomers (TPE), i.e. blends of a thermoplastic with an elastomer; the properties of these materials depending on the composition, the processing conditions and possible cross-linking agents.<sup>200</sup> Blends of NR with petroleum-derived synthetic polymers, such as polyolefins or PS have been reported, and more recently, blends with biobased materials, such as thermoplastic starch, soy meal or polyhydroxybutyrate (PHB) have been considered, showing interesting properties.<sup>200-204</sup>

To date, however, the physical and mechanical properties of PLA/rubber blends have received little attention.<sup>96-99</sup>

In view of the reported works on toughening PLA, the possibility of producing a ductile PLA by blending with natural rubber is studied in this chapter. The objective is to improve the physical and mechanical properties of PLA and, thus to optimise the materials for specific end-use applications. The processing conditions, compatibility, phase morphology, crystallisation, rheological and mechanical properties of PLA/NR blends are assessed in this chapter.

# **III.3.** EXPERIMENTAL SECTION

#### **III.3.1.** Materials and sample preparation

PLA was provided by NatureWorks<sup>®</sup>. The selected grade, PLA 2002D (D-content 4.25 %, MI = 5-7 g/10 min,  $\rho = 1.24$  g·cm<sup>-3</sup>) is a semicrystalline extrusion material with a residual monomer content of 0.3 %. It was dried overnight at 80 °C prior to use in a ventilated oven. NR was kindly supplied by Malaysian Rubber (Berhad, Malaysia) under the trade name CV60 (Mooney viscosity: ML(1 + 4) 100 °C = 60,  $\rho = 0.91$  g·cm<sup>-3</sup>).

PLA/NR blends were prepared by melt blending in a Haake Rheomix 9000 internal mixer. PLA was introduced in the mixer and allowed to melt for 3 min before adding NR. The blending time was counted after the NR addition. The optimal processing conditions (temperature of 160 °C, rotor speed of 60 rpm and blending time of 15 min) were determined based on the morphology of the blend. Subsequently, the materials were compression-moulded into 0.4 mm thick sheets in a Collin P200P press. The samples were initially compressed at 10 bars at 170 °C for 2 min, then at 150 bars for 2 min and were finally cooled under pressure at 150 bars for 2 min, resulting in amorphous materials (verified by XRD measurements).

#### **III.3.2.** Characterisation

## • Structural characterisation

The determination of PLA molecular weight was performed by Size Exclusion Chromatography (SEC) in CHCl<sub>3</sub> (3 ml·min<sup>-1</sup>) at 30 °C using a HPLC Perkin Elmer setup, made of a pump series 200, a refractive index detector series 200a, a column oven series 200, a network chromatography interface NCI 900 COLUMN. Calibration was performed using narrow distributed polystyrene standard.

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured after immersion in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd 80/20) in order to prevent electrical discharge during observation. The rubber droplet size was determined by image analysis.<sup>205</sup> Typically, 200 droplets were analysed per sample and the average Feret's diameter was calculated.

# • Physical properties

Measurements of the refractive indices of the materials were carried out using an Abbe refractometer from Atago. 1-bromonaphthalene was used as a contact liquid and at least 6 specimens of each film were tested to determine a mean value of the results.

The crystallisation process was examined in a Mettler Toledo DSC822 differential scanning calorimetry apparatus. The following procedure was adopted: samples of about 10 mg were firstly heated from room temperature to 180 °C at a scan rate of 10 °C ·min<sup>-1</sup> to erase the thermal history, then they were rapidly cooled to -90 °C, and finally a second heating scan from -90 °C to 200 °C at 10 °C ·min<sup>-1</sup> was carried out. The experiments were performed in a nitrogen atmosphere.

The crystallisation behaviour of PLA was also monitored in an optical polarising microscope (Carl Zeiss Amplival microscope) equipped with a Linkam THMS 600 automatic heating and freezing stage thermal control. Samples were sandwiched between microscope cover slips and the isothermal crystallisation at 130 °C from melt state was studied.

Thermal degradation measurements were performed using a Mettler Toledo thermogravimetric analyser (TGA, model TA Q500). The temperature program was run from 30 °C to 650 °C at a heating rate of 10 °C ·min<sup>-1</sup> in air atmosphere (20 ml·min<sup>-1</sup>).

# Rheological properties

The rheological measurements were performed using an Advanced Rheometer AR1000 from TA Instrument with parallel plate geometry of 20 mm of diameter. Tests

were carried out in dynamic mode of shearing at 160 °C from 0.01 Hz to 100 Hz frequency range. The experiments were performed in the linear viscoelastic region.

Mechanical properties

Tensile tests of the samples were measured according to ASTM D 3379-75 specifications on an Instron dynamometer (model 3366) at 23 °C, and at a cross-head speed of 10 mm·min<sup>-1</sup>. Dog-bone style samples were prepared from the sheets obtained by compression-moulding. At least five specimens of each sample were tested to determine a mean value of the results.

# **III.4.** RESULTS AND DISCUSSION

#### III.4.1. Optimisation of processing

## III.4.1.1. Morphology of the blends

Most polymers are not miscible with other polymers as both entropy and enthalpy factors are usually unfavourable and lead to heterogeneous systems with a multiphase morphology. However, numerous two phase systems have very useful properties. The properties of the blend are not only dependent on the physical properties of each component but also on the dispersed phase microstructure and the interfacial chemistry.<sup>206</sup> To attain a desired benefit, it is necessary to optimise the processing conditions, i.e. temperature, time, and rotor speed, in melt state as it will affect the morphology and the physical properties of the materials.

Melt processing is the procedure generally used to prepare polymer blends. During processing, the components are melt-blended, and the minor phase is broken up to form the dispersed phase. Here, the processing window was evaluated for PLA/NR blends setting the rubber concentration at 10 wt.-%. One of the drawbacks of processing PLA in the molten state is its low thermal stability that readily undergoes random main chain scission. So, the first parameter to study is the temperature.

Three blends were prepared at different temperatures, 160, 180 and 200 °C, while the rotor speed and blending time were fixed at 60 rpm and 15 min, respectively.

Figure III.1 shows the ESEM micrographs of the fracture surfaces of PLA/NR blends. All the blends show a phase separated morphology where the rubber particles form small dispersed droplets with low interfacial adhesion with the PLA matrix, which constitutes the continuous phase (the microvoids of the SEM images are the result of the removal of the dispersed NR droplets during fracture). Similar morphology has been obtained by Zhang *et al.*<sup>99</sup> for PLA/NR blends and was attributed to the immiscibility of the non-polar NR and the polar PLA.

Table III.1 shows an increase of the NR average droplet size when increasing the processing temperature. Also, the dispersion of the droplet size becomes broader. These results agree with previous studies on the effects of the processing parameters in the morphology of immiscible blends.<sup>207, 208</sup> Wu *et al.*<sup>207</sup> proposed a correlation between the average diameter of the dispersed phase (*d*) with the viscosity ratio (*K*) of the dispersed phase ( $\eta_d$ ) over the matrix viscosity ( $\eta_m$ ), the shear rate ( $\gamma$ ) and the interfacial tension ( $\gamma$ ):

$$d = \frac{4\gamma K^{\pm 0.84}}{\gamma \eta_m} \tag{III.1}$$

The exponent of *K* is negative for K < 1 and positive for K > 1. Other authors modified this equation taking into account the effect of the dispersed phase concentration, or that the average diameter is not exactly an inverse function of the shear rate.<sup>208, 209</sup> Nevertheless, decreasing the matrix viscosity by increasing the temperature will result in an increase of the average droplet size of rubber domains in the blend. Moreover, a decrease of the viscosity of the matrix facilitates the coalescence of the droplets of the dispersed phase as the contact time required for drop coalescence is lower.<sup>210</sup>

Thus, the temperature was fixed at 160 °C in this study.



Figure III.1. Morphology and distribution of NR droplet size in the PLA/NR blends for different processing temperatures (a) 160 °C, (b) 180 °C and (c) 200 °C.

The influence of rotor speed and blending time over blend morphology were also studied. Three rotor speeds (30, 60 and 90 rpm) and two blending times (10 and 15 min) were tested. Table III.1 suggests that these parameters hardly vary the blend morphology. Similar results have been reported in the literature, for instance see refs.<sup>211, 212</sup> Thus, the rotor speed was fixed at the intermediate value of 60 rpm and the blending time at 15 minutes. The mechanical properties suggested that the samples prepared under these conditions were more homogeneous as the standard error was less than 5 %.

Variables				Average
Temperature,	Rotor speed,	Blending time,	NR concentration,	droplet size,
°C	rpm	min	wt%	μm
160	60	15	10	$1.15\pm0.40$
180	60	15	10	$2.30\pm0.70$
200	60	15	10	$2.30\pm0.90$
160	30	15	10	$1.20 \pm 0.40$
160	90	15	10	$1.25\pm0.40$
160	60	10	10	$1.15\pm0.35$

Table III.1. Average droplet size of NR in the blend as a function of processing variables, for a NR concentration of 10 wt.-%.

#### III.4.1.2. Polymer degradation

The possible thermal degradation of the two polymers at the chosen processing temperature was evaluated by thermogravimetric analysis. From dynamic conditions (Figure III.2.a), it is observed that the onset degradation temperatures for PLA and NR are well above the processing temperature (338.7 °C and 335.8 °C, respectively). Nevertheless, it is not recommended to process NR at temperatures higher than 200 °C as the possibility of NR oxidation becomes significant and may affect the ageing of the materials.<sup>200</sup> No significant weight loss is observed for both polymers during isothermal treatment at 160 °C (Figure III.2.b).



Figure III.2. Thermal degradation of PLA and NR evaluated by TGA in air atmosphere for (a) dynamic condition and (b) isothermal condition at 160 °C.

Moreover, it is well known that one of the limitations of PLA towards its wider industrial application is the thermal and mechanical degradation that the polymer suffers during processing. The chain length reduction by hydrolysis or alcoholysis reactions strongly depends on traces of residual monomer, water or residual organometallic compounds used during polymerisation.<sup>213</sup> Hence, it is very important to consider PLA degradation during processing.

PLA was processed alone at 160 °C for 15 min and at a rotor speed of 60 rpm. Its possible degradation during melt processing was evaluated by viscosity measurements and resulted in a significant decrease of the complex viscosity in the Newtonian region after processing, from  $21.0 \times 10^3$  Pa·s to  $6.3 \times 10^3$  Pa·s. This decrease suggests a clear reduction of the molecular weight of approximately 30 % due to chain scission processes, according to the relation  $\eta_0 = KM_W^{3.7}$ . The results were confirmed by SEC as the average molecular weight of PLA shifts from  $13.6 \times 10^4$  to  $9.0 \times 10^4$  after processing.

Later, the influence of this molecular weight reduction on crystallisation and mechanical properties of PLA was evaluated. Isothermal crystallisation was studied by polarised optical microscopy: the samples were melted at 180 °C for 2 minutes and cooled to 130 °C at 30 °C ·min<sup>-1</sup> and photos were taken at different times of isothermal treatment. Figure III.3 shows the development of spherulites after 30 min in the case of pristine PLA compared to 10 minutes in the case of processed PLA. This result establishes that the processing can induce a significant increase of the crystallisation rate due to the presence of smaller chains.<sup>49, 214</sup>



Figure III.3. Photos taken by optical polarised microscope. Isothermal crystallisation (cooled from 180 °C to 130 °C) of pristine PLA at (a) 0 min, (b) 30 min, (c) 1 h, (d) 2 h and processed PLA at (e) 0 min, (f) 10 min, (g) 15 min and (h) 1 h.

Moreover, it should also be considered that the addition of NR to PLA could have a certain influence over PLA degradation during processing. Figure III.4 shows the evolution of the torque of PLA and PLA/NR blend in order to analyse this possible degradation. Feeding PLA into the internal mixer drastically increases the torque that then starts to decrease as the polymer melts and reaches a plateau. The torque evolution for the blend follows a similar trend until the addition of NR when the torque increases slightly, but achieves a similar value. This behaviour suggests that NR does not induce a further degradation of PLA.



Figure III.4. Torque evolution at 160 °C for PLA and PLA/NR 10 wt.-% blend.

#### III.4.2. Effect of NR concentration

# III.4.2.1. Morphology

Three blends at 5, 10 and 20 wt.-% of natural rubber were prepared to analyse the effect of the NR concentration on the morphology of the blend. It is of interest to note that the transparency of PLA is not completely lost after blending (Figure III.5).



Figure III.5. Photographs of films of about 150  $\mu$ m for (a) PLA and (b) PLA/NR blend at 10 wt.-%.

The addition of NR produces only a slight yellowish coloration of the blend and translucent material is obtained at low thickness. Refractive indices of  $1.4537 \pm 0.0013$ ,  $1.5209 \pm 0.0008$  and  $1.4579 \pm 0.0013$  have been measured for PLA, NR and PLA/NR 10 wt.-% blend, respectively and are in agreement with those reported in the literature.<sup>13, 215</sup>

Figure III.6 shows the ESEM micrographs of the fracture surfaces of the PLA/NR blends. It is worth to note that the size of the rubber particles is similar in the case of PLA/NR 5 wt.-% and 10 wt.-% but increases for a concentration of 20 wt.-% from 1.15 to 2.00  $\mu$ m (Table III.2).

In general, in an immiscible binary polymer blend, the size of the dispersed phase increases as a function of the concentration of the minor phase in the blend, due to coalescence phenomena.<sup>210</sup> Increasing the dispersed phase concentration leads to the development of a phase inversion. It is well known that the particle size in blends with dispersed structure is governed by the competition between their break-up and coalescence.<sup>210</sup> Several theoretical and experimental approaches in homogeneous steady

shear or extensional flow have been developed to predict the final blend morphology.<sup>209</sup> However, flow field in internal mixers is not homogeneous and the stress varies in different areas. Small drops can appear in high shear regions due to break-up, while increased droplet interactions at high concentration of the dispersed phase will result in large drops due to coalescence, resulting in a broader distribution size. So, the distinction of both phenomena, break-up and coalescence, in polymer blends is a complex issue.



Figure III.6. Morphology and distribution of rubber droplet size in PLA/NR blends at different NR concentrations (a) 5 wt.-%, (b) 10 wt.-% and (c) 20 wt.-%.

NR concentration,	Average droplet size,
wt%	μm
5	$1.20 \pm 0.40$
10	$1.15\pm0.40$
20	$2.00 \pm 0.70$

Table III.2. Average droplet size of NR in the blend as a function of the NR concentration.

## III.4.2.2. Crystallisation behaviour

Figure III.7 shows the DSC heating curves of PLA and PLA/NR blends. The results confirm the immiscible behaviour of the blends since no changes are observed in the glass transition temperature ( $T_g$ ) of PLA with the NR content. Interestingly, a cold-crystallisation exothermic peak and a melting endothermic peak are observed in both 10 wt.-% and 20 wt.-% PLA/NR blends. These results suggest that the incorporation of NR enhances the crystallisation ability of PLA. Similar results were reported by Li *et al.*<sup>96</sup> for PLA/PU blends.



Figure III.7. DSC heating curves of PLA and PLA/NR blends (second heating scan).

	T <sub>g, NR</sub> ,	T <sub>g, PLA</sub> ,	T <sub>c</sub> ,	ΔH <sub>c</sub> ,	T <sub>m</sub> ,	ΔH <sub>m</sub> ,
	°C	°C	°C	$J \cdot g^{-1}$	°C	J·g <sup>-1</sup>
Pristine PLA	-	58.4	-	-	-	-
Processed PLA	-	59.6	-	-	150.0	0.1
PLA/NR 5 wt%	-	59.2	-	-	151.2	0.4
PLA/NR 10 wt%	-73.0	57.7	127.6	-9.7	151.0	9.9
PLA/NR 20 wt%	-72.8	59.4	123.5	-17.0	151.3	20.3

Table III.3. DSC data of PLA and PLA/NR blends (second heating scan).

The isothermal crystallisation of the blends was further analysed via rheological measurements. This study was motivated by the extremely low crystallisation rate of PLA, which results in a low heat flow often within the DSC equipment resolution limits.<sup>216</sup> Khanna *et al.*<sup>217</sup> were the first to use rheological measurements to determine polymer crystallinity and since then this technique has been used on a wide range of systems.<sup>218, 219</sup> Small increments in the polymer crystallinity result in an increase of complex viscosity due to both the filler effect of the crystals and the physical crosslink of the polymer chains within the entangled system.<sup>216</sup> For the experiments, the blends were melted inside the rheometer at 180 °C for 2 min to erase thermal history and then quenched at 120 °C. The evolution of complex viscosity was then monitored as a function of time. Tests were carried out at 1 Hz and within the linear viscoelastic region at small strain values to avoid shear-induced crystallisation. It should be noted that the linear viscoelastic region evolved as the samples crystallisation of the samples.

Figure III.8 represents the evolution of the ratio of the measured viscosity by the initial viscosity of the blends. The addition of NR increases PLA crystallisation rate confirming the nucleating effect of NR over PLA. Similar behaviour of PLA crystallisation has been reported in thermoplastic-PLA blends.<sup>85, 220</sup>



Figure III.8. Evolution of complex viscosity during isothermal crystallisation.

The crystallisation behaviour of a crystallisable matrix in immiscible blends can be affected by two major phenomena which are the migration of impurities during meltmixing and the nucleating activity of the interface.<sup>18</sup> As the concentration of NR increases in the blend, the amount of nuclei that can migrate varies as well and the nucleation density in the crystallisable phase increases. However, increasing the NR concentration results in the formation of larger droplets and thus, in a lower total interfacial contact area. Two phenomena are then in competition which are the increase of nuclei able to migrate and the reduction of contact area between the two polymers. Here, it appears that the increase of nuclei concentration is the predominant effect.

The crystallisation degree of the samples crystallised in the rheometer was then determined by DSC. Figure III.9 represents the first heating scan of the crystallised blends at 10 °C·min<sup>-1</sup>. The slight increase of crystallinity is attributed to the nucleating effect of NR (Table III.4). A decrease of few degrees of the melting temperature with NR concentration could attest to the formation of smaller spherulites due to the nucleating effect of NR.<sup>221</sup>



Figure III.9. Melting curves of crystallised PLA/NR blends.

Table III.4. DSC data of PLA and PLA/NR blends after crystallisation.

	T <sub>m</sub> , °C	$\Delta H_m, I \cdot \sigma^{-1}$
Processed PLA	152.8	23.6
PLA/NR 5 wt%	151.5	24.8
PLA/NR 10 wt%	150.6	25.2
PLA/NR 20 wt%	150.3	25.5

# III.4.2.3. Rheological properties

The rheological study of the blends is of crucial importance to understand the processability of the materials. Moreover, the composition and morphology have a direct impact on the rheological properties. Figure III.10 shows the viscoelastic behaviour of PLA, NR and PLA/NR blends.



Figure III.10. Rheological properties of PLA and PLA/NR blends (a)  $G'(\omega)$ , (b)  $\eta^*(\omega)$  and (c) Cole-Cole diagrams.

PLA follows the characteristic terminal zone behaviour, i.e.  $G' \propto \omega^2$  with a zero shear viscosity of 6 x 10<sup>3</sup> Pa·s. Meanwhile, the absolute value of the complex viscosity  $\eta^*$  of the PLA/NR blends increases with the concentration of NR in the terminal zone, as well as the storage modulus G'. More interestingly, a secondary plateau is observed for the blends with a NR concentration of 10 wt.-% and 20 wt.-%, which can be attributed to a new relaxation phenomenon. The Cole-Cole diagram (Figure III.10.c,  $\eta''(\omega)$  vs  $\eta'(\omega)$ ) clearly shows two relaxation mechanisms for PLA/NR 10 wt.-% and 20 wt.-% blends. The first one, at high frequencies, is attributed to the PLA matrix with a relaxation time  $\lambda_m$  of 0.3 s. The characteristic times of the secondary plateau are estimated to be 25 s and 100 s for PLA/NR 10 wt.-% and PLA/NR 20 wt.-% blends, respectively, and are attributed to the relaxation time of the droplets.<sup>222, 223</sup>

# III.4.2.4. Mechanical properties

The tensile behaviour of the materials is shown in Figure III.11 and Table III.5. PLA is a rigid and brittle polymer with a very low elongation at break of 5 %. The material breaks after yield without necking. The addition of NR in the PLA matrix changes the brittle fracture of PLA to a ductile fracture with formation and propagation of a neck while stretching and the yield fracture is suppressed.



Figure III.11. Average curves of the mechanical properties of PLA and PLA/NR blends.

	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
Pristine PLA	$2874 \pm 108$	$63.1 \pm 1.1$	$3.3 \pm 0.4$
Processed PLA	$3136 \pm 38$	$58.0 \pm 1.5$	$5.3 \pm 0.7$
PLA/NR 5 wt%	$2480 \pm 61$	$50.4 \pm 1.6$	$48 \pm 22$
PLA/NR 10 wt%	$2036\pm47$	$40.1 \pm 1.5$	$200 \pm 14$
PLA/NR 20 wt%	$1837\pm78$	$24.9\pm0.9$	$73 \pm 45$

Table III.5. Mechanical properties of PLA and PLA/NR blends.

It is very interesting to note that a drastic increase of the elongation at break to 200 % is obtained with the addition of 10 wt.-% of NR. Hence, in this particular case, the interfacial adhesion between the PLA and NR phases is not a key factor to improve mechanical properties as low interactions between the two phases were observed. Figure III.12 shows the fractured sections along the tensile direction for PLA and PLA/NR 10 wt.-% blend after stretching. PLA breaks at very low elongations and the fracture

surface is very smooth. Ito *et al.*<sup>224</sup> studied the deformation mechanism of PLA under uniaxial tensile deformation and demonstrated that both shearing deformation and the formation of surface crazes occurred simultaneously with plastic deformation. However, the addition of the rubber leads to a large plastic deformation with formation of a neck. This result suggests that NR behaves as a stress concentrator and debonding could occur in the initial stage of stretching at the particle-matrix interface due to the poor interfacial adhesion. The stress concentration results in the formation of a yield point at which a stable plastic deformation takes place. After the yield point, a typical neck starts to form and then extends in a "cold drawing" process. In addition, the material undergoes some whitening in the necked zone, which reflects a fine-scale cavitation process. The undeformed material contains cavities due to the poor adhesion between PLA and NR, which are clearly increased during the material deformation. The addition of the rubber particles significantly lowers the yield stress, arising from softening and formed voids.

Thus, both the release of the strain constraint, due to the formation of voids, and the decrease of yield stress result in the relaxation of stress concentration, and in the significant increase of the ductility of the material. Further details of the deformation mechanisms of the samples are reported in *Chapter V*.



Figure III.12. Fractured surface of stretched materials (a) PLA and (b) PLA/NR 10 wt.-% blend.

The concentration of 10 wt.-% of NR seems to be optimal since a further increase of the rubber content in the blend decreases the elongation at break to approximately 70 %. As expected, Young's modulus and tensile strength of the blends decrease with the addition of NR.

To understand the results of the mechanical properties of PLA/NR 20 wt.-%, the ESEM micrographs of the blend were analysed before and after compression-moulding, as this processing step was used to prepare the samples for mechanical properties (Figure III.13).

Compression-moulding leads to a dramatic increase of the average droplet size up to  $4.0 \pm 2.1 \,\mu\text{m}$  and to a broader size distribution due to the coalescence of NR droplets. This behaviour has been reported for other polymer blends and demonstrates that the coalescence of dispersed phase in immiscible blends is not prevented by the high viscosity of polymers.<sup>210, 225</sup> Hence, the coalescence of the NR particles in PLA/NR 20 wt.-% blend during compression-moulding increases so much the droplet size that the improvement of PLA mechanical properties by NR becomes ineffective. This coalescence effect occurs in less proportion for PLA/NR 5 wt.-% and PLA/NR 10 wt.-% blends due to the lower concentration of rubber and, thus, hardly influences the mechanical properties.



Figure III.13. Comparison of PLA/NR 20 wt.-% blend morphology before and after compression-moulding.

# **III.5.** CONCLUSIONS

The addition of natural rubber allows straightforward production of ductile PLA, using a simple blending followed by a compression-moulding technique. The processing conditions were fixed at 160 °C, 60 rpm and 15 min of blending time. The optimal NR content to improve the brittleness of PLA was found to be 10 wt.-%; at this concentration, the rubber droplets provided an optimum balance between their coalescence and their enhancement of both the material physical and mechanical

behaviour. The tensile testing of the optimal sample showed a drastic increase in the elongation at break from 5 % to 200 % without sacrificing the transparency of the material. Moreover, natural rubber could be acting as a nucleating agent favouring the crystallisation ability of PLA. The study confirms PLA/NR blend as a viable material to overcome the two main drawbacks of PLA for its use in the packaging sector.
# Chapter IV. PHYSICOCHEMICAL PROPERTIES OF PLA/NR/ORGANOCLAY BIONANOCOMPOSITES \*

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## IV.1. SUMMARY

Novel poly(lactic acid) bionanocomposites with tuneable properties were successfully prepared by melt blending PLA with natural rubber and several montmorillonites (MMT). The organoclays were preferentially located at the interface acting as compatibilisers between both polymer phases. This location resulted in a marked improvement of the physical and mechanical properties of the system. Moreover, these properties can be controlled as a function of the nanofiller surface properties and the blending procedure used.

## **IV.2.** INTRODUCTION

In the previous chapter, blending PLA with NR appeared to be a practical strategy to improve PLA brittleness. However, a lack of compatibility between the two polymers was observed. It is well known that the final properties of immiscible polymer blends are strongly influenced by both the size and interface of the dispersed phase and, hence, compatibilisers are often required in order to improve the morphology. While organic molecules and block copolymers are most commonly used, recent studies have introduced inorganic solid particles as a new type of compatibiliser.<sup>189, 227</sup> In particular, layered silicates have been reported to improve the morphology of immiscible blends.<sup>228-230</sup> Moreover, the addition of nanoclays to the PLA/NR blend could also present a practical way to improve the gas barrier properties of the material.

