

Supporting Information

Strengthening Eco-Friendly Packaging from Pectin by Filling with Poly(ϵ -caprolactone) Nanoparticles and Tailoring the Degree of Methyl-Esterification

Names of authors:

Marcos Vinicius Lorevice^{a,b,1,*}; Graziela Solferini Baccarin^{a,b}; Juliana R. Souza^{a,b}; Pedro Ivo Cunha Claro^{b,c}; Márcia Regina de Moura^d; Caio Gomide Otoni^{c,*}; Luiz Henrique Capparelli Mattoso^{a,d}

Author affiliations:

^aPPGQ, Department of Chemistry, Federal University of São Carlos – Rodovia Washington Luís km 235, São Carlos, SP 13566-905, Brazil (Lorevice: marcos.lorevice@lnnano.cnpem.br; Baccarin: gsbaccarin@estudante.ufscar.br; juhregline@gmail.com)

^bNational Nanotechnology Laboratory for Agriculture (LNNA), Embrapa Instrumentation – Rua XV de Novembro 1452, São Carlos, SP 13560-970, Brazil. (Mattoso: luiz.mattoso@embrapa.br)

^cPPG-CEM, Department of Materials Engineering, Federal University of São Carlos – Rodovia Washington Luís km 235, São Carlos, SP 13566-905, Brazil (