Here, the idea is to develop a novel and industrially scalable organoclay filled PLA/NR blend bionanocomposite prepared by melt blending. This study is aimed at understanding the influence of several clays, presenting different surface properties and hydrophicility on the properties of an immiscible PLA/NR blend.<sup>231</sup> The control of the nanofiller surface property and the mixing procedure could force the location of the clay in the blend. Thus, this location and the interactions of the nanoparticles with both polymers will determine the ultimate physicochemical properties of the nanocomposite. The chapter presents a thorough study based on both experimental and theoretical approaches to understand the best strategy to attain the desired properties. Here, it is focused on optimising the mechanical and barrier properties since they will benefit PLA bionanocomposite applications.

## **IV.3.** EXPERIMENTAL SECTION

## IV.3.1. Materials and sample preparation

PLA polymer 2002D was provided by NatureWorks<sup>®</sup> (D-content 4.25 %, MI = 5-7 g/10 min,  $\rho = 1.24 \text{ g}\cdot\text{cm}^{-3}$ ). Natural Rubber (NR) was kindly supplied by Malaysian Rubber under the trade name CV60 (Mooney viscosity: ML(1 + 4) 100 °C = 60,  $\rho = 0.91 \text{ g}\cdot\text{cm}^{-3}$ ). Three montmorillonites, one un-modified, Cloisite<sup>®</sup> Na<sup>+</sup>, and two organomodified, denoted as Cloisite<sup>®</sup> 15A and Cloisite<sup>®</sup> 30B, provided by Southern Clay Products were used as fillers (Table IV.1).<sup>232</sup> C30B was chosen for its good compatibility with PLA (see *Chapter II*) while C15A was used for its large basal spacing and good compatibility with NR.<sup>233</sup> CNa<sup>+</sup> was employed for sake of comparison.

Table IV.1. Technical characteristics of the layered silicates (data provided by the manufacturer).<sup>232</sup>

Clay	Organic modifier	Modifier concentration (meq/100g clays)	Basal spacing, d (Å)
Cloisite <sup>®</sup> Na <sup>+</sup> (CNa <sup>+</sup> )	-	-	11.7
Cloisite <sup>®</sup> 15A (C15A)	2M2HT <sup>a</sup>	125	31.5
Cloisite <sup>®</sup> 30B (C30B)	MT2EtOH <sup>b</sup>	90	18.5

 $^a$  2M2HT: dimethyl dihydrogenated tallow quaternary ammonium cation. Tallow:  $\sim 65$  % C18,  $\sim 30$  % C16,  $\sim 5$  % C14.

<sup>b</sup> MT2EtOH: methyl bis-2-hydroxyethyl quaternary ammonium cation. Tallow: ~ 65 % C18, ~ 30 % C16, ~ 5 % C14.

PLA and clays were dried overnight at 80 °C in a ventilated oven prior to use. Composites were prepared by melt blending in a Haake Minilab twin screw extruder. NR concentration was fixed at 10 wt.-%, and the clay loading was varied from 1 to 5 wt.-%. In this case, the materials were dried mixed before melt blended in the extruder due to the difficulty of introducing NR into the extruder. An optimal processing window was selected: temperature of 180 °C, rotor speed of 100 rpm, and a blending time of 15 min, based on the PLA degradation, the NR droplet distribution and the clay dispersion. Subsequently, the materials were compression-moulded into 0.4 mm thick sheets in a Collin P200P press. The samples were initially compressed at 10 bars at 180 °C for 2 min, then at 150 bars for 2 min and were finally cooled under pressure at 150 bars for 2 min, resulting in amorphous materials (verified by XRD measurements).

#### **IV.3.2.** Characterisation

#### • Structural characterisation

The determination of PLA molecular weight was performed by Size Exclusion Chromatography (SEC) in CHCl<sub>3</sub> (3 ml·min<sup>-1</sup>) at 30 °C using a HPLC Perkin Elmer setup, made of a pump series 200, a refractive index detector series 200a, a column oven series 200, a network chromatography interface NCI 900 COLUMN. Calibration was performed using narrow distributed polystyrene standard.

Experiments were also performed using a 6890N gas chromatograph equipped with a mass spectroscopic detector from Agilent, an injecting system from Industrie Laboratoire Service and a HP-5ms column. Helium was used as carrier gas and the samples were heated from 60 °C to 315 °C at 30 °C·min<sup>-1</sup>. The identification of the compounds was made by comparison of their mass spectra with the Spectral Database for Organic Compounds (SDBS).<sup>234</sup>

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd 80/20). The nanoclay dispersion was also studied by transmission electron microscopy (Philips Tecnai 20 microscope at an acceleration voltage of 200 kV). Ultra-thin sections of the samples were prepared by cryo-ultramicrotomy at -140 °C (Leica EM UC6). The rubber droplet size was determined by SEM and TEM image analysis using ImageJ.<sup>205</sup> Typically, 200 droplets were analysed per sample and the average Feret's diameter was calculated.

X-ray diffraction (XRD) was also used to characterise the nanocomposites on a nanostructured level. The experiments were performed in a D8 Advance equipment from Bruker with a CuK $\alpha$  radiation at  $\lambda = 1.54$  Å (40 kV and 40 mA). Measurements were carried out in a  $2\theta$  range from 1 ° to 10 ° at a speed of 0.2 second per point.

# • Physical properties

Contact angle measurements were carried out in a Krüss G10 optical contact angle meter. Distilled water and diiodomethane were used as testing liquid. Contact angles of ten droplets at equilibrium were considered in order to obtain an average value.

Crystallisation behaviour of the materials was investigated by differential scanning calorimetry (Mettler Toledo DSC822). The following procedure was adopted: samples of about 10 mg were firstly heated from room temperature to 200 °C at a scan rate of 40 °C  $\cdot$ min<sup>-1</sup>. The samples were kept 3 min at this temperature to erase thermal history, and then were rapidly cooled to 25 °. Finally a second heating scan from 25 °C to 200 °C at 2 °C  $\cdot$ min<sup>-1</sup> was carried out. The experiments were performed in a nitrogen atmosphere.

Dynamic mechanical analysis was performed on a TA instruments (model Q800) in tensile mode at 3 Hz as a function of temperature from -90 °C to 150 °C at a heating rate of 2 °C·min<sup>-1</sup>.

Thermal degradation measurements were performed using a Mettler Toledo thermogravimetric analyser (TGA, model TA Q500). The temperature program was run from 30 °C to 650 °C at a heating rate of 10 °C  $\cdot$ min<sup>-1</sup> in nitrogen atmosphere (20 ml·min<sup>-1</sup>).

# Rheological properties

Rheological measurements were performed using an Advanced Rheometer AR2000 from TA Instruments with parallel plate geometry of 25 mm of diameter. Tests were carried out in dynamic mode of shearing at 180 °C from 0.01 rad·s<sup>-1</sup> to 100 rad·s<sup>-1</sup> frequency range in nitrogen atmosphere.

# Mechanical properties

Tensile tests of the samples were measured according to ASTM D 3379-75 specifications on an Instron dynamometer (model 3366) at 23 °C, and at a cross-head speed of 10 mm·min<sup>-1</sup>. At least five specimens of each sample were tested.

#### Gas barrier properties

Gas barrier properties were determined using a barometric permeation method at a constant temperature of 30 °C. The upstream and downstream pressures were kept at 3 bar and below  $10^{-2}$  mbar, respectively. For the permeation experiments, helium, oxygen and carbon dioxide were used, where helium permeation was only used to check the absence of pinholes. The gas permeability coefficients *P* were determined from the slope of downstream pressure versus time plotted once steady state had been achieved, according to the expression:

$$P = \frac{K_0(B \times t)}{P_0} \tag{IV.1}$$

where  $K_0$  is an apparatus constant that includes parameters such as temperature, cell permeation area and volume of the system, *B* is the slope of downstream pressure versus time, *t* is the film thickness and  $P_0$  is the upstream pressure.

## • Disintegration study

Disintegration study was carried out following the European standard ISO 20200 which considers the disintegration degree of plastic materials under simulated composting conditions in a laboratory-scale test at 58 °C, 50 % of humidity and in aerobic conditions. ISO 20200 defines as disintegrated a sample that achieves in 90 days the 90 % of disintegration, which means that no more than 10 % of the original dry weight has to be retained in a 2 mm sieve. A specific quantity of compost inoculum, supplied by Gesenu S.p.a., was mixed together with the synthetic biowaste, prepared with sawdust, rabbit food, starch, sugar, oil and urea as reported in Table IV.2. The water content of the substrate was around 50 wt.-% and the aerobic conditions were guaranteed by mixing it softly.

Components	%
sawdust	20
rabbit food	15
starch	5
compost inoculum	5
sugar	2.5
oil	1.5
urea	1
deionized water	50

Table IV.2. Compost composition.

Compression moulded films of 20 mm x 20 mm x 0.30 mm were buried into the organic substrate at 4-6 cm depth in the perforated boxes and incubated at 58 °C. The tested samples were taken out at selected times, washed and dried in an oven at 37 °C for 24 h.

The blends chosen for the disintegrability study were PLA, PLA/NR, PLA/NR/CNa<sup>+</sup>, PLA/NR/C15A and PLA/NR/C30B at 3 wt.-% of nanoclays. The disintegrability value was obtained by normalising the weight of the samples, at different stages of incubation, with respect to the initial ones. Infrared spectra of the samples were measured in a Jasco FT-IR 615 spectrometer in attenuated total reflectance (ATR) mode before and after different times of disintegration in composting conditions.

## IV.4. RESULTS AND DISCUSSION

### **IV.4.1.** Optimisation of processing

The optimal conditions for processing the materials in the extruder were determined considering a PLA/NR/C30B nanocomposite with 3 wt.-% of C30B. This montmorillonite was chosen for this study as it is the organoclay which could be more easily exfoliated (see *Chapter II*). Three temperatures (160 °C, 180 °C, 200 °C), three

rotor speeds (50 rpm, 100 rpm, 150 rpm) and three blending times (10, 15, 20 min) were tested. The dispersion state of the organoclay in each nanocomposite was determined by XRD, meanwhile the average NR droplet size was measured from SEM images. Moreover, PLA was processed alone in the same conditions and its degradation was evaluated by rheological measurements, determining the complex viscosity in the Newtonian zone (called Newtonian viscosity).

Table IV.3 shows that the PLA Newtonian viscosity strongly depends on the processing conditions, demonstrating the susceptibility of PLA degradation to the processing conditions.

Moreover, a slight increase of the NR droplet size is observed with the increase of the temperature, as reported in *Chapter III*. A rotor speed higher than 50 rpm also seems to be required in order to obtain a good distribution of the NR droplets while no real influence of the blending time is noted.

Comments on the difference between NR droplet size in the PLA/NR blend or in the nanocomposite are reported in the next section.

	Variables		PLA Newtonian	Average NR
Temperature,	Rotor speed,	Blending time,	viscosity,	droplet size,
°C	rpm	min	Pa.s	nm
160	100	15	5490	$330\pm90$
180	100	15	3080	$360 \pm 90$
200	100	15	2470	$570 \pm 190$
180	50	15	4450	$520 \pm 150$
180	150	15	2310	$410\pm100$
180	100	10	4280	$460 \pm 150$
180	100	20	2615	$450\pm110$

Table IV.3. Average droplet size of NR in the PLA/NR/C30B nanocomposite and PLA Newtonian viscosity as a function of the processing variables.

Figure IV.1 reports the XRD spectra for C30B and for the nanocomposites. C30B displays a diffraction peak at  $2\theta = 4.8$  °, corresponding to an interlayer distance of 18.8 Å. All the nanocomposites presents a shift of this peak at lower angles ( $2\theta \sim 2.6$  °, with a 2<sup>nd</sup> order reflection at about 5.2 °), revealing an intercalated morphology of the

nanocomposites. Exfoliated nanocomposites are obtained for a blending time of 20 min or for a processing temperature of 200 °C, due to the low viscosity of PLA that facilitates the polymer chain penetration into the clay gallery.

In view of the obtained results and considering the three criteria, i.e PLA degradation, NR droplet size and C30B exfoliation, the processing conditions were fixed to a temperature of 180 °C, a rotor speed of 100 rpm and a blending time of 15 min.



Figure IV.1. Evaluation of C30B dispersion by XRD measurements as function of (a) processing temperature at 100 rpm for 15 min, (b) rotor speed at 180 °C for 15 min and (c) blending time at 180 °C and 100 rpm.

Figure IV.2 shows the evolution of the torque in the extruder during blending for pure PLA, PLA/NR and PLA/NR/C30B for the selected processing conditions. Surprisingly, a reduction of the torque and the extrusion pressure is observed in the case of the blends. To discard that this observation was due to PLA degradation, NR phase

was removed from the blend by dissolving selectively PLA from the blend using dioxane as a solvent. The solution was then filtered to remove NR droplets and dried under vacuum. An average molecular weight of about  $11.0 \times 10^4$  was then obtained in both cases.

Thus, it appears that NR could act in the extruder as a lubricant for the blend, limiting friction effects and local overheating. This effect was probably not observed in the case of the internal mixer due to the differences of the surface effect in both equipments.



Figure IV.2. Evolution of torque during blending in the twin screw extruder for PLA, PLA/NR blend and PLA/NR/C30B 3 wt.-%.

The complex nature of NR could explain this effect.<sup>19</sup> Natural rubber contains a nonnegligible amount of lipids, proteins and fatty acids derived by the hydrolysis of phospholipids during storage, and these small molecules can easily migrate to the surface.<sup>235</sup> This migration was evaluated by a simple experiment: the blend was immersed in acetone for few minutes at the outlet of the extruder, and the acetone, which is a poor solvent for both PLA and NR, was then analysed by GC-MS.

Figure IV.3 shows the mass spectra of the acetone at various retention times. Molecules of isoprene as well as lactide (residual monomer) and oligomers of PLA are identified at retention time of 8.5 and 8.2 min, respectively. Additionally, molecules of fatty acids such as palmitic acid and linoleic acid appear at retention times of 5.9 and 6.5 min, respectively. These molecules were not observed in the case of NR extracted



with acetone prior to mixing. The migration of small molecules at the surface of the blend acting as a lubricant during processing is then confirmed.

Figure IV.3. Mass spectra of the acetone in which the blend was immersed at retention times of 6.0, 6.5, 8.2 and 8.5 min.

## IV.4.2. Morphology and location of the nanoparticles

Several studies have demonstrated that nanoparticles can stabilise immiscible polymer blends.<sup>189, 229, 230, 236</sup> Fenouillot *et al.*<sup>189</sup> critically reviewed different phenomena responsible for this stabilisation and identified the following factors: the reduction of the interfacial tension between the polymers, the inhibition of coalescence by the presence of the rigid fillers around the dispersed polymer, the change of viscosity ratio between the two polymers, and the filler-polymer interaction. It was also demonstrated that a key factor to understand the observed compatibilisation mechanism was the nanofiller location in the polymer blend. Hence, the nanoparticle location at the thermodynamic equilibrium was estimated by calculating the wettability parameter w, which depends on the interfacial tensions between the components:

$$w = \frac{\gamma_{P-2} - \gamma_{P-1}}{\gamma_{1-2}}$$
 (IV.2)

where  $\gamma_{P-n}$  is the interfacial tension particle-polymer (in this case, 1 is natural rubber and 2 is referred to PLA), and  $\gamma_{1-2}$  the interfacial tension between the two polymers. If w > 1, the particles will mainly be located in polymer 1; if w < -1, the particles will be present in polymer 2; and if -1 < w < 1, the particles will be concentrated at the interface.<sup>236</sup> Due to the experimental difficulty of determining the interfacial tension between components, it is usually calculated with theoretical models such as the Girifalco-Good equation:<sup>189</sup>

$$\gamma_{ij} = \gamma_i + \gamma_j - 2\varphi_{\sqrt{\gamma_i \gamma_j}}$$
(IV.3)

where  $\gamma_i$  and  $\gamma_j$  are the surface energies of the *i* and *j* components, and  $\varphi$  a parameter depending on the molar volumes of the components. Good approximations can be obtained by taking  $\varphi = 1.^{237, 238}$  Thus, the surface energies of PLA and NR were determined by contact angle measurements (Table IV.4.a) and applying the Owens and Wendt equation:

$$\gamma_L (1 + \cos\theta) = 2\sqrt{\gamma_i^d \gamma_L^d} + 2\sqrt{\gamma_i^p \gamma_L^p}$$
(IV.4)

where  $\gamma_L$  is the surface tension of the testing liquid,  $\theta$  the average contact angles,  $\gamma_i^d$ and  $\gamma_i^P$  the dispersion and polar contributions of  $\gamma_i$ , respectively, and  $(\gamma_i = \gamma_i^d + \gamma_i^P)$  is the surface tension of the polymer.<sup>239</sup> The surface tension values of PLA and NR at room temperature were calculated to 40.2 and 26.2 mJ·m<sup>-2</sup>, respectively, which agree with those reported in the literature.<sup>240, 241</sup> The evolution of the surface tension of polymers with the temperature is approximated using the general relation:<sup>242, 243</sup>

$$d\gamma/dT = -0.06 \ mJ \cdot m^{-2} \cdot K^{-1}$$
(IV.5)

The value of  $\gamma_{PLA}$  and  $\gamma_{NR}$  at 180 °C (processing temperature) are then reported in Table IV.4.b.

The clay surface energies are taken from literature.<sup>244</sup> Applying the equation (IV.2), the wettability parameter can then be calculated to predict the equilibrium position of

the clays in the blend (Table IV.4). The results indicate that CNa<sup>+</sup> and C30B would be located in the PLA phase and C15A at the interface. It is of interest to point out that the thermodynamic consideration is an estimation and that kinetic effects of mixing process should also be taken into account.<sup>229, 236</sup>

a.		V	Water		Diiodomethane	
$\theta_{PLA}$	, ,	7	74 ± 1		45 ± 4	
$\theta_{NR}$	0	9	$92 \pm 2$		$66 \pm 2$	
b.	PLA	NR	CNa <sup>+</sup>	C15A	C30B	
γ, mJ.m <sup>-2</sup>	30.81	16.75	44.00	25.40	34.50	
$\gamma$ pla/nr	2.1	3				
$\gamma$ pla/mmt			1.17	0.26	0.10	
$\gamma$ NR/MMT			6.45	0.89	3.17	
W			-2.49	-0.30	-1.44	
Location			PLA phase	Interface	PLA phase	

Table IV.4. (a) Contact angle values for PLA and NR and (b) surface energies and interfacial tension between the components - Equilibrium location of the clays in the PLA/NR blend.

Scanning and transmission electron microscopes were used to corroborate the theoretical considerations. Figure IV.4 shows SEM micrographs for the PLA/NR blend and its composites reinforced with the different clays at a concentration of 3 wt.-%.



Figure IV.4. SEM images of (a) PLA/NR blend and its composites at 3 wt.-% of filler (b) PLA/NR/CNa<sup>+</sup>, (c) PLA/NR/C15A and (d) PLA/NR/C30B.

The rubber particles form small dispersed droplets (~ 940 nm) in the PLA matrix, as reported in *Chapter III*. The addition of the unmodified  $CNa^+$  clay does not affect the NR droplet morphology, while the organoclays drastically decrease the NR particle size. As expected, a more homogeneous morphology with finer and uniform dispersion of the rubber phase is obtained with the addition of C15A and C30B (~560 nm and 360 nm, respectively).

The location of the different clays as a function of their chemical modification was determined by TEM inspection. CNa<sup>+</sup> is present in the PLA phase forming big agglomerates (Figure IV.5), while both organoclays are preferentially located at the PLA/NR interface at low concentration (Figure IV.6). As the organoclay concentration is increased, the location of C15A is found at both the interface and NR phase, due to the presence of a non-polar surfactant, while C30B is present at both the interface and PLA phase. As previously mentioned, despite the high viscosity of NR, the rubber chains could easily insert within the galleries of the C15A organoclay, giving rise to an

exfoliated morphology.<sup>230, 233, 245</sup> These results agree well with the previous theoretical considerations.



Figure IV.5. TEM image of PLA/NR/CNa<sup>+</sup> 3 wt.-%.



Figure IV.6. Location of C15A at (a) 1 wt.-%, (b) 3 wt.-%, (c) 5 wt.-% (top) and of C30B at (d) 1 wt.-%, (e) 3 wt.-% and (f) 5 wt.-% (bottom) using TEM.

Two effects have to be considered in order to explain the decrease of the rubber droplet size when adding the nanoclays, which are a compatibilising effect and a change of the viscosity ratio of the blend phases. As already discussed, the addition of 1 wt.-%

of C15A or C30B to the blend results in a similar rubber droplet size and in their location at the interface. Hence, the compatibilising effect of the clays could be considered to be then predominant. When the clay concentration is raised, the change of the viscosity ratio between the two phases is expected to play an increasing role. The presence of C30B in the PLA phase increases the PLA viscosity and facilitates the droplet break-up of the dispersed high viscosity rubber phase, inducing a further decrease of rubber droplet size. On the contrary, NR droplet size is not affected by the C15A loading fraction though their morphology appears to be deformed and elongated at 5 wt.-%. These results are in agreement with the observations of Filippone *et al.*<sup>246</sup> who showed that co-continuity of a organoclay-rich minor phase PA6 in a HDPE matrix was obtained and that the spatial arrangement of this minor phase was guided by the filler. Similarly, Hong *et al.*<sup>247</sup> observed that the change of the viscosity ratio and the coalescence suppression effect affected the droplet size, depending on the location of organoclays in PBT/PE blend.

Moreover, the degree of intercalation/exfoliation of the montmorillonites in the nanocomposites was evaluated more precisely by XRD analysis and TEM images (Figure IV.7). C15A presents a high intensity diffraction peak at  $2\theta = 3^{\circ}$ , corresponding to an interlayer distance of 30 Å. A peak is also detected at  $2\theta = 7.2^{\circ}$ , due to remaining unmodified clays with an interlayer distance of 12.2 Å. A clear displacement at lower angles of the main diffraction peak is observed in the nanocomposites ( $2\theta = 2.4^{\circ}$ , with a  $2^{nd}$  order reflection at 4.8°), confirming an intercalation of the polymer chains into the interlayer space. An interlayer distance of 36.7 Å is then calculated for the C15A nanocomposites. Likewise, C30B displays a diffraction peak at  $2\theta = 4.8^{\circ}$ , corresponding to an interlayer distance of 18.8 Å, that shifts to  $2\theta = 2.6^{\circ}$  for the nanocomposites (d = 33.3 Å). The intercalation of both clays seems to be independent of the clay concentration. Nevertheless, a good dispersion of the organoclays is observed by TEM measurements (Figure IV.7).



Figure IV.7. XRD analysis and TEM images (at 3 wt.-% loading) of (a) C15A nanocomposites and (b) C30B nanocomposites.

## **IV.4.3.** Rheological properties

The viscoelastic behaviour of nanocomposites strongly depends on the inter-particle and particle-polymer interactions and, thus, provides useful information about the nanostructure. Hence, rheological properties have widely been used to determine the degree of dispersion and exfoliation of organoclays in nanocomposites, and it is extensively recognised that the percolation threshold, i.e. the filler concentration required to obtain the transition from liquid-like to solid-like behaviour, decreases with the dispersion state of the clays.<sup>150</sup>

Figure IV.8 shows the variation of the storage modulus and viscosity as a function of the angular frequency at 180 °C for the PLA/NR blend and its composites.



Figure IV.8. Influence of (a) nanoclay type at 3 wt.-%, concentration of (b) C15A, (c) C30B and (d) composition of the blends over the rheological properties of the materials.

The addition of 3 wt.-% of CNa<sup>+</sup> does not affect the viscoelastic response of the PLA/NR blend (Figure IV.8.a). A conventional liquid-like behaviour at low frequencies is noticed and is attributed to a poor dispersion and lack of interaction of the clay with any of the polymers. However, a drastic change in the viscoelastic response is observed by the addition of both organoclays, C15A and C30B.

The nanocomposites exhibit a solid-like behaviour with the formation of a plateau for the storage modulus G' and an increase of the absolute complex viscosity  $\eta^*$  at low frequencies (yield stress fluid). This behaviour is observed for concentrations of 3 and 5 wt.-% of organoclay in the nanocomposite (Figure IV.8.b and c). Additionally, the percolation threshold, at low frequencies, occurs between 1 and 3 wt.-% loading fraction. Different types of interactions should be considered in ternary systems, the particle-particle interactions and the dispersed polymer drop-drop hydrodynamic interactions. Droplet bridging through clay particles can also be a cause of the solid like behaviour.<sup>248, 249</sup>

In order to understand these phenomena and the possible interactions between the system components, the effects of each component, NR and C15A, on the rheological properties of PLA were separately studied (Figure IV.8.d). It is observed that the elastomeric phase hardly varies the rheological behaviour of PLA, while the addition of 3 wt.-% of C15A significantly increases the viscosity of the polymer matrix and leads to the formation of a plateau at low frequencies. It is worth noting that these effects are more pronounced when the organoclay is added to the polymer blend. Therefore, the solid-like behaviour observed in the blend composites should be attributed not only to particle-particle interactions but also to the formation of a tridimensional network of neighbouring NR droplets that do not coalesce due to a unique clay layer interface. This structure is observed in TEM micrographs (Figure IV.9). The observed tridimensional network would be a relatively loose packed net due to the low concentration of NR and, hence, the increase of the secondary plateau would also be related to the presence of localised areas of high clay concentration surrounding the NR droplets.



Figure IV.9. NR droplet stabilisation through clay layer interface for PLA/NR/C15A 3 wt.-% nanocomposite as seen by TEM.

#### IV.4.4. Dynamic mechanical analysis

Figure IV.10 shows the storage modulus and *tan*  $\delta$  of PLA/NR blend and its composites, over the temperature range from -100 to 150 °C. The *E*' curve of the blend exhibits two drops corresponding to the glass transition temperature of their constituents, revealing the immiscibility of the system. As expected, natural rubber decreases the modulus of PLA, being this effect stronger at temperatures above the rubber  $T_g$  (-70 °C). The addition of the three clays results in an enhanced stiffness of the blend, noticed as a sensible increase of the modulus value (Figure IV.10.a). This effect is more pronounced for the two organoclays, C15A and C30B, where the reinforcing effect gradually increases with the filler concentration (Figure IV.10.b and c).

Both organoclays show a similar reinforcing effect at temperatures below the NR  $T_g$ , but C30B exhibits a stronger effect in the temperature range between the  $T_g$  of both polymers (from -70 °C to 60 °C). In fact, the storage modulus difference between the PLA/NR blend and the PLA/NR/C15A nanocomposite tends to zero from NR  $T_g$  to the PLA  $T_g$  and, it appears that the reinforcing effect decreases with increasing temperature. Moreover, a shift of the NR  $T_g$  from -64.7 °C to -59.4 °C is observed by the addition of 3 wt.-% of C15A (Figure IV.10.d). This shift indicates that C15A reduces the rubber chain mobility due to the formation of strong nanofiller-rubber interactions and shows a greater affinity for the elastomeric phase. These results are in agreement with the observations of Arroyo *et al.*<sup>230</sup> who reported an exfoliated structure for NR/C15A nanocomposites while an intercalated structure was observed with C30B.

Thus, it appears that C15A has stronger interactions with the NR phase than with the PLA phase, resulting in a higher reinforcing effect on the blend at temperatures below

the  $T_g$  of NR. This effect is progressively reduced as a function of temperature, which indicates a weakening of the thermo-mechanical stability of the material.<sup>131</sup>

On the other hand, C30B does not change the  $T_g$  of the polymers. It has been demonstrated that C30B could show an exfoliated morphology in PLA.<sup>132</sup> However in this case, the real concentration of C30B in the PLA phase would be lower than the concentration of C15A in the NR due to its location both at the interface and PLA phase. Then, no changes in the PLA  $T_g$  are observed with the addition of C30B.



Figure IV.10. Temperature dependence of E' with (a) nanoclay type at 3 wt.-%, concentration of (b) C15A and (c) C30B and (d-e) *tan*  $\delta$  for the nanocomposites at 3 wt.-% of nanoclays.

#### **IV.4.5.** Crystallisation behaviour

It was concluded in *Chapter III* that NR droplets act as a nucleating agents for the PLA matrix, inducing cold crystallisation in dynamic conditions and accelerating the isothermal crystallisation rate. Likewise, the effect of the montmorillonites over the crystallisation behaviour of the blend was studied using the same tools. Dynamic crystallisation was evaluated by DSC measurements. Nevertheless, the heating rate was reduced to 2 °C·min<sup>-1</sup> in order to facilitate PLA crystallisation. The isothermal crystallisation of the nanocomposites was also analysed via rheological measurements. As for PLA/NR blends, the nanocomposites were melted inside the rheometer at 180 °C for 2 min to erase the thermal history and then quenched at 120 °C. The evolution of complex viscosity was then monitored as a function of time at 1 Hz and within the linear viscoelastic region.

Figure IV.11 shows the DSC heating curves of the materials. All samples display the PLA  $T_g$  at 58 °C. When compared with *Chapter III*, reducing the heating rate leads to cold crystallisation of PLA for all materials. The nucleating effect of NR is evidenced by the reduction of PLA crystallisation temperature which decreases from 119.4 °C for processed PLA to 115.5 °C for the PLA/NR blend (Table IV.5). The presence of two melting peaks is also detected for the blend. As reported in the literature review, the presence of two peaks during PLA melting has often been ascribed to a recrystallisation process, i.e. the change of small and imperfect crystals into more stable crystals through melting and recrystallisation.<sup>54</sup> Therefore, the nucleating effect of NR generates the formation of less perfect spherulites that present this particular fusion behaviour.

The addition of 3 wt.-% of  $CNa^+$  induces a further decrease of the crystallisation peak while the two melting peaks are even more pronounced (Figure IV.11.a). It was reported from TEM observations that  $CNa^+$  forms agglomerates in the PLA phase. Thus, it can be concluded that these agglomerates also display a nucleating effect over the PLA matrix. However, the addition of 3 wt.-% of C15A and C30B leads to the opposite effect. The cold crystallisation temperature increases from 115.5 °C for the PLA/NR blend up to 121.1 °C with the addition C15A. For C30B, PLA  $T_c$  increases up to 119.3 °C, being then equal to the value of processed PLA  $T_c$ .

The effect of the clay concentration is reported in Figure IV.11.b and c. For both organoclays, it appears that the crystallisation temperature gradually increases for 1 and

3 wt.-% while slightly decreases at 5 wt.-%. Further experiments would be needed in order to fully understand this behaviour, which could be related to the formation of agglomerates at high clay concentrations.



Figure IV.11. Dynamic crystallisation of PLA/NR/MMT nanocomposites (second heating scan). Influence of (a) type of clays at 3 wt.-%, (b) C15A concentration and (c) C30B concentration.

	T <sub>c</sub> ,	$\Delta H_{c}$ ,	T <sub>m1</sub> ,	T <sub>m2</sub> ,	$\Delta H_{mtot}$ ,
	°C	J·g⁻¹	°C	°C	$J \cdot g^{-1}$
Processed PLA	119.4	- 20.9	149.7	-	-
PLA/NR	115.5	- 25.6	148.4	152.8	22.5
PLA/NR/CNa <sup>+</sup>	113.5	- 24.6	147.6	153.5	22.3
PLA/NR/C15A 1 wt.%	119.1	-20.5	149.1	153.3	20.6
PLA/NR/C15A 3 wt%	121.1	- 19.4	149.6	153.9	19.2
PLA/NR/C15A 5 wt%	117.4	- 20.1	148.8	154.7	19.6
PLA/NR/C30B 1 wt%	118.1	- 20.8	149.2	153.2	21.6
PLA/NR/C30B 3 wt%	119.3	- 20.7	149.3	153.2	20.7
PLA/NR/C30B 5 wt%	119.0	- 20.6	149.4	153.4	19.6

Table IV.5. DSC data of PLA/NR/MMT nanocomposites (second heating scan).

Isothermal crystallisation of the materials was then carried out in order to confirm the effect of the different types of montmorillonites at 3 wt.-% loading. Figure IV.12.a shows the evolution of the ratio of the measured viscosity to the initial viscosity of the materials. As reported in *Chapter III*, the crystallisation rate of PLA is strongly enhanced with the addition of 10 wt.-% of NR. The incorporation of 3 wt.-% of CNa<sup>+</sup> leads to a further reduction of crystallisation rate. Moreover, the retarding effect of C15A and C30B is confirmed by the rheological measurements. The slowest crystallisation rate is observed for PLA/NR/C15A 3 wt.-% nanocomposite.

The crystallisation degree of the samples crystallised in the rheometer was then determined by DSC. Figure IV.12.b represents the first heating scan of the crystallised blends at 10 °C·min<sup>-1</sup>, showing a decrease of few degrees of the melting temperature with the addition of NR and CNa<sup>+</sup> (Table IV.6). Such decrease confirms the nucleation effect of the two components and the formation of smaller spherulites.  $T_m$  further increases with the addition of C15A.



Figure IV.12. (a) Evolution of complex viscosity during isothermal crystallisation and (b) melting curves of crystallised materials for 3 wt.-% of clays.

Table IV.6. DSC data of PLA/NR/MMT 3 wt.-% nanocomposites after crystallisation.

	T <sub>m</sub> ,	ΔH <sub>m</sub> ,
	°C	$J \cdot g^{-1}$
Processed PLA	155.3	19.0
PLA/NR	150.1	22.2
PLA/NR/CNa <sup>+</sup>	150.9	25.4
PLA/NR/C15A	153.3	26.4
PLA/NR/C30B	151.1	26.3

Moreover, the crystallisation form of PLA in the different materials was assessed by X-ray diffraction (Figure IV.13). The typical  $\alpha$ -form is observed for all materials, confirming that neither NR droplets nor the organoclays affect the PLA crystallisation form.



Figure IV.13. XRD of crystallised materials after 45 minutes of isothermal crystallisation at 110 °C.

The analysis of PLA crystallisation in ternary systems has to consider the specific distribution of the fillers. The crystallisation of PLA has been reported by a few authors in similar ternary nanocomposites, such as PLA/PCL/organoclays nanocomposites.<sup>250</sup> Wu *et al.*<sup>250</sup> observed that the addition of 30 wt.-% of PCL into the PLA matrix favoured cold crystallisation of PLA. The addition of 3 wt.-% of organoclays located in the PLA phase further decreased the PLA  $T_c$  and increased the crystallisation degree. An additional study by Ojijo *et al.*<sup>192</sup> on the crystallisation behaviour of PLA/PBSA/MMT nanocomposites showed that PBSA droplets also acted as a nucleating agent for the PLA matrix (30 wt.-% of PBSA), with the blend displaying smaller and more spherulites than neat PLA. Nevertheless, the effect of filler addition (6 wt.-%) seemed to be dependent on the type of organoclays. The addition of C30B and CNa<sup>+</sup> eased PLA crystallisation in the PLA/PBSA blend during cooling process while C15A, C20A and C25A hindered the crystallisation when compared to PLA/PBSA blend. However, no clear explanation was given by the authors and the location of the clays in the blend was not assessed.

Considering the location of the organoclays, it can hardly be suggested that the inhibiting effect of PLA crystallisation is due to physical hindrance of PLA chains by the organoclays, especially in the case of C15A where the organoclays are not observed in the PLA phase. Therefore, it should be considered that the location of the organoclays at the PLA/NR interface inhibited the nucleating effect of NR droplets. It has been concluded in *Chapter III* that two major phenomena have to be taken into

account in order to understand the nucleating effect of NR droplets: the migration of impurities during melt-mixing and the nucleating activity of the interface. The location of the organoclays at the polymer interface could limit the nuclei migration and also reduce the nucleating activity of the interface.

## **IV.4.6.** Mechanical properties

The tensile behaviour of the materials is shown in Table IV.7. As previously observed, the addition of NR in the PLA matrix changes the brittle fracture of PLA to a ductile fracture with formation and propagation of a neck while stretching. An elongation of 160 % is observed with the addition of 10 wt.-% of NR, while Young's modulus and tensile strength decrease. This elongation is slightly lower than the one observed for PLA/NR blends in *Chapter III* and is attributed to the processing difference.

	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
Processed PLA	$2710 \pm 110$	$65 \pm 2.5$	$3.9 \pm 0.9$
PLA/NR	$2240\pm50$	$42.9 \pm 1.1$	$161 \pm 17$
PLA/NR/CNa <sup>+</sup>	$2200 \pm 40$	$42.0 \pm 2.5$	$33 \pm 12$
PLA/NR/C15A 1 wt%	$2200\pm10$	$37.5\pm0.8$	$196 \pm 4$
PLA/NR/C15A 3 wt%	$2290\pm40$	$30.1 \pm 0.9$	$82 \pm 6$
PLA/NR/C15A 5 wt%	$2050\pm80$	$27.3 \pm 0.8$	$42 \pm 8$
PLA/NR/C30B 1 wt%	$2210\pm60$	$38.2 \pm 0.1$	$118 \pm 21$
PLA/NR/C30B 3 wt%	$2420\pm20$	$39.6 \pm 1.5$	$7.6 \pm 1.1$
PLA/NR/C30B 5 wt%	$2630\pm50$	$38.1 \pm 0.9$	$2.7 \pm 0.5$

Table IV.7. Mechanical properties of the materials.

The addition of CNa<sup>+</sup> results in a sharp decrease of the elongation at break with no improvement of either Young's modulus or tensile strength, which is due to the poor dispersion of the clay and the formation of big agglomerates. The addition of the organoclays to the blend drastically changes the mechanical response of the material with a different behaviour among them. C15A gives rise to a marked increase of the

elongation at break, of up to 200 % with 1 wt.-%, without changing the modulus and strength. However, this value drops to 80 % and 42 %, when increasing the nanoclay concentration to 3 wt.-% and 5 wt.-%, respectively. On the other hand, the addition of C15A hardly varies the Young's modulus but a significant decrease of the maximum tensile strength (corresponding to the yield strength) is observed. The incorporation of C15A suppresses the neck formation and leads to a more homogeneous deformation of the blend. In order to understand the effect of the organoclay on the deformation mechanism, a detailed study by *in-situ* synchrotron X-ray scattering experiments under uniaxial stretching is reported in the next chapter.

The nanocomposites containing C30B exhibit a gradual increase in the modulus value with organoclay content, that is in concordance with the DMA results. The functional groups present on the surface of the C30B organoclay tend to form hydrogen bonds with the carbonyl groups of PLA chain segments.<sup>132</sup> These bonds would result in an increase of the Young's modulus due to the strong affinity of the organoclay with the continuous phase, but also in an embrittlement of the material and, in consequence, in a clear decrease of the deformation at break of the blend. Similarly, Tiwari *et al.*<sup>251</sup> demonstrated that the contribution of MMT to the modulus of a PP/PS blend increased as the PP content increased due to the affinity and reinforcing effect of MMT to the PP matrix.

## **IV.4.7.** Barrier properties

Polymer-layered silicate nanocomposites are expected to have excellent barrier properties to gases as the addition of the nanoparticles to the polymer creates a tortuous pathway that hinders the migration of the molecules through the material.<sup>21</sup> This reduction of permeability depends on the aspect ratio of the nanoparticles and, therefore, nanoclays are often chosen for such application. The Nielsen theoretical model is frequently used to predict the relative permeability coefficient value.<sup>162</sup> However, this theoretical model only applies to homogeneously dispersed nanoparticles and perpendicularly oriented to the gas flux. In this case, the specific distribution of the nanoclays surrounding the NR droplets should be considered. A limited number of articles describes the permeability properties of ternary systems, and they do not discuss the influence of particles location over the resulting permeability properties.<sup>194, 252</sup>

Table IV.8 shows the permeability coefficients of the materials, at 3 wt.-% loading of nanoclays for the composites. The addition of NR to PLA increases the  $O_2$  and  $CO_2$  permeability of PLA. The experimental oxygen permeability values are then compared with those obtained from Maxwell law (Equation (IV.6)). This law has been developed to calculate the permeability coefficient of a biphasic system composed of a continuous phase containing spherical dispersed domains, from the volume fractions and the permeability coefficients of each component involved in the blend.<sup>253</sup>

$$\frac{P_{blend}}{P_{c}} - 1 = 3\phi_{d} \left[ \frac{(P_{d} / P_{c}) + 2}{(P_{d} / P_{c}) - 1} - \phi_{d} \right]^{-1}$$
(IV.6)

with  $P_{blend}$ ,  $P_c$  and  $P_d$  the permeability of the blend, the continuous and the dispersed phases, respectively, and  $\Phi_d$  the volume fraction of the dispersed phase.

In the case of  $O_2$ , the theoretical permeability value of the blend can be calculated from the permeability values of PLA and NR,  $P_{O_2 PLA} = 0.54$  barrers and  $P_{O_2 NR} = 26$ barrers (value taken from literature, see ref.<sup>133</sup>). Thus, the permeability value calculated for the PLA/NR blend is equal to 0.77 barrers. This value is lower than the experimental one (1.01 barrers) probably due to the formation of a diffusive gas pathway at the PLA/NR interface as a result of the poor adhesion between PLA and NR. In the Maxwell law, the blend is considered to be ideal and the contribution of an interface effect is not taken into account.

Considering the permeability data of Table IV.8 and taking into account the uncertainty on the permeability values (about 5 %),  $O_2$  and  $CO_2$  can be considered to have the same trends after C30B addition. A marked reduction of gas flux is obtained and this result can be assigned to its better compatibility with PLA, as previously discussed. However, similar or increased permeability values are obtained with C15A (from 1.01 to 0.96 for  $O_2$  and from 2.3 to 2.97 for  $CO_2$ ). The increase of  $CO_2$  permeability value can probably be assigned to the higher solubility of  $CO_2$  compared to that of  $O_2$ . The increase of  $CO_2$  solubility has already been observed in some nanocomposites and was mainly attributed to the presence of tactoids or intercalated structures.<sup>254, 255</sup> Thus, the areas of high C15A concentration surrounding and inside the NR droplets could be responsible for such increase.

Considering the Maxwell law and the composition of the blend, i.e a low permeable continuous phase with dispersed permeable nodules, the most interesting strategy to improve the gas barrier properties is to decrease further the permeability of the continuous phase as it dominates the gas transport mechanism. To confirm this strategy, the location of the clays at 3 wt.-% was forced in the PLA phase by pre-blending C30B into PLA for 10 min before adding NR, referred as [(PLA/C30B)NR]. For comparison, the permeability of the NR droplets was tried to be reduced by pre-blending NR with C15A in an open two-roll mill [PLA(NR/C15A)]. The objective of these two steps was to control the particle location in the PLA/NR blend.

Figure IV.14 shows the TEM images of the effect of blending order for C30B. An increase of nanoclays present in the PLA phase can be observed when pre-blending C30B with PLA. Therefore, it can be concluded that the location of the clays can be controlled by the kinetic effects of process mixing to some extent. A further decrease of the material permeability is obtained when pre-blending C30B with PLA (Table IV.8) whereas pre-blending C15A with NR does not affect the permeability properties when compared to simultaneous mixing.

	$P_{O_2}$ , barrers	$P_{CO_2}$ , barrers
Processed PLA	0.54	1.3
PLA/NR	1.01	2.30
PLA/NR/C15A 3 wt%	0.96	2.97
PLA/NR/C30B 3 wt%	0.86	2.11
PLA(NR/C15A) 3 wt%	1.03	3.08
(PLA/C30B)NR 3 wt%	0.68	1.86
$10^{-10}$ <sup>3</sup> (CTD) $10^{-2}$	)	

Table IV.8. Permeability coefficients for O<sub>2</sub> and CO<sub>2</sub> of PLA/NR blend and its nanocomposites at 3 wt.-% of organoclay.

Barrers:  $10^{-10}$  cm<sup>3</sup> (STP)cm/(cm<sup>2</sup>scm<sub>Hg</sub>)



Figure IV.14. TEM images of the nanocomposites at 3 wt.-% loading fraction (a) PLA/NR/C30B and (b) (PLA/C30B)/NR.

## **IV.4.8.** Thermal degradation

The non-oxidative degradation of the materials was studied by thermogravimetric analysis. Usually, the addition of nanoclays to a polymer results in an increase of the degradation temperature by acting as a superior insulator. Moreover, silicate layers could act as a barrier for incoming gases as well as gaseous by-products formed during degradation improving the thermal stability of the materials.<sup>129</sup> Therefore, the thermal degradation properties could be related to the gas barrier properties of the blends.

Table IV.9 reports the thermal degradation data for the nanocomposites and Figure IV.15 shows the weight loss and DTG curves as a function of temperature of the materials when adding a 3 wt.-% of nanoclays. A decrease of the degradation temperature is noted when adding CNa<sup>+</sup> to the blend. This is attributed again to the poor dispersion of this clay in the blend and to the presence of tactoids which cannot act as an efficient gas barrier. However, a shift in the thermal degradation towards higher temperatures of up to 12 °C for 3 wt.-% organoclay is observed (Table IV.9). It appears that the highest value is obtained for the addition of C30B. Moreover, the same tendency as for the permeability properties is observed when changing the blending order and the highest degradation temperature is obtained when pre-blending C30B with PLA (Figure IV.15).



Figure IV.15. Thermal stability of the bionanocomposites at 3 wt.-% of clay content.

Table IV.9. Thermal degradation data of the material, reporting the onset degradation temperature and the  $T_{dmax}$  of DTG curves.

	T <sub>onset,</sub> °C	T <sub>dmax,</sub> °C
PLA	350.6	373.5
PLA/NR	350.5	373.4
PLA/NR/CNa <sup>+</sup>	342.8	370.4
PLA/NR/C15A 3 wt%	354.8	382.7
PLA(NR/C15A) 3 wt%	353.5	378.5
PLA/NR/C30B 3wt%	354.9	383.3
(PLA/C30B)NR 3 wt.%	355.4	385.7

### **IV.4.9.** Disintegration in composting conditions

Another critical property for the new bionanocomposites developed in this work is their biodegradability. The disintegration of the samples in composting conditions can be observed in Figure IV.16, where pictures of the samples taken out at different times of composting are reported.

During the first week, whitening and deformation of the surface are detected for all materials. These observations are a signal that the hydrolytic degradation has started. The opacity observed is due to changes of the refractive index which can be attributed to the water absorption and to the low molecular weight compounds formed by the

hydrolytic degradation.<sup>168</sup> Moreover, the formation of holes in the materials or an increase of crystallinity during degradation can also be responsible for the opacity.<sup>40</sup> It should be taken into account that the degradation experiments took place at 58 °C, which is closed to the  $T_g$  of the matrix. This could increase the chains mobility, inducing the crystallisation of the PLA matrix.

At the 10<sup>th</sup> day, fragmentation and weight loss of the samples are already observed for PLA, PLA/NR and PLA/NR/CNa<sup>+</sup>. These phenomena occur from the 14<sup>th</sup> day for the composites containing the organoclays. Figure IV.17 reports the evolution of the material disintegrability with the composting time. It can be observed that after 31 days of composting, all materials reached more than a 90 % of disintegration and they can be considered as disintegrated according to the ISO 20200 standard. A slight delay of PLA/NR blend disintegration is observed when compared to PLA, without affecting the disintegration percentage at the end of the experiment. The addition of the unmodified clay does not affect the disintegration rate of the blend unlike the two organoclays which greatly slow down the process.



Figure IV.16. Disintegration of the samples at different times of composting.



Figure IV.17. Evolution of disintegration of the materials with the composting time.

It has been demonstrated that natural rubber undergoes microbial degradation and possible biodegradation involving oxidative cleavage of the double bond of the polymer backbone.<sup>101, 102</sup> However, the rubber biodegradation is a slow process and this explains the observed results for the blend when compared to PLA.

The effect of the organoclay addition to biodegradable materials such as PLA has also been reported in the past few years; however, no clear conclusions can be made, as reported in *Chapter II*. In this case, both organoclays retard the disintegration of PLA/NR blend and the slowest rate is observed for C15A. TEM images showed that C30B is more homogenously dispersed in the PLA matrix than C15A. Therefore, C30B presented better improvement of the barrier properties and thermal degradation than C15A. However, the hydrophilicity of C30B and its terminal hydroxylated groups could accelerate the hydrolysis of PLA and counterbalance the barrier effect.

Figure IV.18 shows the FT-IR spectra of PLA and PLA/NR/C15A at different incubation times. Both materials present at the beginning of the experiment the typical sharp band at 1750 cm<sup>-1</sup> of the carbonyl group stretching (-C=O) and the -C-O-stretching band of the -CH-O- group at 1182 cm<sup>-1</sup> of PLA. Observing the PLA spectra evolution, a new band appears at 1600 cm<sup>-1</sup> corresponding to the carboxylate ion, while the band at 1260 cm<sup>-1</sup> corresponding to the -C-O- stretching disappears (14 days). These observations have previously been reported and are due to the depletion of the lactic acid and oligomers by the microorganism leaving a carboxylate ion at the end of the chain.<sup>256, 257</sup> Moreover, after 17 days of incubation, the characteristic bands of PLA

spectra nearly have disappeared and the FT-IR spectrum shows new absorption bands at 1038 cm<sup>-1</sup>, 1640 cm<sup>-1</sup> and 3300 cm<sup>-1</sup>, which are typical absorption bands of microbial mass probably adhered to the PLA surface.<sup>258, 259</sup>



Figure IV.18. FT-IR spectra of (a) PLA and (b) PLA/NR/C15A as function of the disintegration time.

Similar evolution is observed for PLA and PLA/NR/C15A nanocomposite, however the process of degradation is slower for the nanocomposite, as seen in Figure IV.18.b. Moreover, a new band progressively appears at 830 cm<sup>-1</sup> (cis-1,4-double bond), due to the increasing concentration of NR in the blend as PLA degrades.

## **IV.5.** CONCLUSIONS

The addition of natural rubber and montmorillonites to the PLA matrix allowed a straightforward production of bionanocomposites with tuneable properties by melt blending. It appeared that both organoclays, C15A and C30B, acted as compatibilisers for the PLA/NR blend because of their preferential location at the interface, forming a solid barrier and preventing the coalescence of NR droplets. However, different properties were obtained depending on the nanoclays used. While C15A allowed a further increase of the elongation at break of the PLA/NR blend, the addition of C30B produced stiffer materials. This behaviour was attributed to the different interactions of the nanoclays with the two polymers. Moreover, a more marked improvement of permeability properties was obtained with C30B due to its better compatibility with
PLA. These properties can further be improved by changing the mixing procedure and, hence, obtaining a specific location of the clays. Therefore, it can be concluded that new PLA/NR blend nanocomposites with different desired properties can be achieved by an appropriate choice of the nanoclays used and of the mixing procedure.

# Chapter V. DEFORMATION MECHANISMS IN PLA/NR/ORGANOCLAY BIONANOCOMPOSITES AS REVEALED BY SYNCHROTRON X-RAY SCATTERING \*

\* Part of the work described in this chapter has been accepted for publication in *Soft Matter* (DOI:10.1039/c2sm25729G, 2012).

## V.1. SUMMARY

The micromechanical deformation mechanisms of a poly(lactic acid) (PLA)/natural rubber (NR) blend (PLA/NR 90/10 wt.-%) and its organoclay filled bionanocomposites have been investigated by small and wide angle X-ray scattering (SAXS-WAXS) under tensile conditions. The addition of NR to the PLA matrix changed the brittle fracture of PLA to a ductile deformation through the debonding of the rubber droplets. Otherwise, the formation of cavities between PLA and NR was hampered by the nanoclays since they were mainly located at the polymer interface. In this case, nanoclays acted as craze nucleation sites. At 1 wt.-% of filler concentration, the crazes were able to fully develop in the blend and to evolve into stable microvoids which kept growing and orienting in the tensile direction. These mechanisms also explained the progressive plastic deformation of the polymer chains and the preferential orientation of the nanoclay platelets.

## V.2. INTRODUCTION

Recently, it has been demonstrated that the nanoparticles behave as effective compatibilisers for immiscible polymers through their preferential location at the polymer interfaces, reducing the interfacial tension and preventing the coalescence of the dispersed phase.<sup>189, 229, 260-262</sup> Moreover, Vo *et al.*<sup>229</sup> demonstrated that such ternary blends can be stiffer, stronger and also tougher than the binary blends suggesting a change in their deformation mechanisms. Dasari *et al.*<sup>228</sup> proposed an analysis of the micro and nanoscale deformation behaviour for nylon 66/SEBS-g-MA/organoclay ternary nanocomposites using microscopy analysis of the fracture surface. However, microscopy analysis only provides snapshot information of the deformation mechanism with no real time monitoring and requires an extensive and laborious sample preparation after breaking.

Deformation mechanisms can be investigated *in-situ* by combining scattering techniques using synchrotron light with stress-strain experiments in a simultaneous fashion.<sup>263, 264</sup> This approach has already been used to study polymer blends and polymer nanocomposites since it enables linking the macroscopic deformation to the structural changes at both microscopic and mesoscopic levels.<sup>264-266</sup> However, to the

best of the author's knowledge, no reports regarding nanoparticle filled polymer blend are found in the literature.

The previous chapters reported the production of ductile PLA through the addition of natural rubber (NR). Significant improvement of the mechanical properties of these PLA/NR blends can be further obtained by incorporation of small amount of organoclays, especially for the C15A. This effect was attributed to the preferential location of the organoclays at the PLA/NR interface. This chapter aims to provide a understanding of the micromechanical deformation mechanism better of bionanocomposites based on organoclay C15A filled PLA/NR blends during uniaxial stretching by using simultaneous synchrotron small angle and wide angle scattering (SAXS, WAXS) techniques. Therefore, this analysis enables obtaining information at different length scales relevant for the deformation mechanism. On one hand, WAXS can be used to provide information about length scales associated to inter-chain correlations of the polymer matrix. On the other hand, SAXS can provide structural information about microvoid formation, crazing, shear yielding or debonding phenomena. Moreover, additional information about organoclay orientation can be obtained from the intermediate angle range of the scattering and from there a precise picture about the evolution with deformation of the PLA/NR interface can be inferred.

The simultaneous combination of this battery of techniques with the stress-strain experiment enables the precise description of the deformation mechanism in this class of bionanocomposites.

## V.3. EXPERIMENTAL SECTION

#### V.3.1. Materials and sample preparation

The samples were prepared as described in *Chapter IV*, the NR concentration in the blend was fixed at 10 wt.-%, and the organoclay (C15A) loadings were 1 and 3 wt.-%.

#### V.3.2. Characterisation

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured

after immersion in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd 80/20) in order to prevent electrical discharge during observation. The study of the dispersion of the nanoclays was carried out using transmission electron microscopy (TEM) (Philips Tecnai 20 microscope at an acceleration voltage of 200 kV). Ultra-thin sections of the samples were prepared by cryo-ultramicrotomy at -140 °C (Leica EM UC6).

# V.3.3. Time resolved wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) using synchrotron light

Time-resolved WAXS and SAXS were performed at the Spanish beamline BM16-CRG of the European Synchrotron Facility (ESRF) in Grenoble, France.<sup>267</sup> The X-ray wavelength was  $\lambda = 0.9795$  Å. Data were collected using a MarCCD165 detector in 1024 x 1024 pixels resolution mode (effective pixel size of 158.7 µm) at a sample to detector distance of 309.5 mm and 1397.4 mm for WAXS and SAXS, respectively. The experimental data were corrected for the X-ray absorption and background scattering. It should also be noted that the intensity was normalised by the sample thickness, *t*, at each step calculated from the Beer-Lambert law:

$$I = I_o exp(-\mu t) \tag{V.1}$$

The absorption coefficient  $\mu$  was determined for the undeformed samples and assumed to be constant during stretching.<sup>268</sup>

## Mechanical properties

*In-situ* WAXS and SAXS measurements were recorded simultaneously during longitudinal deformation of the samples by means of a Linkam tensile stage (Linkam Scientific Instruments Ltd.) at a speed of 5 mm·min<sup>-1</sup>.

## • Data analysis

2D WAXS and SAXS patterns were analysed following different approaches in order to obtain as much structural information as possible about the stretching mechanism at the molecular level. From the 2D WAXS pattern (Figure V.1.a) information about orientation of polymer chains can be extracted. By enlarging the pattern at middle angles (Figure V.1.b), the characteristic diffraction maximum of the nanoclay is clearly visible and the orientation of the nanoclay can be estimated. Further enlargement of the angular range provides access to smaller angles (Figure V.1.c) where mostly information about microvoids can be obtained.



Figure V.1. Example of scattered intensity for an oriented sample (PLA/NR/C15A 3 wt.-% at 50 % strain) (a) WAXS 2D pattern: orientation of polymer chains, (b) orientation of nanoclays and (c) SAXS 2D pattern: microvoid formation and orientation.

## SAXS analysis:

- microvoid formation and orientation

2D SAXS images (for example Figure V.1.c) were integrated to obtain the scattering intensity (*I*) as a function of the scattering vector q ( $2\theta$  is the scattering angle)

$$q = \frac{4\pi}{\lambda} \sin\theta \tag{V.2}$$

Moreover, the analysis was focused on a *q*-range from 0.1 to 1.2 nm<sup>-1</sup> in order to study the microvoid formation and orientation. Thus, the total integrated intensity  $I_{tot}$  is defined by:

$$I_{tot} = \int_{0.1}^{1.2} I(q) dq$$
 (V.3)

In order to estimate the orientation fraction, 2D SAXS images were also divided in four quadrants, as pictured in Figure V.2.a.<sup>269, 270</sup> The meridional and equatorial scattered intensities were calculated as two total integrated intensities  $I_{mer}$  and  $I_{eq}$  over a q-range from 0.1 to 1.2 nm<sup>-1</sup> and over azimuthal angles ( $\varphi$ ) from -45 ° to 45 ° and 135 °

to 225 ° and from 45 ° to 135 ° and 225 ° to 315 °, respectively. According to Figure 2a,  $I_{mer} = I_1 + I_3$  and  $I_{eq} = I_2 + I_4$  and the oriented fraction is defined as  $I_{or} = I_{eq} / (I_{eq} + I_{mer})$ .



Figure V.2. (a) Example of SAXS analysis of 2D patterns (PLA/NR/C15A 3 wt.-% at 100 % strain). (b) Integrated intensity as a function of the azimuthal angle  $\varphi$  in order to calculate the Herman's orientation function.

- nanoclay orientation

The Herman's orientation function can be used to estimate the degree of orientation of crystalline lamellae, or even polymer chains, from the resulting anisotropic response of scattering or spectroscopic tools.<sup>269, 271</sup> In this case, this function was employed to study the orientation of the nanoclays through the deformation induced anisotropy of the scattering associated to the average interlayer space of the nanoclays. The *q*-range for integration was taken from q = 1.4 nm<sup>-1</sup> to q = 2.0 nm<sup>-1</sup>.

The Herman's orientation function  $f_2$  is defined as:

$$f_2 = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \tag{V.4}$$

$$\left\langle \cos^2 \varphi \right\rangle = \frac{\sum_{\varphi_i=0}^{90^{\circ}} I_i \sin \varphi_i \cos^2 \varphi_i}{\sum_{\varphi_i=0}^{90^{\circ}} I_i \sin \varphi_i}$$
(V.5)

Where

with  $I_i$  the scattered intensity at the *i*th azimuthal angle  $\varphi_i$  (see Figure V.2.b). The initial and final angles were chosen as 90 ° and 180 ° to avoid the shadow of the beam stop. In this case,  $f_2$  is equal to 1 and -0.5 when the scattered intensity is concentrated along the meridian and the equator, respectively. The value of 0 is obtained for isotropic patterns.

## WAXS analysis: polymer chain orientation

The Herman's orientation function was used in a similar way to determine the orientation of the disordered polymer chains during stretching through the amorphous halo observed in the 2D WAXS patterns (Figure V.1.a). The *q*-range for integration was taken from q = 7.8 nm<sup>-1</sup> to 14.2 nm<sup>-1</sup>.

## V.4. RESULTS AND DISCUSSION

## V.4.1. Morphology of the materials

Figure V.3 shows SEM and TEM images of the materials. As reported in *Chapter IV*, the organoclay is mainly located at the interface acting as an effective compatibiliser for the immiscible polymer blend.



Figure V.3. Morphology of (a) PLA/NR blend, (b) PLA/NR/C15A 3 wt.-% nanocomposite and (c) location of C15A in PLA/NR/C15A 3wt.-% by TEM.

# V.4.2. Microstructure deformation mechanism as revealed by simultaneous WAXS, SAXS and stress-strain experiments

The tensile behaviour of the materials at a deformation rate of 5 mm·min<sup>-1</sup> is shown in Figure V.4 and Figure V.5.a. The addition of NR in the PLA matrix changes the brittle fracture of PLA to a ductile one with formation and propagation of a neck while stretching. The stress reaches the maximum value at the yield point (strain 5 %) and then, rapidly decreases, followed by a stable propagation up to fracture, reaching 200 % elongation. Interestingly, a further increase of the elongation at break of up to 270 % is obtained with the addition of 1 wt.-% C15A. However, this value drops to 120 % when increasing the nanoclay concentration to 3 wt.-%. The addition of the nanoclays also results in the disappearance of the neck and in the homogeneous deformation of the sample, as seen in Figure V.4.



Figure V.4. Samples stretched at different elongations (a) PLA, (b) PLA/NR, (c) PLA/NR/C15A 1 wt.-% and (d) PLA/NR/C15A 3 wt.-%.

These observed changes led to the analysis of the microstructure deformation mechanisms of PLA/NR/C15A nanocomposites during uniaxial stretching by *in-situ* synchrotron WAXS/SAXS techniques. Simultaneous SAXS and WAXS patterns are presented in Figure V.5.b and c.



Figure V.5. (a) Mechanical properties of the PLA/NR blend and its nanocomposites. The pictures present *in-situ* simultaneous (b) SAXS patterns and (c) WAXS patterns at selected elongation values. The arrows indicate the stretching direction.

SAXS patterns of stretched PLA are shown in Figure V.5.b (first row). Figure V.6.a represents the 1D-SAXS intensity of PLA at different elongations in the equatorial direction. PLA is a brittle material with failure resulting from the formation of crazes, which are defined as microcracks bridged by small fibrils.<sup>272</sup> Crazing is a commonly observed process of polymer deformation and is both a cause of failure and a mechanism of energy absorption, depending of the craze formation and concentration. The generation of high density of crazes can result in a tough system while few crazes can also develop into cracks, precursor of failure. SAXS is an efficient technique to identify crazes because of their cross-like SAXS signature, resulting from the scattering of the craze fibrils in the equatorial direction and of the crack planes in the meridional direction. The maximum observed at q = 0.26 nm<sup>-1</sup> for 10 % strain in the scattered equatorial intensity suggests the development of crazes during stretching (Figure V.6.a). In fact, it corresponds to the average correlation length between consecutive fibrils formed across the plane of craze.<sup>273</sup>

As previously shown, the addition of NR to the PLA matrix results in a large increase of the elongation at break. SAXS patterns of stretched PLA/NR blend are shown in Figure V.5.b (second row). Prior to deformation, the PLA/NR blend presents a slight isotropic scattered intensity. At the yield point, the blend exhibits a sharp meridional intensity and equatorial streak close to the beam stop, which could indicate the formation of crazes in the PLA matrix prior to the yield point and the appearance of the first microvoids. As stretching progresses (up to 20 % strain), the SAXS intensity increases in the equatorial direction (Figure V.6.b), while no increase of the signal is observed in the meridional one (Figure V.5.b second row). This effect suggests that the formed microvoids are oriented parallel to the direction of the applied stress. This corresponds, at macroscopic scale, to the whitening of the blend as a consequence of microvoid formation, and also to the formation of a neck due to the microscopic localisation of the stress at the yield point. When the specimens are further stretched, no significant changes in the SAXS patterns are observed due to the propagation of the neck through the sample.

Neither a peak nor a shoulder are observed in the 1D-scattered intensity in the equatorial direction (Figure V.6.b). However, an increase of the intensity at low q-value is observed in the equatorial direction. The absence of equatorial intensity maximum for

PLA/NR blend (Figure V.6.b) in comparison with its presence for PLA (Figure V.6.a) is a clear indication of changes in the mechanisms of deformation.

Previous scattering studies on polystyrene/elastomer blends by Magalhaes *et al.*<sup>273</sup> reported a similar effect which was attributed to non-crazing processes and to the formation of irregular cavities. Consequently, it can be deduced that crazing is not the main deformation process for PLA/NR blend as opposite to PLA. Cavitation and debonding are the two other traditionally proposed deformation mechanisms for thermoplastic/elastomer blends, depending on the phase morphology and adhesion.<sup>198</sup> Since it was shown in *Chapter III* that the adhesion between PLA and NR is poor, then debonding should prevail as the main deformation mechanism here.



Figure V.6. 1D-SAXS intensity (linear scale) integrated in the equatorial region at different elongations for (a) PLA and (b) PLA/NR blend.

Some important changes can be observed when comparing the SAXS patterns of the nanocomposites and PLA/NR blend (Figure V.5.b, third and fourth row). First of all, an orientation of the scattering intensity in the meridional direction is observed at low elongations, which means that the microvoids are oriented perpendicular to the direction of the applied stress. After 10 % strain, a cross like pattern appears. Subsequently, for higher strain, the equatorial intensity becomes even stronger and the signal in the meridional direction decreases.

The 1D-SAXS equatorial intensity for the PLA/NR/C15A for 1 wt.-% and 3 wt.-% of nanoclays are shown in Figure V.7.a and b, respectively. For 1 wt.-%, a shoulder appears at low angles for strains higher than 20 % which evolves to a maximum for

strains between 50 % and 100 %. This maximum then tends to disappear progressively for strains higher than 100 % until the sample failure. Similar observations are made for 3 wt.-% fraction loading of nanoclays. The appearance of this maximum could result from the scattering of the craze fibrils and indicates that the addition of nanoclays tends to suppress the debonding process of rubber droplets in favour of craze formation.



Figure V.7. 1D-SAXS intensity (linear scale) integrated in the equatorial region at different elongations for (a) PLA/NR/C15A 1 wt.-%, (b) PLA/NR/C15A 3 wt.-% and (c) PLA/C15A 3 wt.-%.

Moreover, additional experiments were carried out for a nanocomposite of PLA/C15A at 3 wt.-% clay loading, for which the sample rupture occurs at elongations lower than 15 % (Figure V.7.c). The absence of peak in equatorial intensity demonstrates that the craze formation in the PLA matrix is inhibited in favour of cavitation, probably at the interface between the clays and the matrix.

Therefore, it can be concluded that the reason for crazing mechanisms in the PLA/NR/C15A bionanocomposites is the combined effect of NR and C15A. These results also suggest that the nanoclays located at the PLA/NR interface (Figure V.3) act as a compatibilising agent hindering the formation of voids between the two phases.

Figure V.8 represents the evolution of the oriented fraction of microvoids of PLA/NR blend and nanocomposites as a function of the applied strain. In the case of PLA/NR blend, a rapid initial orientation of the voids takes place until a strain of about 30 %. Subsequent strain has no further effect. On the contrary, for PLA/NR/C15A nanocomposites, the oriented fraction of voids progressively increases with strain until break. No effect is observed on C15A concentration. These results are in agreement with the macroscopic observation of a more homogenous deformation of nanocomposites in comparison to that of the blend.



Figure V.8. Oriented fraction of microvoids in PLA/NR blend and its nanocomposites.

On another hand, Figure V.9 shows the evolution of the total integrated intensity (integrated from q = 0.1 to  $1.2 \text{ nm}^{-1}$ ) as a function of elongation. In a first approach, the increase of the intensity can be attributed to the void formation since the scattered intensity is determined by the differences of electron density. In fact, the X-ray scattering intensity is proportional to the square of the electron density contrast. Given that void electron density is about two orders of magnitude lower than those of the polymers, then the observed increase of the total integrated intensity can be assigned to an increase of microvoid concentration.<sup>274</sup>

In the case of the PLA/NR blend, the integrated intensity increases up to 20 % and then decreases reaching a stable plateau value corresponding to the propagation of the neck. Since the intensity is normalised by the sample thickness, the reduction of the sample volume could not be the explanation for this decrease of intensity. Therefore, it is proposed that the voids reach a size as large as to be beyond the resolution. The total integrated intensity of the nanocomposites is significantly higher than that of the PLA/NR blend. Moreover, a slight increase is observed with the concentration of nanoclays. A maximum is reached at 100 % strain for 1 wt.-% clay loading, meanwhile the sample breaks before showing any maximum for 3 wt.-% loading.



Figure V.9. Variation of total integrated intensity over q = 0.1 to 1.2 nm<sup>-1</sup>.

From the scattering analysis (Figure V.8 and Figure V.9), it is concluded that the formation and orientation of microvoids in PLA/NR blend occur at the first stage of the sample deformation, up to about 30 % strain. Thus, at this initial stage, the stress is concentrated around the NR droplets and debonding gives rise to the formation of the first microvoids. As deformation increases, the voids stabilise allowing the propagation of the neck along the sample.

Furthermore, the strong increase of total integrated intensity of the nanocomposites when compared to that of the PLA/NR blend (Figure V.9) clearly demonstrates that the nanoclay platelets could act as preferential sites to induce the craze formation. For 1 wt.-% of C15A, the concentration and density of crazes increase and grow stable until 100 % strain. Beyond this point, the intensity decreases probably due to the progressive rupture of polymer fibrils of the crazes and to their disappearance to form larger voids

or "cracks" which keep growing and orienting in the tensile direction. For 3 wt.-% of organoclays, the progressive transformation of crazes to cracks results in the mechanical failure of the sample, explaining the reduction of the elongation at break with the clay concentration. Thus, it appears that an optimal number of crazes able to grow stable are generated for 1 wt.-% nanoclay.

# V.4.3. Nanoclay orientation as revealed by intermediate angle X-ray scattering

The orientation of the nanoclays was analysed according to the Herman's orientation function  $f_2$ . SAXS patterns and  $f_2$  are presented as a function of the elongation in Figure V.10. Close inspection of X-ray patterns (Figure V.10.a) indicates that the nanoparticles progressively orient themselves in the direction of the applied stress, attesting also of the orientation of the PLA/NR interface.





Further observation of these SAXS patterns reveals that the diffraction maximum of the nanoclays not only becomes oriented but also broadens with stretching. This effect can be visualised in Figure V.11, where the equatorial intensity for the PLA/NR/C15A 3 wt.-% nanocomposite is represented. Two reflections with a maximum intensity at  $q = 1.68 \text{ nm}^{-1}$  (1<sup>st</sup> order), and 3.4 nm<sup>-1</sup> (2<sup>nd</sup> order) corresponding to the layered structure of the nanoclays are observed and do not suffer any modification upon stretching. On the contrary, a clear broadening of the main peak and a disappearance of the 2<sup>nd</sup> order are clearly evidenced, suggesting that a loss of the nanoclay crystalline perfection occurs during stretching without delamination of the clays.<sup>275</sup>



Figure V.11. Equatorial X-ray intensity (logarithmic scale) at intermediate angles for PLA/NR/C15A 3 wt.-% nanocomposite.

## V.4.4. Orientation of the polymer chains as revealed by WAXS

The Herman's orientation function was calculated from the scattering patterns in the WAXS angular region (Figure V.5.c). In this range (q-range from 7.8 nm<sup>-1</sup> to 14.2 nm<sup>-1</sup>) the amorphous halo of both PLA and natural rubber can be detected. Analysis of this halo was used to evaluate the polymer chain orientation during deformation (Figure V.12). Since the observed halo includes both the PLA and the NR contributions, it is not possible to isolate them from the WAXS pattern.

For the PLA/NR blend, a strong orientation development is observed from 0 to 50 % of elongation. Formation and orientation of voids also take place at this elongation range. In fact, these two phenomena permit to lower the yield strength and facilitate the

orientation of polymer chains. Elongation of the PLA matrix can occur due to the dissipation of energy by the void formation giving rise to a ductile fracture mechanism. No further orientation is observed for elongations higher than 50 %. However, a slight change occurs after 150 % elongation. This change could correspond to the end of the neck propagation. After that, further orientation of the voids (Figure V.8) and of the polymer chains (Figure V.12) take place, resulting in strain hardening by the extension of the molecular network until the sample breaks.<sup>276</sup>

A similar qualitative effect is observed for the nanocomposites with a shift towards higher elongations. As previously discussed, the concentration of crazes increases when adding the nanoclays, resulting in a higher dissipation of the applied energy through the formation and growth of voids. Therefore, the energy attributed to the plastic deformation of the polymeric matrix materials is lowered, explaining the decrease of the polymer chain orientation when increasing the nanoclay concentration (Figure V.12). These observations also explain the reduction of the flow stress with the filler concentration in the mechanical properties of the materials.



Figure V.12. Herman's orientation function versus elongation for PLA/NR blend and its nanocomposites (from WAXS patterns).

## V.4.5. Comparison with other montmorillonites

This chapter was focused on the nanocomposites based on C15A as the objective was to explain the synergy of NR combined with this organoclay. Nevertheless, it is of interest to understand the tensile behaviour of the materials reinforced with CNa<sup>+</sup> and

C30B. For this purpose, the SAXS patterns of the nanocomposites at 3 wt.-% clay loading are reported in Figure V.13, while the 1D-SAXS intensities at different elongations in the equatorial direction are observed in Figure V.14. The elongation at break of PLA/NR/C30B 3 wt.-% is of about 20 %, while PLA/NR/CNa<sup>+</sup> deforms up to 30 %.



Figure V.13. SAXS patterns of (a) PLA/NR/CNa<sup>+</sup> and (b) PLA/NR/C30B at 3 wt.-% clay loading at different elongations.

The SAXS patterns of PLA/NR/CNa<sup>+</sup> display a behaviour similar to PLA/NR. The intensity is rapidly oriented and increased in the equatorial direction, indicating the formation of irregular cavities. As in the case of PLA/NR blend, the debonding of the NR droplets could occur. Nevertheless, the premature failure of the nanocomposites also indicates that the void formation could be generated by the unmodified clays.

In the case of C30B, a cross like pattern is observed at 10 % of elongation, as for the PLA/NR/C15A nanocomposite. An increase of the equatorial intensity is also observed (Figure V.14). Due to the location of some clays at the interface, a mechanism similar to C15A should then develop, but an early failure of the sample occurs. Therefore, this behaviour is attributed to the presence of clays in the PLA matrix, which could act as defect points leading to the sample rupture.



Figure V.14. 1D-SAXS intensity (linear scale) integrated in the equatorial region of (a)  $PLA/NR/CNa^+$  and (b) PLA/NR/C30B at 3 wt.-% clay loading at different elongations.

## V.5. CONCLUSIONS

The influence of the addition of organoclay to a PLA/NR blend over the deformation micromechanisms has been studied through *in-situ* SAXS and WAXS measurements under tensile conditions, enabling a deeper understanding on how the bionanocomposite can be more ductile than the simple PLA/NR blend. The deformation mechanisms of each material were analysed and can be itemised as follows: (1) PLA is a brittle material with a failure through the formation of crazes. (2) PLA/NR is a ductile blend in which debonding associated to the formation of voids occurs when stretching. (3) PLA/NR/C15A bionanocomposites upon deformation exhibit craze formation since the location of the nanoclays at the PLA/NR interface hinders the formation of voids between the two phases. The nanoclays act as preferential sites for the craze formation and their number increases with the filler concentration.

Nonetheless, while PLA matrix cannot stand formation of crazes or cavities without mechanical failure, the presence of organoclays favours the generation of a large number of crazes in PLA/NR blend that are able to develop higher deformations. This mechanism allows under elongation a progressive orientation of polymer chains, nanoparticles and interfaces. Moreover, it appears that 1 wt.-% of nanoclay is the optimum concentration in this blend regarding the mechanical properties. Higher organoclay concentration precludes craze development and their transformation into cracks results in the sample mechanical failure. Thus, a clear synergy effect is revealed

in the mechanical reinforcement mechanism of the PLA matrix obtained with the addition of NR and the right amount of nanofillers.

The proposed deformation mechanisms are represented and summarised in Figure V.15. Moreover, they could be applied to other polymer blend nanocomposites in which the nanofiller is located at the interface between immiscible polymers.



Figure V.15. Scheme of the proposed deformation mechanisms for (a) PLA, (b) PLA/NR blend and (c) PLA/NR/C15A bionanocomposite.

## Chapter VI. CELLULOSE NANOCRYSTAL EXTRACTION AND MODIFICATIONS

## VI.1. SUMMARY

Cellulose nanocrystals (CNC) were obtained from acid hydrolysis of commercial microcrystalline cellulose (MCC). The length of the rod-like crystals was  $250 \pm 80$  nm. Two surface modification reactions were carried out in order to facilitate the incorporation of the nanocrystals in the polymer matrix. The first reaction consisted on the surface grafting of a long alkyl chains (18 carbon atoms) while the second modification resulted in PLA chain grafting onto the cellulose whiskers by ring opening polymerisation. The grafting efficiency of both reactions was fully characterised using a wide range of techniques.

## VI.2. INTRODUCTION

As reported in Chapter II, cellulose nanocrystals can be extracted from various sources and can lead to the production of bionanocomposites with excellent properties combined with biodegradability. Here, commercial microcrystalline cellulose was selected as a starting material. This method has the advantage of allowing a rapid production of a relatively large quantity of cellulose nanocrystals. In fact, Bondeson et al.<sup>118</sup> optimised the acid hydrolysis conditions of MCC with the idea of designing a CNC high yield reaction for extrusion process of bionanocomposites. However, the dispersion of CNC into polymer matrices remains challenging and modifications of the CNC surface are often required. Given the obtained results with layered silicates, two modification reactions were planned. Since the montmorillonite modified with cations possessing two alkyl tallows (C15A) displayed interesting mechanical properties, the CNC surface was grafted with long alkyl chains following the chemical modification proposed by Siguiera et al.<sup>277</sup> Additionally, the layered silicate nanocomposite study showed that obtaining a reinforced PLA matrix maintaining high deformation under tensile conditions remained an issue. Thus, the preparation of a nanohybrid consisting of CNC grafted with short chains of PLA could be a solution as such chains could help maintaining the material flexibility. Such nanohybrids were prepared by ring opening polymerisation and their preparation is reported in this study.

### VI.3. EXPERIMENTAL SECTION

### VI.3.1. Materials

Microcrystalline cellulose (MCC), sulphuric acid (96 %), n-octadecyl isocyanate, dibutyltin dilauryl, L-lactide, Tin (II) 2-ethylhexanoate, chloroform, dichloromethane anhydrous and toluene anhydrous, were provided by Sigma-Aldrich. Acetone and ethanol were purchased from Chimie-Plus.

#### VI.3.2. Extraction of cellulose nanowhiskers

Cellulose nanocrystals (CNC) were produced from sulfuric acid treatment of microcrystalline cellulose (MCC) following the procedure of Bondeson *et al.*<sup>118</sup> Hydrolysis was carried out in a 65 wt.-% sulphuric acid solution at 44 °C for 130 min under vigorous stirring. The MCC content during hydrolysis was fixed to 10 wt.-%. The reaction was stopped by cooling the suspension with ice cubes. Repeated centrifugation cycles (Sigma laboratory centrifuges 6K15, 10000 rpm, 10 min, 4 °C) with deionised water were then carried out to wash the suspension (at least five washings). Sedimented CNC were redispersed in clean water between each centrifugation cycle using an Ultra turrax (T25 basic, Ika Werke). Finally, the suspension was dialysed against deionised water for about 5 days until the wash water reached a constant pH and the recovered CNC suspension was neutralised using a 1 wt.-% NaOH solution. The aqueous suspension was kept at 4 °C after adding a few drops of chloroform as an anti-bacterial agent. The yield reaction was about 20 %.

#### VI.3.3. Grafting of n-octadecyl isocyanate

The CNC surface grafting with n-octadecyl isocyanate was adapted from Siquiera *et al.*<sup>277</sup> The aqueous suspension containing 3 g of cellulose was solvent-exchange by successive centrifugation steps from deionised water to acetone, and from acetone to anhydrous toluene. Redispersion of the CNC after each centrifugation was carried out using the ultra-turrax. This process avoids drying the CNC, which would lead to strong aggregation of the crystals reducing the available surface for the reaction. Afterward, CNC were dispersed in 350 mL of anhydrous toluene in a three-necked round-bottom flask equipped with a reflux condenser. 2 mL of catalyst (dibutyltin dilauryl) were added and the system was kept under nitrogen atmosphere to avoid the absorption of

humidity by the CNC. The reaction medium was heated to 90 °C and the n-octadecyl isocyanate was added drop by drop. Due to the reactivity of isocyanate towards water, the reaction was carried out with an excess of 10 eq. of isocyanate compared to the OH groups available on the CNC surface (estimated as 10 %). The temperature was then increased to 110 °C and the reaction was allowed to proceed for 30 min. Finally, a centrifugation protocol consisting in several cycles with different solvents (1 cycle of toluene, 4 cycles of dichloromethane, 3 cycles of ethanol) was performed to remove the secondary products and the un-reacted isocyanate. Modified CNC with long carbon chains is denoted as C18-g-CNC.

### VI.3.4. Grafting of PLA chains by in-situ ring opening polymerisation

The CNC surface grafting with PLA chains by *in-situ* ring opening polymerisation of L-lactide was adapted from Goffin *et al.*<sup>145</sup> The aqueous suspension containing 1.4 g of cellulose was solvent-exchange by successive centrifugation steps from deionised water to acetone, and from acetone to anhydrous toluene. Redispersion of the CNC after each centrifugation was carried out using the ultra-turrax. 1.4 g of CNC were dispersed in 60 mL of anhydrous toluene in the last step. Meanwhile, 10 g of L-lactide were dissolved in 20 mL of anhydrous toluene at 50 °C in a two-necked round-bottom flask equipped with a reflux condenser. The CNC suspension was then added to the system kept under nitrogen atmosphere. The temperature was increased to 80 °C and 0.2 g of Tin(II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>) was introduced in the reaction flask using a syringe. After 24 hours of reaction, the polymerisation was stopped adding a few drops of hydrochloric acid at 0.1 mol·L<sup>-1</sup>. Finally, the secondary products, un-reacted L-lactide and the non-grafted polymer were removed using a centrifugation protocol, established after having testing several possibilities (4 cycles of methanol, 4 cycles of ethanol and 2 cycles of acetone). Modified CNC with PLA chains is denoted as PLA-g-CNC.

#### VI.3.5. Characterisation

An environmental scanning electron microscope (ESEM), model Quanta 200 FEI, with accelerating voltage of 10 kV was used to characterise the MCC while a Zeiss Ultra 55 Field Emission Gun Scanning Electron Microscope (FEGSEM) was used for the unmodified CNC.

TEM images of unmodified and modified cellulose nanowhiskers were also obtained in a LEO 910 microscope with a bioscan camera model 792. The samples were prepared by drop-casting a previously sonicated diluted suspension of CNC in water (in order to avoid the damage of the carbon grid) and allowing the water to evaporate. The samples were stained with a 2 wt.-% uranyl acetate solution for about 5 min.

X-Ray diffraction (XRD) was used to evaluate the crystallinity of the cellulose nanowhiskers. The experiments were performed in a D8 Advance equipment from Bruker with a CuK $\alpha$  radiation at  $\lambda = 1.54$  Å (40 kV and 40 mA). Measurements were carried out in a range from 1 ° to 30 ° of 2 $\theta$  at 0.2 second per point.

Fourier transform infrared spectra (FT-IR) were obtained on a Perkin-Elmer Spectrum One and with a resolution of 4 cm<sup>-1</sup>. FT-IR spectra were recorded by depositing the cellulose powder directly on the surface crystals with the ATR configuration.

XPS studies were performed on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser, operated on a constant pass energy mode and non-monochromatized Mg X-ray radiation (hv = 1253.36 eV) at 10 mA and 12 kV. The samples were first placed in a copper holder mounted on a sample rod in the pre-treatment chamber of the spectrometer and then degassed at room temperature for 1 h before being transferred to the analysis chamber. Data analysis was performed with the XPS peak program.

Elemental analysis of the sample was carried out in a Leco CHNS-932 apparatus in order to determine the weight percentage of carbon, hydrogen, nitrogen, and sulphur present within a sample. The experiments were performed by heating about 2 mg of sample to 1000 °C. The amounts of C, H, N and S were measured by an IR absorption detection system and the percentage of nitrogen by a thermal conductivity detector.

Thermogravimetric analysis-mass spectroscopy (TGA-MS) measurements were performed using a Mettler Toledo thermogravimetric analyser (TGA, model TA Q500) coupled to a Pfeiffer Vacuum ThermoStar TM mass spectrometer, in order to analyse the products resulting from the decomposition of the sample. The temperature program was run from 30 °C to 900 °C at a heating rate of 5 °C·min<sup>-1</sup> in helium atmosphere (20 ml·min<sup>-1</sup>).

Contact angle measurements were carried out in a DataPhysics instrument equipped with a CCD camera. Distilled water was used as testing liquid.

## VI.4. RESULTS AND DISCUSSION

## VI.4.1. Characterisation of unmodified cellulose nanowhiskers

The acid hydrolysis of MCC leads to the removal of the amorphous cellulose and to the production of rod-like nanocrystals, as shown in Figure VI.1. Individual cellulose whiskers obtained from water suspension can be observed. The stability of CNC colloidal suspension in water depends on the dimension and polydispersity of the crystals, but also on their surface charges, due to the presence of sulphate groups remaining from the hydrolysis.<sup>22, 278</sup> The average length of cellulose nanowhiskers determined by image analysis (ImageJ software<sup>205</sup>, 200 measurements) was  $250 \pm 80$  nm (Figure VI.1.b). The value of the diameter is reported in the literature to be between 5 and 10 nm, and is in agreement with the images.<sup>23, 118</sup>



Figure VI.1. Images of (a) microcrystalline cellulose and (b) nanocrystalline cellulose obtained through acid hydrolysis with the distribution of nanocrystal length.

The thermal degradation of CNC was analysed by thermogravimetric analysis coupled with mass spectroscopy (Figure VI.2). The initial weight loss of approximately 10 % can be ascribed to the presence of absorbed water. Then, the degradation occurs in a broad temperature range, being separated in two defined processes. The first one occurs between 230 °C and 300 °C while the second one is a high temperature (from 350 °C to 650 °C) and slow process, resulting in a large amount of residues. This behaviour has been observed by other authors and attributed to the presence of sulphate groups remaining from the acid hydrolysis.<sup>138, 279</sup>

The effect of acid washing over the cellulose pyrolysis has been reported years ago, by studying the possible flame retardancy effect of sulphuric acid in the pyrolysis and combustion of cellulose.<sup>280-284</sup> The authors explained that the presence of inorganic acids increased the yield char at the expense of flammable tars but lower the onset of the thermal degradation.

In fact, sulphuric acid can react with the cellulose hydroxyl groups to form sulphate ester. As the temperature increases, the ester decomposes forming an organic sulphate and leading to the dehydration of the cellulose, facilitated by the low energy required to eliminate the sulphate acid in the sulphated anhydroglucose units. Thus, sulphuric acid could be considered as a dehydration catalyst. Moreover, decompositions involving the dehydration reaction increase the formation of gas, char, acid and carbonyl compounds, such as hydroxyacetaldehyde. This dehydration mechanism occurs at the expense of other degradation mechanisms, such as depolymerisation. The depolymerisation mechanisms lead to the formation of levoglucosan and other volatile products. These observations have been made for cellulose impregnated with acid solution and the authors analysed the char residue by FT-IR or the gaseous products of pyrolysis by mass spectroscopy.<sup>280, 281, 284</sup>

Thus, the sulphuric acid hydrolysis for the preparation of the cellulose nanowhiskers is expected to have a strong influence over the degradation of the cellulose. Roman *et al.*<sup>146</sup> studied the effect of hydrolysis conditions on the thermal degradation behaviour of bacterial cellulose. They demonstrated that the introduction of sulphate groups at the crystal surface during acid hydrolysis caused a significant decrease of the degradation temperature. Two processes were identified, the first one being attributed to the degradation of more accessible, highly sulphated regions while the second one was

related to the breakdown of the unsulphated crystal interior. Similarly, Wang *et al.*<sup>279</sup> studied the hydrolysis conditions of MCC and neutralisation procedures of the CNC. The nanowhiskers with detectable sulphate acid groups presented the two-step process, as the result of a primary pyrolysis catalysed by acid sulphate groups and of a low charring process of the solid residue.

Here, the identification of the degradation process is carried out by thermogravimetric analysis coupled to mass spectroscopy. Signals for m/z = 48 and m/z = 64 are detected at about 280 °C during the first degradation step of CNC and can be attributed to sulphate species.<sup>281</sup> At higher temperature, between 300 and 400 °C, carbon dioxide and monoxide are detected (m/z = 25 and 44), as well as masses related to anhydro sugars such as levoglucosan (m/z = 43, 57, 60, 70, 73 and 144) and levoglucosenone (m/z = 39, 42, 52, 53, 96).<sup>285</sup> Mass at m/z = 60 could also be related to acetic acid and hydroxyacetaldehyde.<sup>286</sup> A slow degradation process is observed at temperatures higher than 400 °C, as well as a gradual increase of the signal intensity for m/z = 44, corresponding to CO<sub>2</sub>. This process is then attributed to the charring process of the solid residue.



Figure VI.2. TGA analysis coupled with mass spectroscopy of CNC.

#### VI.4.2. Surface modification: grafting of n-octadecyl isocyanate

The grafting of long carbon chains onto the nanocrystal surface results from the reaction of n-octadecyl isocyanate with the hydroxyl groups of cellulose. However, isocyanate groups are highly reactive with water resulting in the formation of

disubstituted urea and carbon dioxide (Scheme VI.1). Hence, the reaction was carried out with an excess of isocyanate to counterbalance this possibility.

Scheme VI.1. Surface grafting reaction of n-octadecyl isocyanate with hydroxyl groups on the CNC surface and secondary reactions.

## VI.4.2.1. Characterisation of the grafting reaction

Figure VI.3 shows the FT-IR spectra of CNC, C18-g-CNC and waste by-products removed during the dichloromethane centrifugation cycles. CNC spectrum shows the typical absorption bands of cellulose: -O-H group at 3300 cm<sup>-1</sup>, -C-H and -CH<sub>2</sub>- at 2850 and 2900 cm<sup>-1</sup> and -C-O- at 1030 cm<sup>-1</sup>. After the grafting reaction, two intense bands at 2920 and 2850 cm<sup>-1</sup> attributed to the -CH<sub>2</sub>- and -CH<sub>3</sub> groups confirm the presence of long alkyl chains. Moreover, the grafting efficiency is demonstrated by the appearance of a new signal at 1704 cm<sup>-1</sup> associated to the carbamate group formed during the reaction. The removal of the excess of isocyanate is verified by the absence of the isocyanate group signal at 2260 cm<sup>-1</sup>. Moreover, the analysis of the by-products confirms the formation of long chains of diurea, observed as two strong absorption bands at 1610 and 1570 cm<sup>-1</sup> corresponding to the amide function groups. The absence of these two bands in the final product validates the efficiency of the centrifugation cycles as a washing method.



Figure VI.3. FT-IR spectra of unmodified cellulose nanowhiskers, modified with long carbon chains and secondary products.

XPS was also used to determine the surface chemical composition and bonding of CNC and C18-g-CNC. Carbon, oxygen, nitrogen and sulphur signals are present at 285 ( $C_{1s}$ ), 533 ( $O_{1s}$ ), 400 ( $N_{1s}$ ) and 170 ( $S_{2p}$ ), respectively. The  $C_{1s}$  spectra of unmodified and modified cellulose nanocrystals are shown in Figure VI.4 and the O/C, N/C and S/C ratios as well as the relative amount of surface functional group from deconvolution curves are reported in Table VI.1.



Figure VI.4. High resolution  $C_{1s}$  XPS spectra of (a) CNC and (b) C18-g-CNC. Curves inside are the deconvoluted curve fits of the spectra.

a.			
	С	NC	C18-g-CNC
O/C	0.	.58	0.43
N/C 0.		0.02	
S/C	0.0	008	0.006
b.			
Binding energy, eV	Assignment	CNC	C18-g-CNC
284.8	C-C	39 %	48 %
286.5	C-O	45 %	37 %
287.9	O-C-O/C=O	16 %	15 %

Table VI.1 (a) Atom ratio and (b) assignment of binding energy (BE) and atomic bond contribution (%) after deconvolution of the C<sub>1s</sub> XPS spectra.

The O/C ratio of CNC is lower than that deduced from the theoretical formula  $((C_6H_{10}O_5)_n \text{ giving a O/C ratio of 0.83})$  but agrees well with the values reported in the literature.<sup>277, 287</sup> This difference can be due to remaining hydrocarbon impurities. The presence of sulphate is also detected. After deconvolution of the C<sub>1s</sub> signal, the unmodified CNC exhibits three peaks, attributed to C-C bond (284.8 eV), C-O (286.5 eV) and O-C-O (287.9 eV). This third peak is related to the presence of impurities such as residual lignin, extractive substance or long-chain acids.<sup>288</sup>

After surface treatment, the N/C ratio increases while the O/C ratio decreases. Moreover, both the increase of the signal intensity of the C-C bond in the  $C_{1s}$  deconvoluted signal and the decrease of the C-O one effectively confirm the grafting of the crystal surface with long carbon chains. As expected, no evolution of the O-C-O/C=O bonds is observed.

The efficiency of surface grafting was demonstrated by FT-IR and XPS analysis while the amount of grafted carbon chain can be deduced from elemental analysis and thermogravimetry coupled to mass spectroscopy.

The content of the N element in C18-g-CNC ( $N_{C18-g-CNC}$ ) was determined to be 1.1 % by elemental analysis, while the theoretical N element content in the n-octadecyl isocyanate ( $N_{C18}$ ) is 4.7 %. Thus, the content x of grafted chains could be evaluated with the following equation:

$$xN_{C18} = N_{C18-g-CNC}$$
 (VI.1)
Hence, a content of 23 wt.-% of grafted carbon chains is obtained.

A corroboration of this result was carried out by TGA analysis, as shown in Figure VI.5. The first strong degradation step is attributed to the degradation of CNC, as m/z signals previously observed for the unmodified cellulose nanocrystal degradation are detected at 280 °C. This temperature is lower than for unmodified CNC (signals detected between 300 and 350 °C), which indicates a decrease of thermal stability after the grafting reaction. This behaviour has been reported by Uschanov *et al.*<sup>289</sup> for cellulose modified with long-chain fatty acids by esterification reaction and was attributed to a change of crystallinity in the surface structure, owing to the modification reaction (see structural analysis). Signals at 450 °C are observed for m/z = 29 + n14 and can be attributed to the fragmentation and degradation of the grafted carbon chains. Moreover, the signal at m/z = 56 could indicate the formation of the CH<sub>2</sub>NCO<sup>+</sup> cation. The amount of grafted chains is then also estimated to be around 20 %.



Figure VI.5. TGA profile coupled with mass spectroscopy of C18-g-CNC.

# VI.4.2.2. Structural analysis of C18-g-CNC

Figure VI.6 shows the TEM images of unmodified CNC and C18-g-CNC. Both samples were prepared from dilute aqueous suspensions of the whiskers sonicated before casting onto the TEM grid.

C18-g-CNC are less individualised than unmodified CNC. In fact, C18-g-CNC are less stable in water due to the presence of long carbon chains, resulting in the formation of nanowhisker agglomerates.



Figure VI.6. TEM images of (a) unmodified CNC and (b) C18-g-CNC.

WAXD analysis of the nanocrystals was carried out in order to verify that the crystalline structure was maintained after the chemical modification (Figure VI.7). Both CNC and C18-g-CNC display the typical diffraction peaks of cellulose I crystalline form (14.8 °, 16.5 °, 22.5 ° and 34.5 °). However, the diffraction peaks of C18-g-CNC are less sharp that the unmodified one, probably due to the formation of the grafted layer at the CNC surface and changes of the surface crystallinity.



Figure VI.7. XRD of unmodified CNC and C18-g-CNC.

Finally, the changes of the nanocrystal hydrophilicity were evaluated by contact angle measurements with water (Figure VI.8). Surface grafting induces an increase of

the contact angle from 65 to 92 °. Therefore, important changes of the crystal polarity are expected and should facilitate its dispersion in low polar solvents and polymers.



Figure VI.8. Contact angle measurement of a water drop onto CNC and C18-g-CNC.

#### VI.4.3. Surface modification: grafting of PLA chains

PLA grafting onto cellulose nanocrystals by ring opening polymerisation has been reported by Goffin *et al.*<sup>145</sup> However, they did not carry out any washing procedure of the obtained nanocrystals and mixed directly the nano-hybrids with PLA to produce the bionanocomposites. The polymerisation conditions (Scheme VI.2) were adapted by adding a purification protocol to remove residual monomer and non-grafted polymer. The advantage of this procedure when compared to a Soxhlet extraction is that a lower amount of nanofillers is lost through the Soxhlet cartridge.



Scheme VI.2. Surface grafting reaction of PLA chains onto cellulose nanocrystals by ring opening polymerisation.

#### VI.4.3.1. Characterisation of the grafting reaction

Figure VI.9.a reports the absorption bands of the reagents, i.e. L-LA and CNC, as well as a typical PLA spectrum while Figure VI.9.b displays the FT-IR signals of the obtained PLA-g-CNC and waste by-products from the acetone centrifugation cycles.

The absence of L-LA absorption band at 1240 and 1270 cm<sup>-1</sup> in the FT-IR spectra of the final PLA-g-CNC suggests the effective removal of residual monomer during the centrifugations. Chloroform centrifugation steps were tried as a method to remove residues of non-grafted PLA polymer. However, PLA-g-CNC crystals did not sediment in chloroform even after several centrifugation cycles. In fact, PLA-g-CNC formed a stable suspension in chloroform 48 hours after dispersion; while both unmodified CNC and unmodified CNC mixed with PLA sedimented (see Figure VI.10). This is a clear evidence of the successful grafting of PLA onto CNC surface.

As an alternative to chloroform, centrifugation cycles were carried out using acetone, which partially dissolves PLA. The spectra of the by-product present in the supernatant displays the typical PLA spectra (see Figure VI.9.b) with a strong signal around 1730 cm<sup>-1</sup> arising from the stretching frequency of PLA carbonyl group. Moreover, the absence of the absorption band of O-H group at 3300 cm<sup>-1</sup> indicates the absence of cellulose in the supernatant. Finally, the purified PLA-g-CNC displays the characteristic absorption bands of PLA as well as the weak band at 3300 cm<sup>-1</sup> of O-H groups of the cellulose.



Figure VI.9. FT-IR spectra of (a) PLA, L-LA and unmodified CNC and (b) CNC modified with PLA chains and secondary products.



Figure VI.10. Suspension in chloroform of (a) unmodified CNC, (b) unmodified CNC + PLA and (c) PLA-g-CNC 48 hours after stopping the stirring.

The amount of PLA chains present in the final PLA-g-CNC was evaluated by elemental analysis.<sup>144</sup> The content of the C element in CNC ( $C_{CNC}$ ) and PLA-g-CNC ( $C_{PLA-g-CNC}$ ) were determined to be 38.6 % and 46.7 % respectively, while the theoretical C element content in the PLA ( $C_{PLA}$ ) is 50 %. Thus, the content x of grafted PLA could be evaluated with the following equation:

$$xC_{PLA} + (1-x)C_{CNC} = C_{PLA-g-CNC}$$
(VI.2)

Finally, a content of 70 wt.-% of PLA in PLA-g-CNC is obtained.

Figure VI.11.a shows the thermal degradation of PLA-g-CNC, while Figure VI.11.b represents the degradation of the free PLA that has been eliminated during the centrifugation cycles. The peak detected for the polymer in the derivative of weight loss is located at 260 °C, which is much lower than the thermal degradation of the PLA pellets, probably due to differences between the molecular weights of the two polymers. PLA-g-CNC thermal degradation displays two processes (Figure VI.11.a). The first degradation step takes place from 200 °C to 290 °C and can be attributed to the PLA. The second degradation process occurs from 290 °C to 320 °C, corresponding then to cellulose degradation. Therefore, the amount of PLA contained in PLA-g-CNC estimated by TGA is also around 60-70 %.



Figure VI.11. TGA analysis of (a) PLA-g-CNC and (b) PLA.

# VI.4.3.2. Structural analysis of PLA-g-CNC

Figure VI.12 shows TEM images of the nanocrystals before and after PLA grafting. The morphology of the nanocrystals does not appear to be modified after the reaction. However, the nanocrystals are more agglomerated due to the presence of superficial PLA chains. Similar observations have been reported for PCL grafting.<sup>290</sup>



Figure VI.12. TEM images of (a) unmodified CNC and (b) PLA-g-CNC.

The XRD pattern of the PLA-g-CNC is reported in Figure VI.13. The two strong peaks located at  $2\theta = 16.8$  ° and 19.2 ° are the characteristic reflections of PLA crystalline  $\alpha$ -form.<sup>51</sup> Moreover, weaker reflections are reported at 12.5 °, 14.8 °, 22.5 °.<sup>291</sup> Thus, the CNC diffraction signal at 14.8 ° and 16.5 ° are masked by the PLA crystalline diffraction. Cellulose and starch nanocrystals grafted with PCL by ring opening polymerisation present similar behaviour and no signal of nanoparticle crystals

was detected due to PCL high crystallinity.<sup>143, 144</sup> However, the unusual shape of the peak at 22.5 ° suggests that both CNC and PLA participate to the signal.



Figure VI.13. XRD of PLA-g-CNC.

Finally, as for C18-g-CNC, the changes of the nanocrystal hydrophilicity were analysed by contact angle measurements with water. Surface grafting induces an increase of the contact angle from 65 to 79 °C confirming the surface modification.



Figure VI.14. Contact angle measurement of a water drop onto CNC and PLA-g-CNC.

# VI.5. CONCLUSIONS

The extraction of nanocrystalline cellulose was performed from acid hydrolysis of commercial microcrystalline cellulose, obtaining rod-like crystals of  $250 \pm 80$  nm length. The grafting of alkyl chains onto the cellulose nanowhiskers obtained by the reaction between the hydroxyl groups of the cellulose and n-octadecyl isocyanate was successfully demonstrated by FT-IR and XPS. Moreover, the amount of grafted carbon chains was estimated to be 20 % by elemental analysis and thermogravimetric analysis, resulting in new hydrophobic properties of C18-g-CNC. Grafting of PLA chains was

carried out by ring opening polymerisation. A special care was taken during the washing procedure in order to eliminate the remaining monomer and the non-grafted polymer. The amount of PLA in the PLA-g-CNC was finally estimated to be 70 %. The efficiency of the grafting was more difficult to demonstrate, however the high stability of PLA-g-CNC suspension in chloroform as well as the changes of the crystal surface properties are clear indications of the grafting success.

# Chapter VII. **PREPARATION AND PROPERTIES OF PLA/NR/CELLULOSE NANOCRYSTALS BIONANOCOMPOSITES**

# VII.1. SUMMARY

PLA/NR/cellulose nanowhisker composites were prepared using the three types of cellulose nanocrystals (CNC), i.e. the unmodified CNC and the two surface modified CNC developed in the previous chapter. A novel method of material processing was optimised combining solvent casting and extrusion in order to obtain a homogeneous dispersion of the nanofillers in the PLA/NR blend. The CNC modifications determined the affinity of the crystals towards the polymers and reflected on the ultimate properties.

# VII.2. INTRODUCTION

PLA/NR nanocomposites based on montmorillonites were studied in detail in *Chapter IV*. Interesting properties were obtained and could be tailored depending on the organoclays used. A compatibilising effect of the organoclays in the PLA/NR blend was also reported. Nonetheless, it could be of interest to substitute these mineral fillers by biodegradable nanoparticles extracted from renewable resources. Cellulose nanowhiskers have already been a preferred option to reinforce the PLA matrix, leading to interesting properties such as improved crystallisation or mechanical properties, when good compatibilisation and dispersion were achieved.<sup>135, 139</sup> Nevertheless, the processing of PLA/CNC nanocomposites remains challenging because of the degradation of both the fillers and the matrix.

This chapter details the development of new PLA/NR/CNC bionanocomposites. A special care was taken in the chosen processing method in order to achieve the best dispersion of the fillers. Moreover, the behaviour of CNC fillers in a polymer binary blend is reported for the first time. As for montmorillonite nanocomposites, the location and the interactions of the nanoparticles with the two polymers are expected to determine the ultimate properties of the nanocomposite. Especially, thermal, mechanical and disintegration properties are discussed along the chapter.

#### VII.3. EXPERIMENTAL SECTION

#### VII.3.1. Materials and sample preparation

PLA polymer 2002D was provided by NatureWorks<sup>®</sup> (D-content 4.25 %, MI = 5-7 g/10 min,  $\rho = 1.24$  g·cm<sup>-3</sup>). Natural Rubber (NR) was kindly supplied by Malaysian Rubber under the trade name CV60 (Mooney viscosity: ML(1 + 4) 100 °C = 60,  $\rho = 0.91$  g·cm<sup>-3</sup>).

Two methods were used to prepare the nanocomposites, i.e. direct extrusion or solvent casting combined with extrusion. For direct extrusion, CNC were lyophilised for 48 h (lyophilisador Telstar Lioalfa-6), forming a foam that was then pulverised in an analytical grinder from IKA. The obtained powder was mixed with PLA/NR blend in the extruder. For solvent casting combined with extrusion, a pre-blend of PLA/CNC was first prepared. For this purpose, CNC were solvent exchange from water to acetone and from acetone to chloroform by several centrifugation cycles. The suspension was sonicated for 3 x 3 min with an ultrasonication probe (Sonics Vibracell) in an ice bath to avoid temperature rise and was added to a PLA dissolution in CHCl<sub>3</sub> previously prepared. PLA/CNC mixture was then stirred for 1 hour and sonicated for 15 min using on/off cycles in order to avoid overheating. PLA/CNC mixture was then casted and CHCl<sub>3</sub> was allowed to evaporate for 2 days at room temperature, 5 hours under vacuum at 40 °C and dried over night before used in a ventilated oven at 80 °C. PLA/CNC film was cut into small pieces, extruded with NR and compression moulded.

NR concentration was fixed at 10 wt.-% and the cellulose nanocrystal loading was varied from 1 to 5 wt.-%. Samples prepared by direct extrusion were coded \_E while no specific indication in nomenclature was made for the samples prepared by combining solvent casting and extrusion.

#### VII.3.2. Characterisation

Structural Characterisation

The morphology of the samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. All the samples were cryo-fractured in liquid nitrogen and the fracture surface was sputter coated with gold/palladium (Au/Pd

80/20). The nanoclay dispersion was also studied by transmission electron microscopy (Philips Tecnai 20 microscope at an acceleration voltage of 200kV). Ultra-thin sections of the samples were prepared by cryo-ultramicrotomy at -140 °C (Leica EM UC6). The rubber droplet size was determined by image analysis using ImageJ.<sup>205</sup> Typically, 200 droplets were analysed per sample and the average Feret's diameter was calculated.

# • Physical properties

The crystallisation process was examined in a Mettler Toledo DSC822 differential scanning calorimetry. The following procedure was adopted: samples of about 10 mg were firstly heated from room temperature to 200 °C at a scan rate of 40 °C·min<sup>-1</sup>, maintained at this temperature for 3 min to erase the thermal history, then, were rapidly cooled to 20 °C. Finally, a second heating scan from 20 °C to 200 °C at 2 °C·min<sup>-1</sup> was carried out. The experiments were performed in nitrogen atmosphere.

Dynamic mechanical analysis was performed on a Mettler Toledo DMA 861<sup>e</sup> in tensile mode at 1 Hz as a function of the temperature from -90 °C to 150 °C at a heating rate of 2 °C  $\cdot$ min<sup>-1</sup>.

Thermal degradation measurements were performed using a Mettler Toledo thermogravimetric analyser (TGA, model TA Q500). The temperature program was run from 30 °C to 650 °C at a heating rate of 10 °C·min<sup>-1</sup> in nitrogen atmosphere (20 ml·min<sup>-1</sup>).

# Rheological properties

Rheological measurements were performed using an ARES Advanced Rheometric Expansion System rheometer with parallel plate geometry of 25 mm of diameter. Tests were carried out in dynamic mode of shearing at 180 °C from 0.01 rad·s<sup>-1</sup> to 100 rad·s<sup>-1</sup> frequency range.

# Mechanical properties

Tensile tests of the samples were measured according to ASTM D 3379-75 specifications on an Instron dynamometer (model 3366) at 23 °C, and at a cross-head speed of 10 mm·min<sup>-1</sup>. At least five specimens of each sample were tested.

# • Disintegration study

Disintegration study was carried out following the European standard ISO 20200 (see *Chapter IV*). Compression moulded of 20 mm x 20 mm x 0.30 mm films were buried into the organic substrate at 4-6 cm depth in the perforated boxes and incubated at 58 °C. The tested samples were taken out at selected times, washed and dried in oven at 37 °C for 24 h. The blends chosen for the disintegrability study were the nanocomposites prepared by solvent casting combined with extrusion with 3 wt.-% of nanofillers. The disintegrability value was obtained normalising the weight of the samples, at different stages of incubation, with respect to the initial ones. Infrared spectra of the sample were measured in a Jasco FT-IR 615 spectrometer in attenuated total refraction (ATR) mode before and after different times of disintegration in composting conditions.

# VII.4. RESULTS AND DISCUSSION

# VII.4.1. Optimisation of processing

The preparation of bioparticle nanocomposites by extrusion process often remains an issue due to the possible thermal degradation of cellulose whiskers. In this study, CNC were neutralised in order to prevent the degradation linked to the sulphate groups introduced during acid hydrolysis, and the same extrusion parameters as for the montmorillonite nanocomposites were applied. However, strong degradation of cellulose nanowhiskers was observed when a PLA/NR/CNC blend was processed by direct extrusion at 180 °C and brown little spots could be seen in the material. Similar observation has been made by Goffin *et al.*<sup>145</sup> Thus, the processing temperature was reduced to 160 °C while time and rotor speed remained unchanged. No visible degradation was observed in this case (see Figure VII.1).



Figure VII.1 PLA/NR/CNC\_E 3 wt.-% nanocomposites extruded at (a) 160 °C and (b) 180 °C.

Moreover, the crystalline structure of CNC could be prone to degradation during processing. Figure VII.2.a shows the XRD spectra for the nanocomposites at 3 wt.-% prepared by solvent casting combined with extrusion as well as PLA/NR/CNC\_E 3 wt.-%. Although the signal of crystalline CNC is very weak compared to the amorphous signal of the matrix, a shoulder is visible at 22.5 °, corresponding to the most intense diffraction peak of cellulose I crystalline form. This signal is more visible for the nanocomposites at 5 wt.-% (Figure VII.2.b). Therefore, it can be concluded that the crystalline structure of cellulose is maintained during processing, independently of the applied process conditions.



Figure VII.2. XRD spectra of pristine CNC and several PLA/NR/CNC nanocomposites.

In order to compare the efficiency of the two blending procedures, a PLA/NR blend was also prepared by casting combined with extrusion and compared with PLA/NR\_E. The morphology of these blends is shown in Figure VII.3, observing minor changes

between them. Although NR average droplet size is very similar in both cases, a slight decrease is observed when compared to the average droplet size of the PLA/NR blend prepared at 180 °C in *Chapter IV* (940  $\pm$  330 nm). As reported in *Chapter III* and *Chapter IV*, increasing processing temperature led to an increase of NR droplet size due to the decrease of the matrix viscosity.<sup>210</sup>

a. 890 ± 230 nm





Figure VII.3. SEM images of PLA/NR blend prepared by (a) extrusion and (b) casting combined with extrusion.

The dispersion of CNC was also evaluated for PLA/NR/CNC 3 wt.-% bionanocomposites prepared by both blending procedures. Rheology has been proven to be an effective tool to inform about the nanocomposite structure and measurements were carried out in frequency sweep mode (Figure VII.4).

A slight difference of complex viscosity is observed between PLA/NR and PLA/NR\_E at low frequencies. PLA chains are subjected to more aggressive conditions in the case of casting combined with extrusion, which explains the slight decrease of viscosity when compared to simple extrusion. Adding 3 wt.-% of CNC does not lead to any changes in the case of direct extrusion, which suggests that nanoscale level dispersion is not achieved. Hence, agglomerates are expected to be present in the samples when redispersing dried CNC in the polymer matrix by direct extrusion. Interestingly, an increase of viscosity and storage modulus at low frequencies is observed when employing the solvent casting-extrusion method. This solid-like behaviour is attributed to the formation of a network structure. Alloin *et al.*<sup>292</sup> compared the rheological properties of poly(oxyethylene)/ramie whiskers at 6 wt.-% prepared by

casting and by extruding a freeze-dried powder of the cellulose whiskers/POE solution. A solid-like behaviour was reported for films prepared by casting while a liquid-like behaviour was observed for films prepared by extrusion. They concluded that the extrusion prevented the formation of a strong whisker network.

Nevertheless, Figure VII.4 shows that the network formation is preserved after extrusion and PLA/NR/CNC bionanocomposites having good dispersion of CNC can be successfully obtained using the adequate process conditions. Thus, combining casting and extrusion has been the preferred process method in this study. Jonoobi *et al.*<sup>293</sup> developed a similar procedure and prepared a masterbatch of PLA/cellulose nanofibres by solvent casting before extrusion in order to improve the nanofibre dispersion.



Figure VII.4. Influence of blending procedure over the rheological properties of the materials.

#### VII.4.2. Morphology of the bionanocomposites

The addition of nanofillers in a polymer blend has been reported to have a profound effect over the final morphology of the blend.<sup>189</sup> This effect was observed and reported in detail for PLA/NR/MMT nanocomposites in *Chapter IV*. The morphology of the resulting materials was found to be dependent on the affinity of the organoclays toward the two polymers and of the filler loading. However, no reports were found regarding the effect of cellulose nanowhiskers over the morphology of polymer blends.

Figure VII.5 shows the morphology of PLA/NR blends filled with 3 wt.-% of the three types of cellulose nanowhiskers. A reduction of the size of NR domains is

observed when compared to the unfilled blend (Figure VII.3), this effect being stronger for unmodified CNC.



Figure VII.5. SEM images of the PLA/NR blend filled with (a) CNC, (b) PLA-g-CNC and (c) C18-g-CNC at 3 wt.-%.

Further evolution of the morphology with the concentration of C18-g-CNC and PLAg-CNC is reported in Figure VII.6. Increasing PLA-g-CNC concentration leads to a progressive reduction of the NR droplet size, while the opposite effect is reported for C18-g-CNC. The largest NR domain is observed for PLA/NR/C18-g-CNC 5wt.-%.



Figure VII.6. Morphology of PLA/NR/C18-g-CNC at (a) 1 wt.-%, (b) 5 wt.-% and PLA/NR/PLA-g-CNC at (c) 1 wt.-%, (d) 5 wt.-%.

The affinity of the different types of CNC and their location in the blend need to be evaluated in order to explain these results. Given the polarity of the cellulose nanowhiskers, CNC affinity towards the PLA phase should be higher than to the NR domains. Moreover, in the case of the organoclay C15A, the presence of alkyl apolar chains in the clay lattices increased the affinity of the clay towards the NR domains. The same effect is then expected for C18-g-CNC. Obviously, grafting PLA chains onto the CNC surface should improve its compatibility with the PLA matrix.

TEM images of PLA/NR blend filled with 3 wt.-% of CNC, 5 wt.-% of PLA-g-CNC and C18-g-CNC at 5 wt.-% are shown in Figure VII.7. TEM contrast between polymers and cellulose nanowhiskers is low and complicates achieving TEM images with high resolution and high contrast. Nevertheless, CNC and PLA-g-CNC can be observed in the PLA matrix (Figure VII.7.a and Figure VII.7.b) even if it is not possible to observe single whiskers. In the case of C18-g-CNC, the PLA matrix appears to be very homogenous, confirming the absence of whiskers in this phase. C18-g-CNC is observed in the NR droplets, as seen in Figure VII.7.c. No whiskers could be seen at the interface between both polymers.



Figure VII.7. TEM images of PLA/NR blend filled with (a) 3 wt.-% CNC, (b) 5 wt.-% PLA-g-CNC and (c) 5 wt.-% C18-g-CNC at two magnifications.

In general, the changes reported over the morphology of the blends can be ascribed to the changes of the viscosity ratio. The location of CNC and PLA-g-CNC in the PLA phase could increase the PLA viscosity and thus, hinder the coalescence of NR droplets facilitating the droplet break-up of the dispersed high viscosity rubber phase. The location of C18-g-CNC did not lead to important changes on the blend morphology at low filler loadings and an increase of NR droplets is observed for 5 wt.-%. This effect could be ascribed to the increase of NR viscosity. Nevertheless, the effect of cellulose nanowhiskers over the blend morphology is not as remarkable as it was for the montmorillonites.

#### VII.4.3. Rheological properties

Very few studies describe the rheological properties of cellulose nanowhisker composites.<sup>152, 292, 294</sup> The authors reported solid-like behaviour when strong interactions existed between the nanofiller and the matrix. As an example, Goffin *et al.*<sup>152</sup> studied PCL/CNC bionanocomposite viscoelastic properties, observing no effect of the pristine CNC while PCL-g-CNC induced a solid-like behaviour at 8 wt.-%. This behaviour was due to the formation of a physical network between the polymer matrix and modified nanowhiskers.

The rheological properties of PLA/NR/C18-g-CNC bionanocomposite are reported in Figure VII.8.a. An increase of storage modulus G' and of the absolute complex viscosity  $\eta^*$  at low frequencies are observed for concentrations of 3 and 5 wt.-% and a solid-like behaviour is observed for 5 wt.-%. Hence, the percolation threshold occurs between 3 and 5 wt.-% loading fraction, confirming the formation of a network structure that gives to the material a better resistance against the applied deformation at low frequency. Figure VII.8.b shows the rheological properties of PLA/NR/PLA-g-CNC bionanocomposites. In this case, G' and  $\eta^*$  increase with the cellulose nanowhisker content, however this increment is lower and does not reach the solid-like behaviour, probably due to the lower content of cellulose nanowhiskers in the modified CNC.

Nevertheless, the increase of the storage modulus and the complex viscosity are an indication that a good dispersion of the cellulose whiskers was achieved in both cases.



Figure VII.8. Influence of the concentration of (a) C18-g-CNC and (b) PLA-g-CNC over the rheological properties of the composite.

# VII.4.4. Dynamic mechanical analysis

An increase of the mechanical properties and of the storage modulus of PLA/cellulose bionanocomposites have been described by several research groups, although no significant changes were observed regarding PLA *tan*  $\delta$ .<sup>135, 141, 142</sup> Figure VII.9 shows the storage modulus and *tan*  $\delta$  of PLA/NR blend and its nanocomposites over a temperature range from -100 to 150 °C.



Figure VII.9. Temperature dependence of (a) E' and PLA  $tan \delta$  with cellulose nanowhisker type at 3 wt.-%, (b) E' and NR  $tan \delta$  with C18-g-CNC concentration and (c) E' and PLA  $tan \delta$  with PLA-g-CNC concentration.

As observed in *Chapter IV*, the E' curve of the blend exhibits two drops corresponding to the glass transition temperature of their constituents. The addition of 3 wt.-% of the different types of CNC results in an increase of the modulus value (Figure VII.9.a). Surprisingly, the stronger increases were observed for unmodified CNC and PLA-g-CNC. For C18-g-CNC, the storage modulus difference between the PLA/NR blend and the nanocomposite tends to zero from NR  $T_g$  to the PLA  $T_g$  and the reinforcing effect decreases with increasing temperature. (Figure VII.9.b). Moreover, while none of the CNC affects the PLA  $T_g$  (Figure VII.9.a), a shift of NR  $T_g$  towards higher temperature is observed with the addition of C18-g-CNC (Figure VII.9.b). This shift confirmed the affinity of C18-g-CNC to the NR phase, reducing the rubber chain mobility due to the formation of strong nanofiller-rubber interactions. For PLA-g-CNC filled nanocomposites, an increase of the storage modulus is observed when increasing the concentration over the entire temperature range while no effect over the polymer  $T_g$  is perceived. In fact, the real concentration of C18-g-CNC in the NR phase is higher than the concentration of PLA-g-CNC in the PLA phase, explaining why no changes are observed in the PLA  $tan \delta$ , even if a good affinity is expected between PLA matrix and PLA-g-CNC.

#### VII.4.5. Crystallisation behaviour

Crystallisation behaviour of the PLA/NR/CNC nanocomposites was studied by DSC dynamic measurements, as pictured in Figure VII.10. No changes of the PLA  $T_g$  are observed with the addition of the cellulose nanowhiskers. It is also noticed that the cold crystallisation temperatures are lower than those reported in *Chapter IV* and the observed differences are attributed to the processing method (Table VII.1).

Figure VII.10.a displays the influence of cellulose nanowhisker types over the crystallisation behaviour of the PLA/NR blend. Significant changes are observed depending on the whisker modifications. The addition of 3 wt.-% of unmodified CNC and C18-g-CNC induces an increase of PLA  $T_c$  while a slight decrease is reported for PLA-g-CNC.

The effect of the two modified cellulose whiskers is more evident in Figure VII.10.b and c where the effect of the increasing concentration of fillers is reported. Clearly, PLA  $T_c$  progressively decreases with the PLA-g-CNC concentration while increases for C18-g-CNC. Thus, an opposite effect of the two nanowhiskers is observed. Both location and affinity of the bioparticles with the two polymers play an important role over the crystallinity behaviour of the nanocomposites. Unmodified CNC and PLA-g-CNC were both located in the PLA phase. However, meanwhile the presence of CNC appears to affect PLA crystallisation, PLA-g-CNC demonstrates a nucleating effect over the PLA/NR blend. A similar observation has been reported by Goffin *et al.*<sup>145</sup> Nevertheless, they also observed a strong decrease of the PLA  $T_g$  due to the presence of

short PLA-grafted or non-grafted chains that could act as plasticisers. Therefore, it was difficult to conclude which effect was more predominant between the nucleation induced by PLA-g-CNC or the plasticisation effect of PLA short chains. In the current study, no changes of the PLA  $T_g$  were observed by neither DMA nor DSC measurements. Thus, the nucleating effect of well dispersed and modified CNC is predominant.

Opposite results are observed with the addition of C18-g-CNC, which are similar to the results obtained with C15A organoclay that hindered PLA crystallisation and inhibited the nucleating effect of NR droplets. From DMA measurements and TEM images, it was demonstrated that C18-g-CNC affinity towards NR was higher than towards PLA. Therefore, similar conclusions can be drawn here, explaining the increasing PLA cold crystallisation temperature.



Figure VII.10. Dynamic crystallisation of PLA/NR/CNC bionanocomposites. Influence of (a) type of modification at 3 wt.-%, (b) C18-g-CNC concentration and (c) PLA-g-CNC concentration.

	T <sub>c</sub> ,	$\Delta H_{c}$ ,	T <sub>m1</sub> ,	T <sub>m2</sub> ,	$\Delta H_{mtot}$ ,
	°C	J∙g⁻¹	°C	°C	J·g⁻¹
PLA/NR_E	109.9	-22.0	146.6	152.8	20.9
PLA/NR	104.9	-22.2	145.2	152.3	21.8
PLA/NR/CNC 3 wt%	106.0	-22.1	145.7	152.6	22.3
PLA/NR/C18-g-CNC 1 wt%	107.1	-22.5	145.6	152.5	21.6
PLA/NR/C18-g-CNC 3 wt%	110.0	-23.2	146.8	153.0	20.2
PLA/NR/C18-g-CNC 5 wt%	111.5	-22.5	147.0	153.2	21.4
PLA/NR/PLA-g-CNC 1 wt%	103.7	-22.1	144.9	152.5	20.3
PLA/NR/PLA-g-CNC 3 wt%	103.0	-20.9	145.6	153.6	20.6
PLA/NR/PLA-g-CNC 5 wt%	100.9	-22.9	145.6	153.9	22.6

Table VII.1 DSC data of PLA/NR/CNC nanocomposites (second heating scan).

#### VII.4.6. Mechanical properties

Retaining the ductile behaviour of the PLA/NR blend obtained in *Chapter III* after the addition of nanofillers was a desired result. Therefore, the study of the mechanical properties of cellulose nanowhisker nanocomposites is critical in the development of these systems.

Firstly, it should be noted that the method of preparation of the materials does not have any major influence over their mechanical properties. PLA and PLA/NR prepared by both methods only display a slight decrease in the tensile strength (Table VII.2).

No real improvements of Young's modulus or tensile strength are observed with the addition of unmodified CNC. The average elongation of this material is not reported in Table VII.2 because of the large deviations of the results, which vary between 8 % up to 148 %. TEM images demonstrated that unmodified CNC are preferentially located in the PLA phase. A good dispersion of the fillers was observed by TEM images and rheological measurements, nevertheless a lack of compatibility between unmodified CNC and PLA matrix could be responsible for the inhomogeneous elongation at break values reported.

The addition of C18-g-CNC leads to a progressive decrease of the Young's modulus and the tensile strength with increasing concentration of whiskers. The elongation at break remains over 150 % for concentrations of 1 wt.-% and 3 wt.-% while decreases to about a third of that value for 5 wt.-%. These mechanical properties are similar to those obtained for C15A montmorillonites and are attributed to the affinity of the C18-g-CNC towards the NR phase. Nevertheless, no significant increase of the elongation at break is observed for low C18-g-CNC contents, as it was the case for C15A.

Interesting results are obtained with the addition of PLA-g-CNC. The tensile strength is maintained with increasing the concentration of nanocrystals while the Young's modulus slightly increases. The elongation at break is also maintained for concentrations of 1 wt.-% and 3 wt.-%, while more heterogeneous results are observed at 5 wt.-%. The presence of PLA grafted short chains on the CNC surface appears to be an effective compatibiliser between CNC and PLA to maintain the ductile property of the PLA/NR blend, even though the PLA-g-CNC are observed to be dispersed in the PLA phase. Moreover, small PLA chains could also help to improve PLA matrix flexibility even if no changes in PLA  $T_g$  were observed.

	Young's modulus, MPa	Tensile strength, MPa	Elongation at break, %
PLA_E	$2514\pm63$	$64.2 \pm 1.7$	$4 \pm 0.4$
PLA	$2553 \pm 68$	$60.4 \pm 1.5$	$4 \pm 1$
PLA/NR_E	$2076\pm106$	$46.6 \pm 1.0$	$183 \pm 17$
PLA/NR	$2045 \pm 86$	$41.1 \pm 0.9$	$166 \pm 22$
PLA/NR/CNC 3 wt%	$2043 \pm 142$	$42.4 \pm 1.1$	from 8 to 148
PLA/NR/C18-g-CNC 1 wt%	$2260 \pm 138$	$39.9 \pm 1.3$	$178 \pm 6$
PLA/NR/C18-g-CNC 3 wt%	$1876 \pm 111$	$33.9\pm0.9$	$152 \pm 12$
PLA/NR/C18-g-CNC 5 wt%	$1785 \pm 77$	$31.1 \pm 0.6$	53 ± 13
PLA/NR/PLA-g-CNC 1 wt%	$1892 \pm 58$	$42.0 \pm 1.0$	$163 \pm 8$
PLA/NR/PLA-g-CNC 3 wt%	$1986 \pm 88$	$41.1\pm0.8$	$167 \pm 20$
PLA/NR/PLA-g-CNC 5 wt%	$2047 \pm 135$	$41.4 \pm 2.1$	from 58 to 191

Table VII.2. Mechanical properties of PLA/NR/CNC nanocomposites.

#### VII.4.7. Thermal degradation

The non-oxidative degradation of the materials was studied by thermogravimetric analysis. Figure VII.11 represents the thermal degradation data of the materials prepared by solvent casting combined with extrusion. It appears that the addition of 3 wt.-% of cellulose nanowhiskers results in a slight decrease of the degradation peak, independently of the type of modification, due to the lower thermal stability of the nanofillers with respect to the polymers. The same effect is observed for all concentrations (Table VII.3)



Figure VII.11. DTG curves of the materials at 3 wt.-% of nanofillers.

	T <sub>onset,</sub> ⁰C	T <sub>dmax,</sub> ⁰C
PLA	352.9	376.0
PLA/NR	351.1	372.9
PLA/NR/CNC 3 wt%	342.8	365.3
PLA/NR/C18-g-CNC 1 wt%	343.7	365.3
PLA/NR/C18-g-CNC 3 wt%	346.2	368.9
PLA/NR/C18-g-CNC 5 wt%	334.8	365.2
PLA/NR/PLA-g-CNC 1 wt%	342.9	363.8
PLA/NR/PLA-g-CNC 3 wt%	340.6	366.3
PLA/NR/PLA-g-CNC 5 wt%	343.5	362.6

Table VII.3. Thermal degradation of the materials.

#### VII.4.8. Disintegration in composting conditions

The study of the disintegration of PLA/NR/cellulose nanowhisker materials was carried out for 3 wt.-% of nanofillers. Additionally, PLA and PLA/NR blend were also studied for comparison.

Figure VII.12 shows the samples taken out at different times of composting, resulting in very similar observations to PLA/NR/MMT nanocomposites. During the first week, whitening and deformation of the surface are detected for all materials. These changes have been attributed to the water absorption and to the formation of low molecular weight compounds formed by the hydrolytic degradation, as well as to hole formation and crystallinity increase (see section IV.4.9). At the 10<sup>th</sup> day, fragmentation and weight loss of the samples are already observed for all the materials except C18-g-CNC nanocomposite, which starts to fragment after the 15<sup>th</sup> day.

Figure VII.13 reports the evolution of the material disintegrability with the composting time. It can be observed that after 31 days of composting, all materials reach a 100 % of disintegration. Moreover, the disintegration rates of PLA and PLA/NR materials prepared by solvent casting and extrusion at 160 °C are very similar to the materials prepared by direct extrusion at 180 °C (see section IV.4.9). As the disintegration in compost strongly depends on the initial molecular weight of the polymer, these results are an indication that similar degradation of PLA occurs during both processing methods. Again, a slight delay of PLA/NR blend disintegration is observed when compared to PLA. Surprisingly, the addition of the unmodified CNC does not affect the disintegration rate of the blend. Although the addition of a hydrophilic filler is expected to accelerate the degradation rate of the PLA/NR material, CNC could also impede water diffusion, explaining the obtained results.<sup>170</sup> The two modified cellulose nanowhiskers delay the disintegration rate, the slowest rate being observed for C18-g-CNC. The modification reaction of cellulose whiskers increased the hydrophobicity of the nanofillers, especially for C18-g-CNC, which could then hinder the hydrolytic degradation.



Figure VII.12. Disintegration of the samples at different times of composting.



Figure VII.13. Evolution of disintegration of the materials with composting time.

Figure VII.14 shows the FT-IR spectra of PLA/NR and PLA/NR/C18-g-CNC at different incubation times. As previously observed, a new band appears progressively at 1600 cm<sup>-1</sup> corresponding to the carboxylate ion, while the band at 1260 cm<sup>-1</sup>

corresponding to the -C-O- stretching disappears (14 days). The process of degradation is slower for C18-g-CNC composites than for PLA/NR blend.

In both cases, the spectra obtained after 23<sup>th</sup> days of experiments corresponds to NR spectra, with a band at 830 cm<sup>-1</sup> (cis-1,4-double bond).



Figure VII.14. FT-IR spectra of (a) PLA/NR and (b) PLA/NR/C18-g-CNC as function of the disintegration time.

# VII.5. CONCLUSIONS

The preparation and properties of new PLA/NR/CNC bionanocomposites were described in this chapter. A special care was attributed to the processing method, as a combination of casting and extrusion was necessary in order to prevent the degradation of the cellulose nanowhiskers and to obtain a good dispersion of the fillers. The addition of the three types of fillers affected the morphology of the blend, reducing the NR droplets in the case of PLA-g-CNC and CNC. These two nanowhiskers displayed a higher affinity to the PLA phase while C18-g-CNC demonstrated strong interactions with the rubbery phase. These different interactions with both polymers explained the effect of the fillers over the PLA crystallisation behaviour. Interestingly, a high elongation under tensile conditions was maintained for the bionanocomposites. Moreover, all materials reached a 100 % of disintegration in composting conditions, even if the introduction of hydrophobic nanofillers delayed the process.

# Chapter VIII. CONCLUSIONS

In this doctoral thesis, new PLA bionanocomposites have been developed in order to improve PLA physical and mechanical properties to broaden its applications without compromising its biocompatible and biodegradable characteristics. For this purpose, layered silicates and cellulose nanocrystals have been incorporated in a PLA/NR biobased blend. Initially, the structure and properties of the PLA/NR blends were studied in detail in order to optimise the blend properties. Subsequently, the influence of the addition of small amounts of organoclays and cellulose nanocrystals over the blend properties was reported. Special attention was attributed to the mechanical properties of the materials all along this work.

The chemical modification of the nanofillers plays a key role when incorporated into the bio-based blend, as it determines their affinity with both polymers and their subsequent location in the blend. For this purpose, different commercial organoclays were selected (CNa<sup>+</sup>, C15A and C30B), considering their affinity with both polymers.

With the same idea, cellulose nanowhiskers (CNC), extracted from commercial microcrystalline cellulose, were superficially modified using grafting reactions. The first studied reaction consisted in the grafting of long alkyl chains onto the cellulose nanowhiskers (C18-g-CNC), obtained by the reaction between the hydroxyl groups of the cellulose and the n-octadecyl isocyanate. Moreover, a grafting of PLA chains was carried out by ring opening polymerisation (PLA-g-CNC). Again, these reactions improved the compatibility with the NR phase and PLA phase, respectively

The following general conclusions regarding the materials can be extracted from this thesis:

• The addition of natural rubber allowed a straightforward production of ductile PLA, using a simple melt blending procedure. The optimal NR content to improve the brittleness of PLA was found to be 10 wt.-%. At this concentration, rubber droplets of about 1 µm diameter were homogenously dispersed in the PLA matrix, providing an optimum balance of both the physical and mechanical behaviour of the material without sacrificing totally the transparency of the material. The tensile behaviour of the blend showed a drastic increase of the elongation at break, through the debonding of the rubber droplets, as demonstrated by synchrotron X-ray scattering experiments. Moreover, natural rubber acted as a nucleating agent favouring the crystallisation ability of PLA.

- The processing conditions of the nanocomposites need to be optimised considering the characteristics of the nanofillers, as the cellulose nanocrystals required a special care in order to avoid their degradation. As a function of the nanofiller modification and the processing method, it was possible to control the dispersion of the nanofillers.
- The addition of the nanofillers drastically modified the morphology of the blend, especially in the case of the organoclays. C15A and C30B acted at low concentration as compatibilisers for the PLA/NR blend because of their preferential location at the polymer interface, forming a solid barrier and preventing the coalescence of NR droplets. In the case of the cellulose nanocrystals, the location of unmodified CNC and PLA-g-CNC in the PLA matrix resulted in a decrease of the NR droplet size.
- The good dispersion of the nanofillers in the polymer blend was effectively demonstrated by rheological measurements, considering both particle-particle and particle-polymer interactions.
- The study of the mechanical properties of the materials was an important part of this work. The further increase of the PLA/NR blend ductility by the addition of small amounts of C15A motivated a deeper analysis of the deformation mechanisms by synchrotron X-ray scattering. For this particular nanocomposite, the formation of cavities between PLA and NR was hampered by the nanoclays since they were mainly located at the polymer blend interface, leading to the formation of stable crazes able to fully develop. Meanwhile, the reinforcement of the PLA matrix by C30B led to a further embrittlement of the materials. Interestingly, the cellulose nanowhiskers mainly maintained a high elongation at break, even if large deviations of the elongation at break were observed for some samples.
- Dynamic mechanical analysis was a powerful tool to evaluate the affinity of the fillers with both polymers. C15A and C18-g-CNC both induced a displacement of the NR  $T_g$  at higher temperatures, indicating a strong interaction with the NR

phase. Stronger increases of the storage modulus were obtained for C30B, CNC and PLA-g-CNC, confirming their affinity to the continuous phase.

- The crystallisation behaviour of the materials strongly depended on the nanofiller location and dispersion. The organoclays and C18-g-CNC inhibited the nucleating effect of the NR droplets while interesting results were obtained for PLA-g-CNC, which promoted PLA crystallisation.
- The best improvement of the barrier properties were obtained when the organoclays were homogeneously distributed in the continuous phase. Chemical modifications of the fillers could help this dispersion, as in the case of C30B. Moreover, changes in the blending procedure could also force this scenario.
- Thermal degradation of the blend in an inert atmosphere was improved with the addition of the organoclays while slightly decreased with the addition of the nanocrystals due to their lower thermal stability when compared to the polymer ones.
- Disintegrability tests in compost demonstrated that all the prepared materials reached more than a 90 % of disintegration after one month of composting and can be considered as disintegrated according to the ISO 20200 standard. The addition of hydrophobic nanofillers could retard the material degradation, without affecting the final disintegration percentage.
- As a general conclusion, it should be underlined that the nanofiller and its chemical modification should be chosen carefully as reinforcement in the PLA/NR bio-based blend depending on the targeted property.
## Capítulo VIII. CONCLUSIONES

En esta Tesis doctoral se han desarrollado nuevos bionanocompuestos de PLA con el fin de mejorar sus propiedades físicas y mecánicas y así ampliar su uso industrial. Para ello, se han incorporado dos tipos de nanocargas, silicatos laminares y nanocristales de celulosa, a una mezcla de PLA/NR. En un primer momento, se estudió la morfología y las propiedades de la mezcla polimérica. Posteriormente, se discutió la influencia de la adición de pequeñas cantidades de montmorillonitas o nanocristales de celulosa sobre la morfología y las propiedades físicas y mecánicas de la mezcla. En particular, se estudió de manera más detallada el mecanismo de deformación de los materiales mediante medidas *in-situ* de dispersión de rayos X por radiación sincrotrón durante el ensayo mecánico.

La modificación química de las nanocargas tiene una importancia clave a la hora de incorporarlas a la mezcla polimérica, determinando su afinidad con los dos polímeros y su localización en la mezcla. Por ello, se emplearon diferentes tipos de organosilicatos comerciales (CNa<sup>+</sup>, C15A and C30B), elegidos según su afinidad con los polímeros, y se modificaron superficialmente nanocristales de celulosa (CNC), extraídos de celulosa microcristalina comercial, mediante reacciones de injerto. La primera reacción estudiada consistió en el injerto de cadenas largas de 18 átomos de carbono (C18-g-CNC), a través de la reacción de los grupos hidroxilos de la celulosa con n-octadecilisocianato. También se injertaron cadenas de PLA mediante reacción de polimerización con apertura del anillo (PLA-g-CNC). Estas dos reacciones tuvieron como propósito mejorar la compatibilidad con la fase NR y la fase PLA, respectivamente.

De los resultados obtenidos durante el estudio, se pueden extraer las siguientes conclusiones.

 La adición de caucho natural permitió la producción de una mezcla dúctil, empleando un método simple y escalable en estado fundido. Una concentración de NR de 10 % en peso se definió como óptima para mejorar la fragilidad del PLA. A esta concentración, se observó la formación de gotas de NR de un tamaño medio de 1 µm homogéneamente distribuidas en la matriz de PLA, proporcionando un balance óptimo de las propiedades físicas y mecánicas del material, sin sacrificar totalmente la transparencia del material. Las propiedades a tracción de la mezcla mostraron un incremento drástico de la deformación a rotura. Adicionalmente, se observó que el NR actuaba como agente nucleante para la matriz de PLA.

- Las condiciones de procesado han de ser elegidas teniendo en cuenta las características de cada nanocarga, como por ejemplo la posible degradación de los nanocristales de celulosa con la temperatura.
- La adición de las nanocargas tuvo una profunda influencia sobre la morfología de la mezcla, especialmente en el caso de los organosilicatos. C15A y C30B actuaron como agentes compatibilizantes debido a su localización en la interfase polimérica, formando una barrera sólida que previene la coalescencia de las gotas de caucho. En el caso de los nanocristales de celulosa, la localización del CNC y del PLA-g-CNC en la matriz de PLA resultó en una disminución del tamaño de las gotas de NR.
- Las medidas reológicas permitieron evaluar de forma rápida la dispersión de las nanocargas en la mezcla polimérica, considerando las interacciones partículapartícula y entre las partículas y los polímeros.
- El estudio de las propiedades mecánicas de los materiales constituyó una parte fundamental del trabajo de esta Tesis. El incremento de la ductilidad de la mezcla al incorporar la organoarcilla C15A nos llevó a analizar en profundidad el mecanismo de deformación de estos nanocompuestos mediante medidas *in-situ* de dispersión de rayos X por radiación sincrotrón. Se observó que la mezcla PLA/NR se deforma mediante la formación de vacíos en la interfase debido a la falta de compatibilidad entre ambas fases poliméricas. Sin embargo, la localización de las nanocargas en la interfase conduce a la formación de grietas que se propagan de forma estable durante la deformación del material. Por su parte, la adición de la organoarcilla C30B, preferentemente localizada en la interfase y en la fase de PLA, tiende a aumentar la tenacidad de la mezcla y disminuir la deformación a rotura del material. Se obtuvieron resultados interesantes con la adición de los nanocristales de celulosa, manteniéndose e incluso aumentándose ligeramente la deformación a rotura del material.

- El estudio de las propiedades mecano-dinámicas permitió determinar de forma concreta la afinidad de las nanocargas con los polímeros. La adición de C15A y C18-g-CNC a la mezcla produjo un aumento de la  $T_g$  del NR mientras que la de C30B, CNC y PLA-g-CNC provocó un aumento del modulo de almacenamiento, confirmando su afinidad por la fase continua.
- El comportamiento cristalino de los materiales dependió de la dispersión y localización de las nanocargas. En general, las cargas estudiadas inhibían el efecto nucleante de las gotas de NR, excepto la PLA-g-CNC que favorecía la cristalización del PLA.
- Los mejores resultados en términos de propiedades barrera se observaron para las nanocargas distribuidas homogéneamente en la fase continua. La modificación química de las cargas ayudó a esta distribución, como en el caso de la C30B. Además, se observó que es posible controlar la localización de las nanopartículas en la mezcla polimérica variando las condiciones del procesado.
- La degradación térmica de la mezcla se mejoró con la adición de los organosilicatos, mientras se redujo con los nanocristales de celulosa, debido a su baja estabilidad térmica.
- El estudio de la desintegración demostró que todos los materiales alcanzaron más de un 90 % de desintegración después de un mes en abono. La adición de nanocargas hidrofóbicas retrasó la degradación, sin afectar al porcentaje final de desintegración.
- Se puede concluir que en función del tipo y naturaleza química de la nanocarga, así como del método de procesado utilizado, es posible preparar materiales con propiedades "a medida".

## **FUTURE WORK**

This thesis studied in great detail the development of nanocomposites based on PLA/NR blend. Nevertheless, some of the properties of the materials, such as their permeability, could be the subject of a deeper analysis.

The permeability of the bionanocomposites based on cellulose nanocrystals should be evaluated. Also, the materials could be crystallised in order to evaluate the contribution of both the crystals and the nanofillers over the barrier properties. Moreover, further analysis would be needed in order to prove the possible application of these nanocomposites for food packaging. Especially, overall and specific migration testing could be carried out considering different stimulants usually employed for food contact materials, such as water, ethanol or vegetable oil.

Finally, the materials prepared during this work demonstrated interesting shape memory properties. Some experiments regarding this behaviour have been started. An intense study would be required to fully understand this behaviour and is undergoing. Nevertheless, some results are shown in this section to provide a clear overview of the ongoing work.

PLA has a theoretically shape-memory effect but difficult to observe due to its high brittleness. Nevertheless, Zhang *et al.*<sup>97</sup> reported this shape memory effect for PLA toughened by polyamide elastomer. The addition of 10 wt.-% of PAE led to an increase of elongation at break of up to 195 %. It appeared that the PAE domains acted as stress concentrators and led to energy-dissipation process, preventing PLA matrix from breaking at high deformation. Moreover, the authors observed that the samples stretched at 100 % of strain can recovered its original state and its mechanical properties when heated above the glass transition temperature of PLA at 60 °C.

The same shape memory effect was observed for the PLA/NR blend and nanocomposites. The samples stretched at 100 % of strain kept their temporary shape after removing the tensile load, due to the low flexibility of PLA at ambient temperature. Moreover, they recovered completely their original shape after 5 min at 65 °C (Figure a). In fact, the PLA chains recovered their randomly coiled state that represents the most probable state for an amorphous linear polymer chain when heating above its  $T_g$ .



Figure a. Samples stretched at 100 % and recovered (noted R) after 5 min at 65 °C (a) PLA/NR, (b) PLA/NR/C15A 1 wt.-% and (c) PLA/NR/C15A 3 wt.-%.

The shape memory effect can be quantified by cyclic investigation. The samples that recovered their initial shape after heating at 65 °C for 5 min were left at 25 °C for one hour and mechanically tested (named R). The comparison of the mechanical properties of the materials during the first and second stretch is reported in Table a.

	Young's	Tensile	Elongation at
	modulus, MPa	strength, MPa	break, %
PLA/NR	$2292 \pm 67$	$43.4 \pm 1.8$	$216 \pm 39$
PLA/NR R	$1844\pm35$	$31.2 \pm 1.2$	$48 \pm 11$
PLA/NR/C15A 1 wt%	$2269\pm53$	$40.6\pm0.5$	$242\pm19$
PLA/NR/C15A 1wt% R	$1588\pm33$	$27.0\pm0.4$	$163 \pm 26$
PLA/NR/C15A 3 wt%	$2185\pm65$	$34.8 \pm 1.7$	$95 \pm 17$
PLA/NR/C15A 3wt% R	$1510\pm65$	$25.0 \pm 1.1$	31 ± 11

Table a. Comparison of mechanical properties of the materials during the first and second stretch (deformation rate of 5 mm  $\cdot$ min<sup>-1</sup>).

It is observed that the mechanical properties of the samples are not completely recovered during the second stretching. The Young's modulus and tensile strength decrease for all samples. Moreover, the elongation at break of the PLA/NR blend dramatically decreases of up to 48 %. Interestingly, a high elongation was maintained for PLA/NR/C15A 1wt.-%.

The deformation mechanisms of the materials, such as debonding and crazing, were identified and described in *Chapter V*. Thus, the materials suffered from damages during stretching, as well as orientation of clays and orientation of polymer chains. During the recovery of their shape, the polymer chains and the clays could regain their initial isotropicity. However, some self-healing properties would be also desirable in order to eliminate the microvoids formed during the first stretching cycle. Different parameters should be considered for this study, such as the recuperation temperature or the stretching elongation before recovery and are under consideration.

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LIST OF PUBLICATIONS

To date, the following publications have been obtained from this thesis:

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- N. Bitinis, R. Verdejo, E. M. Maya, E. Espuche, P. Cassagnau and M. A. López-Manchado, Physicochemical Properties of Organoclay Filled Polylactic Acid/Natural Rubber Blend Bionanocomposites, *Composites Science and Technology*, 2012, 72, 305-313.
- N. Bitinis, A. Sanz, A. Nogales, R. Verdejo, M. A. López-Manchado, T. A. Ezquerra, Deformation Mechanisms in Polylactic Acid/Natural Rubber/Organoclay Bionanocomposites as Revealed by Synchrotron X-ray Scattering, *Soft Matter*, DOI:10.1039/c2sm25729G, 2012.

Other publications:

- R. Verdejo, M. Hernández, N. Bitinis, J. M. Kenny, M. A. López Manchado, Vulcanization Characteristics and Curing Kinetics of Rubber-Organoclay Nanocomposites, Chapter 9 in "Rubber-Clay Nanocomposites", ed. Maurizio Galimberti, John Wiley & Sons, 2011, ISBN: 978-0-470-56210-9.
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### Structure and properties of polylactide/natural rubber blends

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### ARTICLE INFO

### ABSTRACT

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Keywords: Biopolymers Immiscible blends Microstructure Polylactide, PLA, is a biodegradable thermoplastic polyester derived from biomass that has restricted packaging applications due to its high brittleness and poor crystallisation behaviour. Here, new formulations based on natural rubber-PLA blends have been developed. The processing windows, temperature, time, and rotor rate, and the rubber content have been optimised in order to obtain a blend with useful properties. The rubber phase was uniformly dispersed in the continuous PLA marks with a droplet size range from 1.1 to 2.0  $\mu$ m. The ductility of PLA has been significantly improved by blending 10 with natural rubber, NR. The elongation at break improved from 5% for neat PLA to 200% by adding 10 wt% NR. In addition, the incorporation of NR not only increased the crystallisation rate ulas on hanced the crystallisation ability of PLA. These materials are, therefore, very promising for industrial applications. © 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Recently, biodegradable polymers derived from natural resources have gained much interest as they can be an alternative to petroleum based polymeric materials as well as a solution to waste disposal problems. Thus, the development of such materials is a crucial issue in order to reduce the environmental impact of plastic production and waste.

One of these biomaterials is the polylactide (PLA). PLA is a biodegradable thermoplastic polyester derived from biomass such as sugar, corn, beet, which possesses excellent physical and mechanical properties (mbined with biocompatibility and biodegradability properties [1]. Due to its initial production costs, the starting applications of PLA have been focused on high value products such as medical devices [2]. On the other hand, PLA's potential for food packaging is very high due to its transparency, mechanical properties and acceptable moisture processability for dry food stuff [3–5]. Nevertheless, there are some drawbacks, such as its high brittleness and poor crystallisation behaviour that limit its current use in food packaging [6,7]. In order to overcome these limitations, the copolymerization of lactides with other monomers has been a widely used approach, but without any success for commercial application [8–10]. A less expensive and more practical strategy to overcome these drawbacks is the blending of PLA with other polymers. Hence, several synthetic

\* Corresponding author. Tel.: +34 912587424; fax: +34 915644853. E-mail address: Imanchado@ictp.csic.es (M.A. Lopez-Manchado). polymers, such as low density poly(ethylene) [11], poly(propylene glycol) and poly(ethylene glycol) [12,13], polymeric plasticizers [14,15], or biodegradable polymers such as polycaprolactone [16–18], poly(butylene succinate) [19], poly(butylenes adipate)co-terephtalate [20], and poly(ethylene succinate) [21] have been used. However, most of these blends are incompatible and compatibilisers are required in order to attain the desired properties. In addition, most of these polymers are not biocompatible which limits its applications.

On another hand, rubber matrices have commonly been used as a second phase polymer to improve the toughness of brittle thermoplastic materials. The rubber particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately result in a material with improved toughness. In order to impart toughness to polymers, several criteriamust be met: the rubber must be distributed as small domains in the polymer matrix, the rubber must have good interfacial adhesion to the polymer, the glass transition temperature of the rubber must be at least 20 °C lower than the use temperature, the molecular weight of the rubber must not be low, the rubber should not be miscible with the matrix polymer, and the rubber must be thermally stable in the polymer processing temperatures [22–24]. To date, however, the physical and mechanical properties of

To date, however, the physical and mechanical properties of PLA/rubber blends have received little attention and, to the best of our knowledge, natural rubber (NR) has never been used for toughening PLA [25–28]. Natural rubber is a renewable resource derived from a milky colloidal suspension or latex found in the sap of some plants. It exhibits a unique combination of toughness, flexibility, biocompatibility and biodegradability that together with its low

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## Views

Recent Advances in Clay/Polymer Nanocomposites

N. Bitinis, M. Hernandez, R. Verdejo, J. M. Kenny, and M. A. Lopez-Manchado\*

Smectite clays (e.g. montmorillonite), belonging to the structural family called 2:1 phyllosilicates, are the main choice for designing polymer nanocomposites due to their low cost and rich intercalation chemistry allowing them to be chemically modified (organoclays) and to improve the compatibility with the polymer matrix. These hybrid materials, normally called polymeric nanocomposites (PNC), represent a radical alternative to conventional polymer composites and have focused the attention of both academia and industry because of their unexpected properties, and their straightforward synthesis and processing. Such materials on the nanoscale level show significant improvements in mechanical properties, heat distortion temperatures, thermal stability, flame retardancy and enhanced barrier properties. The combination of enhanced properties, weight reduction, and low cost has led to interesting commercial applications such as automotive and packaging, among others. All this justifies the growing interest of both academia and industry in the development of these hybrid materials. In this paper we describe the most significant findings in the clay/polymer nanocomposites field considering three polymer families: elastomers, thermosets and polymers from natural resources or biopolymers.

### 1. Introduction

Composite materials represent one of the most active fields in the polymer industry. Many different types of fillers, carbon black, calcium carbonate, glass fibres and talc in the micrometer size range have been added to polymers to provide an improvement of the final product properties. However, this improvement is only achieved at high filler concentrations, which lead to an increase in the viscosity of the material and, hence, problems in processing. In recent years, it has been observed that the addition of just a small quantity of nano-sized layered silicates greatly improved the properties of virgin polymers without affecting their processability. Layered silicate clays have been found to be effective reinforcing fillers for polymers due to their lamellar structure and high aspect ratio of about 750 m<sup>2</sup>/g. Smectite clays (e.g. montmorillonite), belonging to the structural family called 2:1 phyllosilicates, are the main choice for designing polymer nanocomposites due to their low cost and rich intercalation chemistry allowing them to be chemically modified (organoclays) and to improve the compatibility with the polymer matrix. These hybrid materials, normally called

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polymeric nanocomposites (PNC), represent a radical alternative to conventional polymer composites and have focused the attention of both academia and industry because of their unexpected properties, and their straightforward synthesis and processing.<sup>[1]</sup> The ideal design of a nanocomposite involves individual silicate layers (1 nm thick) homogeneously dispersed in a continuous polymer. The uniform dispersion of nanoelements can lead to an ultra-large interfacial area between the constituents per volume of material. Thus, in PNCs with only a low volume percentage of dispersed nanoparticles, the entire polymer matrix may be considered to be a nanoscopically confined interfacial polymer. Such materials on the nanoscale level show significant improvements in mechanical properties, heat distortion temperatures, thermal stability, flame retardance and enhanced barrier properties. The combination of enhanced properties, weight reduc-

tion, and low cost has led to interesting commercial applications such as automotive and packaging, among others. All this justifies the growing interest of both academia and industry in the development of these hybrid materials.

We will now describe the most significant findings in the clay/polymer nanocomposites field considering three polymer families: elastomers, thermosets and from natural resources or biopolymers.

### 2. Elastomer Nanocomposites

Rubbers, or most specifically called elastomers, are one of the most important commercial polymers. They are formed by long chains with molecular weights of the order of  $1 \times 10^5$  g/mol crosslinked at many points along their length, producing 10–20 crosslinks per primary molecule, giving rise to the formation of a three-dimensional network structure. Their main characteristic is the ability to suffer considerable deformation under stress but upon release of the stress, the rubber article will go back to its original shape, recovering the energy stored during the deformation.

The elastomers are soft and weak materials with a low modulus and strength, so they usually require the inclusion of fillers in order to get a substantial improvement in the physical and mechanical properties of the compound. A wide range of fillers have traditionally been used in the rubber industry, being carbon black and silica the main fillers used in compounding recipes. However, a minimum of 20–30 wt% of conventional fillers is

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### Composites Science and Technology 72 (2012) 305-313



# Physicochemical properties of organoclay filled polylactic acid/natural rubber blend bionanocomposites

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ABSTRACT

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B. Interface B. Mechanical properties D. Transmission electron microscopy (TEM) A novel toughened polylactic acid (PLA) bionanocomposite with tuneable properties was successfully prepared by melt mixing PLA with natural rubber and several montmorillonites (MMTs). The organoclays were preferentially located at the interface acting as compatibilisers between both polymer phases. This location resulted in a marked improvement of the physical and mechanical properties of the system. Moreover, these properties can be controlled as a function of the nanofiller nature and the mixing procedure used.

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#### 1. Introduction

Keywords

Bionanocomposites A. Nanoclays

Polylactic acid (PLA) is a sustainable alternative to petrochemical-derived polymers, since it is produced from renewable re-sources, possesses excellent physical properties and is easily processed [1]. However, several drawbacks such as its brittle behaviour, slow crystallisation rate or low gas barrier properties have limited its applications until now. In our previous study, we demonstrated that blending PLA with Natural Rubber (NR) presents a practical strategy to toughen PLA [2]. The addition of natural rubber allows straightforward production of ductile PLA. The optimal NR content in the blend was found to be 10 wt.%; at this concentration the rubber improves the brittleness and favours the crystallisation ability of PLA. However, a lack of compatibility between the two polymers was observed. It is well known that the final properties of immiscible polymer blends are strongly influenced by both the size and interface of the dispersed phase and, hence, compatibilisers are often required in order to improve the morphology. While organic molecules and block copolymers are most commonly used, recent studies have introduced inorganic solid particles as a new type of compatibilisers [3,4]. In particular, layered silicates have been reported to improve the morphology of immiscible blends [5-7]. Moreover, the addition of nanoclays to

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the PLA/NR blend could also present a practical way to improve the gas barrier properties of the material.

Thus, our approach is to develop a novel and industrially scalable organoclay filled PLA/NR blend bionanocomposite prepared by melt blending. This study is aimed at understanding the influence of several nanofillers, presenting different surface properties and hydrophilicity on the properties of an immiscible PLA/NR blend [8]. The control of the nanofiller surface property and the mixing procedure could force the location of the clay in the blend. Thus, this location and the interactions of the nanoparticles with the blended polymers will determine the ultimate physicochemical properties of the nanocomposite. We carried out a thorough study based on both experimental and theoretical approaches to understand the best strategy to attain the desired properties. Here, we specifically focused on optimising the mechanical and barrier properties since they will benefit PLA bionanocomposite applications.

### 2. Experimental part

### 2.1. Materials and sample preparation

PLA polymer 2002D was provided by NatureWorks<sup>®</sup> (D-content 4.25%,  $\rho$  = 1.24 g/cm<sup>3</sup>). Natural Rubber (NR) was kindly supplied by Malaysian Rubber under the trade name CV60 (Mooney viscosity: ML(1 + 4) 100 °C = 60,  $\rho$  = 0.91 g/cm<sup>3</sup>). Three montmorillonites, one

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Deformation mechanisms in polylactic acid/natural rubber/organoclay bionanocomposites as revealed by synchrotron X-ray scattering

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The micromechanical deformation mechanisms of a polylactic acid (PLA)/natural rubber (NR) blend (PLA/NR 90/10 wt%) and its organoclay filled bionanocomposites have been investigated by small and wide angle X-ray scattering (SAXS-WAXS) under tensile conditions. The addition of NR to a PLA matrix changed the brittle fracture of PLA to a ductile deformation through the debonding of the rubber droplets. Otherwise, the formation of cavities between PLA and NR was hampered by the nanoclays since they were mainly located at the polymer blend interface. In this case, the nanoclays acted as craze nucleation sites. At 1 wt% of filler concentration, the crazes were able to fully develop in the blend and to evolve into stable microvoids, which kept growing and orienting in the tensile direction. These mechanisms also explained the progressive plastic deformation of the polymer chains and the preferential orientation of the nanoclay platelets.

### Introduction

Polylactic acid (PLA) is a linear aliphatic polyester that has found plenty of applications in a broad range of medical procedures, including drug delivery systems and tissue engineering, among others.1-3 However, polylactic acid presents a high brittleness and mechanical weakness, with a very low elongation at break and low impact resistance. Being both biodegradable and biocompatible, the improvement of the mechanical properties of polylactic acid by using different procedures, including blending with other natural or biodegradable polymers or mixing with nanoadditives, appears to be of great intrinsic interest.\*\*

Blending two polymers is a practical way to develop new polymeric materials that effectively combine the properties of the components.7,8 As an example, rubber matrices have commonly been used as a second polymeric phase to improve the toughness of brittle thermoplastic materials, receiving much attention from both academic and industrial areas. The properties of these blends strongly depend on the microscopic morphology which in turn determines the micromechanical deformation mechanisms, such as internal rubber cavitation, rubber droplet/matrix debonding, shear yielding or crazing, the latter being defined as microvoids bridged by small fibrils. $^{9-11}$ 

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Recently, it has been demonstrated that the nanoparticles behave as effective compatibilisers for immiscible polymers through their preferential location at the polymer interfaces, reducing the interfacial tension and preventing the coalescence of the dispersed phase.12-16 Moreover, Vo and Giannelis demonstrated that such ternary blends can be stiffer, stronger and also tougher than the binary blends suggesting a change in their deformation mechanisms.<sup>13</sup> Dasari et al. proposed an analysis of the micro- and nanoscale deformation behaviour for nylon 66/SEBS-g-MA/organoclay ternary nanocomposites using microscopy analysis of the fracture surface.17 However, microscopy analysis only provides snapshot information of the deformation mechanism with no real time monitoring and requires an extensive and laborious sample preparation after breaking. Deformation mechanisms can be investigated "in situ" by combining scattering techniques using synchrotron light with stress-strain experiments in a simultaneous fashion.16,19 This approach has already been used to study polymer blends and polymer nanocomposites since it enables linking the macroscopic deformation to the structural changes at both microscopic and mesoscopic levels.<sup>19-21</sup> However, to the best of our knowledge, no reports regarding nanoparticle filled polymer blends are found in the literature.

In our previous study, we demonstrated the production of ductile PLA through the addition of natural rubber (NR).22 Further improvements of these PLA/NR blends were obtained by developing new bionanocomposites. Bionanocomposites can be considered as a subset of polymer nanocomposites where the nanofillers, the matrix, or both, come from bio-based, renewable resources. In our case, a small amount of organoclays was added to a bio-based polymer blend, allowing a further increase of the

Soft Matter



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## Fluid dynamics of evolving foams<sup>†</sup>

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The physical properties of many multiphase systems are determined by coarsening phenomena. From raindrops to polycrystal grains and foams, the formation and stability of these systems continuously evolve towards lower-energy configurations through events such as coalescence, Ostwald ripening and drainage. Here we propose a procedure to identify and characterise key topological transformations of coarsening phenomena using a physically-based fluid dynamic framework. In situ, real-time foaming processes of a polymeric matrix reinforced with two morphologically different nanofillers, carbon nanotubes and graphene sheets were observed by synchrotron X-ray radioscopy. We obtained detailed information on the evolution of the growth patterns and coarsening events. Filled samples showed differences in both trend and speed compared with the unfilled sample. Furthermore, we found different dominating coarsening phenomena due to the wetting nature of carbon nanoparticles. Our procedure can be extended to sequences of any type of 2D projection or 3D images and to other multiphase systems.

### Introduction

Foaming is a complex process which involves the formation of gas bubbles in a fluid or the nucleation and evolution of both liquid and gas until stabilization occurs. This spatial and temporal evolution involves the interplay of several physical phenomena, such as surface tension, diffusion and viscosity, which is reflected in the dynamics of the liquid and gaseous phases and determines the final cellular microstructure of the system.

Despite the important influence that this cellular topology has on the properties of foams,2 the physics of the foaming phenomena, such as drainage and foam flow, are still unclear, even in the simplest case of the aqueous foams.3 The majority of current studies focusing on foam formation have been carried out on aqueous foams by light scattering techniques or AC conductivity.7 Ideally, the same basic theories should apply to aqueous and non-aqueous foams.8 However, recent studies of the foaming of metal foams involving synchrotron analyses have shown clear differences between aqueous and non-aqueous foams.<sup>9</sup> Banhart et al.<sup>9</sup> showed that drainage due to gravity had only a weak effect on the coarsening phenomena affecting metal foams, while interdependence was observed between drainage and coarsening in aqueous foams.3,10,11

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Here, we report a procedure based on a fluid dynamic framework to identify and characterise key topological transformations in reactive polymer foams. We studied a polymer foam produced by a reactive foaming process.<sup>12</sup> This process involves the simultaneous foaming and polymerization of liquid reactants, presenting a liquid-solid phase transition (see ESI, video S1<sup>†</sup>). The foaming is driven by a gas generated as a by-product of the polymerization reaction. This reaction has to be well controlled in order to balance the rates of both the evolution of the gas and the increase in viscosity:11 if not, the foam will collapse. One practical way in which to improve the stability of reactive foams is to increase the bulk viscosity of the reactants or the surface viscosity of the gas-liquid interface through a colloidal suspension of solid particles.8 These dispersed particles can also act as nucleation sites for bubbles in the early stages of the process and as functional fillers for the final foam.

We have recently studied the use of nanofillers as reinforcements, as they can be physically introduced into cell walls without disrupting the foam cellular microstructure.14,15 Electron microscopy of the foams confirmed that the nanofillers were completely embedded and homogeneously dispersed within the polymer matrix, but also showed a drastic change in the cellular microstructure: from isotropic interconnected open pores to highly anisotropic closed pores.

To better understand the foaming evolution and its dynamics, we carried out in situ foaming experiments using synchrotron radiation, because conventional X-ray sources do not provide the appropriate spatial and temporal resolutions. Synchrotron radiography (SR) has previously been used to study a broad range of physical and technological phenomena: from fuel injection in a running engine<sup>16</sup> to formation of granular jets17 and foaming of metal systems.9 For foaming studies and appropriate spatial sampling distances in the order of several µm, SR allows temporal sampling to be adjusted

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\* Electronic supplementary information (ESI) available: Movies: (S1)
foaming recorded by standard video camera; (S2) foaming recorded by
high resolution radiography. See DOI: 10.1039/b913262g

## **CHAPTER 9**

## VULCANIZATION CHARACTERISTICS AND CURING KINETIC OF RUBBER–ORGANOCLAY NANOCOMPOSITES

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### 9.1 INTRODUCTION

Unvulcanized raw rubbers are entangled high molecular weight viscoelastic liquids, generally not very strong, sticky, easily deformed when warm, brittle when cold, that do not maintain their shape after a large deformation. They are completely soluble in solvents, have a consistency similar to chewing gum and give rise to inelastic deformation being made of long polymeric chains that can move independently to each other. An uncured rubber cannot be used to make articles with a good level of elasticity.

The transformation to a useful rubber article such as tires and mechanical goods is due to the discovery of the vulcanization process by Goodyear [1]. In this process, physical and chemical cross-links are formed between the polymer chains giving rise to the formation of a three-dimensional network structure. The long rubber chains with molecular weight of the order of  $1 \times 10^5$  g/mol are cross-linked at many points along their length, producing 10–20 cross-links per primary molecule, so that the chains can no longer move independently. As a result, viscoelastic liquids are converted to viscoelastic solids with a high elasticity. They are prone to suffer considerable deformation under stress but upon release of the stress, the rubber article can go back to its original shape, recovering the energy stored during the

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<sup>271</sup> 

# RESUMEN

## I. INTRODUCCIÓN

En la actualidad, la posibilidad de sustituir los polímeros convencionales procedentes de hidrocarburos por materiales naturales, abundantes y biodegradables ha generado un enorme interés tanto a nivel industrial como académico.<sup>1, 2</sup> La producción de plásticos, fundamentalmente polietileno, polipropileno, policloruro de vinilo, poliestireno y polietilentereftalato, alcanzó en Europa 57 millones de toneladas en 2010, generando 10.4 millones de toneladas de residuos en vertederos (Figura I.1).<sup>3</sup>

Por este motivo, el desarrollo de materiales "ecológicos" representa una alternativa clave para, por un lado, minimizar el impacto de los plásticos sobre el medio ambiente y por otro, reducir el consumo de combustibles fósiles que tenderán a agotarse en un futuro próximo. Los polímeros producidos a partir de fuentes renovables, biodegradables y no tóxicos, denominados biopolímeros, son una solución especialmente deseable para productos de vida útil corta, debido a su posible degradación por microorganismos.<sup>4</sup> Además, puede emplearse un número elevado de biomacromoléculas presentes en la naturaleza para la preparación de estos biomateriales.<sup>5</sup>

Sin embargo, las propiedades de los biomateriales no se pueden equiparar a las de los termoplásticos convencionales, requiriendo modificaciones para mejorar su competitividad a escala industrial.



Figura I.1. Recuperación de los plásticos en Europa en 2010.<sup>3</sup>

Por otra parte, los nanocompuestos poliméricos han sido objeto de un enorme interés en el campo de la ciencia de los materiales y polímeros. Un nanocompuesto polimérico se define como un material híbrido basado en una matriz polimérica reforzada por fibras, láminas o partículas esféricas con al menos una dimensión a escala nanométrica. El diseño ideal de un nanocompuesto consiste en la dispersión homogénea de nanopartículas individuales en la matriz polimérica. En este caso, se obtendrá una elevada área interfacial por unidad de volumen entre los componentes, y con ello, una mejora importante de las propiedades a mínimas concentraciones de nanopartículas, a diferencia de los materiales compuestos convencionales que requieren altas concentraciones, superiores al 20 % en peso. Especialmente, se han demostrado mejoras significativas de las propiedades mecánicas, estabilidad térmica y propiedades barrera a gases combinadas con una reducción del peso final del material.<sup>6-8</sup>

Los bionanocompuestos son un caso particular de nanocompuestos donde la matriz, las nanocargas o ambos son derivados de fuentes renovables y/o biodegradables. Asimismo, la adición de nanocargas en una matriz biopolimérica, formando un bionanocompuesto, representa una forma práctica de mejorar las propiedades de estos bioplásticos para convertirlos en una alternativa comercial a los polímeros convencionales.<sup>9-11</sup>

De entre las diferentes familias de biopolímeros, los producidos mediante la síntesis química convencional a partir de monómeros procedentes de fuentes renovables son los que se encuentran en una fase de desarrollo más avanzada. Uno de los candidatos más prometedores y con un mayor potencial en la producción a gran escala es el ácido poliláctico, PLA, producido a partir de recursos renovables y biodegradables.<sup>12, 13</sup> Debido a los altos costes de producción iniciales, las primeras aplicaciones del PLA se destinaron a productos de alto valor añadido, tales como aplicaciones médicas.<sup>14</sup> Con el paso de los años, los costes de producción se han ido reduciendo considerablemente al intensificar su producción y al desarrollarse nuevos métodos capaces de producir PLA con alto peso molecular.<sup>15</sup>

El PLA es un biopoliéster alifático polimerizado a partir de monómeros del ácido láctico. Los monómeros se producen a partir de la fermentación de azúcares de maíz, caña de azúcar, remolacha, etc. El PLA exhibe excelentes propiedades para su utilización como plástico de alto consumo, como una alta transparencia o interesantes propiedades de biodegradabilidad o biocompatibilidad.<sup>12, 13, 16</sup> Todas estas características convierten al PLA en un candidato potencial para la fabricación de envases y otros bienes de consumo. Sin embargo, otras propiedades como su elevada fragilidad mecánica, su lenta cristalización o sus bajas propiedades barrera a gases, se han de mejorar para poder ampliar su uso.<sup>17</sup>

## II. OBJETIVOS DE LA TESIS

El objetivo general de esta Tesis doctoral se centra en mejorar las propiedades físicas y mecánicas del PLA para ampliar su rango de aplicaciones, sin deteriorar sus propiedades de biodegradación y biocompatibilidad. Para cumplir con este propósito, se han considerado diferentes aditivos para el desarrollo de nuevos bionanocompuestos de PLA.

El mezclado de dos polímeros presenta una forma práctica de desarrollar nuevos materiales poliméricos y de combinar de forma óptima las propiedades de los dos componentes. Asimismo, los elastómeros se han empleado para mejorar las propiedades mecánicas de termoplásticos y compensar su posible fragilidad, tanto en el campo académico como para aplicaciones industriales.<sup>18</sup> El caucho natural (NR) es un elastómero derivado de fuentes renovables a partir de una suspensión coloidal o látex encontrada en la corteza de algunos árboles.<sup>19</sup> Exhibe una combinación única de propiedades mecánicas y de bajo coste que lo convierte en el candidato ideal para corregir la alta fragilidad del PLA.

Sin embargo, es posible que se requiera de más aditivos para mejorar un mayor número de propiedades del PLA, por lo que el desarrollo de bionanocompuestos basados en mezclas de PLA/NR ha sido considerado. De este modo, dos tipos de nanocargas, silicatos laminares y nanocristales de celulosa, han sido seleccionadas, considerando sus propiedades particulares.

Los silicatos laminares son los nanoelementos inorgánicos más empleados para preparar nanocompuestos, debido a su estructura laminar y su alta relación de aspecto. Las arcillas esmécticas, como las montmorillonitas (MMT), pertenecen a la familia de los filosilicatos 2:1 y constituyen una elección adecuada debido a su bajo coste y sobre todo, a la posibilidad de modificarlas químicamente y mejorar su compatibilidad con la

matriz polimérica. Además, numerosas investigaciones han demostrado que las montmorillonitas mejoran eficientemente las propiedades mecánicas, térmicas y barrera de los bioplásticos y pueden generar un nanocompuesto de PLA con altas prestaciones.<sup>20, 21</sup>

La celulosa es uno de los biopolímeros más abundantes en la Tierra, de la cual se puede extraer nanocristales de alto módulo (CNC).<sup>22, 23</sup> Desde los trabajos pioneros de Favier *et al.*<sup>24</sup> en 1995, ha surgido un enorme interés académico e industrial en el desarrollo de bionanocompuestos poliméricos reforzados con nanocristales de celulosa. A diferencia de los silicatos laminares, estos nanocristales presentan la ventaja de ser renovables y biodegradables, lo que resulta de gran interés para este estudio.

A la vista de los aditivos elegidos para la matriz de PLA, se han definido los siguientes objetivos específicos:

- La optimización y el desarrollo de la mezcla PLA/NR para producir una mezcla de PLA dúctil.
- El desarrollo de bionanocompuestos PLA/NR/MMT y el estudio de la influencia de diferentes montmorillonitas modificadas sobre las propiedades de la mezcla optimizada de PLA/NR.
- La producción y modificación de nanocristales de celulosa para su incorporación a la mezcla polimérica.
- El desarrollo de bionanocompuestos PLA/NR/CNC y el estudio de la influencia de los nanocristales sobre las propiedades de la mezcla PLA/NR.

## III. PLAN DE LA TESIS

La Tesis se ha dividido en 8 capítulos: desde la producción de una mezcla dúctil de PLA/NR hasta el desarrollo de bionanocompuestos de PLA con propiedades óptimas.

El *Capítulo II* consiste en una revisión bibliográfica enfocada a las diferentes formas de mejorar las propiedades del PLA.

En el *Capítulo III* se han estudiado la estructura y las propiedades de la mezcla PLA/NR. Se han considerado las condiciones de procesado para optimizar la morfología de la mezcla y sus propiedades.

El *Capítulo IV* se ha dedicado al estudio de los bionanocompuestos PLA/NR/MMT y está enfocado a la relación entre la microestructura y las propiedades de los nanomateriales. La modificación química de las nanocargas tiene una importancia clave a la hora de incorporarlas a la mezcla polimérica, determinando su afinidad con los dos polímeros y su localización en la mezcla. Asimismo, se emplearon diferentes tipos de organosilicatos comerciales (CNa<sup>+</sup>, C15A and C30B), elegidos según su afinidad con los polímeros.

A la vista de los resultados obtenidos en el *Capítulo IV*, se ha realizado un estudio más detallado de las propiedades mecánicas de los nanocompuestos basados en una montmorillonita específica, la C15A. De esta manera, el *Capítulo V* consiste en el estudio de los mecanismos de deformación del nanocompuesto PLA/NR/C15A mediante medidas *in-situ* de dispersión de rayos-X por radiación sincrotrón.

El *Capítulo VI* reporta la extracción y la modificación superficial de los nanocristales de celulosa mediante reacciones de injerto. La primera reacción estudiada consistió en el injerto de cadenas largas de carbono (C18-g-CNC), a través de la reacción de los grupos hidroxilos de la celulosa con n-octadecilisocianato. También se injertaron cadenas de PLA mediante polimerización con apertura de anillo (PLA-g-CNC). Estas dos reacciones tuvieron como propósito una mejora de la compatibilidad con la fase NR y PLA, respectivamente.

El *Capítulo VII* está dedicado al estudio de los nanocompuestos PLA/NR/CNC y a sus propiedades.

Las conclusiones generales de la Tesis se presentan en el Capítulo VIII.

## IV. CONCLUSIONES Y APORTACIONES FUNDAMENTALES

De los resultados obtenidos durante el estudio, se pueden extraer las siguientes conclusiones y destacar las aportaciones fundamentales de esta Tesis doctoral:

 La adición de caucho natural permitió la producción de una mezcla dúctil, empleando un método de procesado en fundido. Una concentración de NR de 10 % en peso se definió como óptima para mejorar la fragilidad del PLA. A esta concentración, se observó la formación de gotas de NR de un tamaño medio de 1 µm homogéneamente distribuidas en la matriz de PLA, proporcionando un balance óptimo de las propiedades físicas y mecánicas del material, sin sacrificar totalmente la transparencia del material. Las propiedades a tracción de la mezcla mostraron un incremento drástico de la deformación a rotura. Adicionalmente, se observó que el NR actuaba como agente nucleante para la matriz de PLA. Asimismo, el mezclado en fundido de PLA/NR representa una forma simple, rápida, económica y escalable a producción industrial para solucionar dos de las principales limitaciones de PLA, su elevada fragilidad y su lenta cristalización.

- La adición de la nanocargas tuvo una profunda influencia sobre la morfología de la mezcla, especialmente en el caso de los organosilicatos. C15A y C30B actuaron como agentes compatibilizantes debido a su localización en la interfase polimérica, formando una barrera sólida que previene la coalescencia de las gotas de caucho. En el caso de los nanocristales de celulosa, la localización del CNC y del PLA-g-CNC en la matriz de PLA resultó en una disminución del tamaño de las gotas de NR.
- El estudio de las propiedades mecánicas de los materiales constituyó una parte fundamental del trabajo de esta Tesis. El incremento de la ductilidad de la mezcla al incorporar la organoarcilla C15A nos llevó a analizar en profundidad el mecanismo de deformación de estos nanocompuestos mediante medidas *in-situ* de dispersión de rayos X por radiación sincrotrón. Se observó que la mezcla PLA/NR se deforma mediante la formación de vacíos en la interfase debido a la falta de compatibilidad entre ambas fases poliméricas. Sin embargo, la localización de las nanocargas en la interfase conduce a la formación de grietas que se propagan de forma estable durante la deformación del material. De forma más general, el mecanismo de deformación propuesto en este estudio se podría aplicar a otros sistemas de polímeros inmiscibles compatibilizados por nanocargas, explicando los aumentos de tenacidad o ductilidad observados en sistemas similares.

Por su parte, la adición de la organoarcilla C30B, preferentemente localizada en la interfase y en la fase de PLA, tiende a aumentar la tenacidad de la mezcla y disminuir la deformación a rotura del material. Se obtuvieron resultados

interesantes con la adición de los nanocristales de celulosa, manteniéndose e incluso aumentándose ligeramente la deformación a rotura del material.

- El estudio de las propiedades mecano-dinámicas permitió determinar de forma concreta la afinidad de las nanocargas con los polímeros. La adición de C15A y C18-g-CNC a la mezcla produjo un aumento de la  $T_g$  del NR mientras que la de C30B, CNC y PLA-g-CNC provocó un aumento del modulo de almacenamiento, confirmando su afinidad por la fase continua.
- El comportamiento cristalino de los materiales dependió de la dispersión y localización de las nanocargas. En general, las cargas estudiadas inhibían el efecto nucleante de las gotas de NR, excepto la PLA-g-CNC que favorecía la cristalización del PLA.
- Los mejores resultados en términos de propiedades barrera se observaron para las nanocargas distribuidas homogéneamente en la fase continua. La modificación química de las cargas ayudó a esta distribución, como en el caso de la C30B. Además, se observó que es posible controlar la localización de las nanopartículas en la mezcla polimérica variando las condiciones del procesado.
- La degradación térmica de la mezcla se mejoró con la adición de los organosilicatos, mientras se redujo con los nanocristales de celulosa, debido a su baja estabilidad térmica.
- El estudio de la desintegración demostró que todos los materiales alcanzaron más de un 90 % de desintegración después de un mes en abono. La adición de nanocargas hidrofóbicas retrasó la degradación, sin afectar al porcentaje final de desintegración.
- Se puede concluir que en función del tipo y naturaleza química de la nanocarga, así como del método de procesado utilizado, es posible preparar materiales con propiedades "a medida".

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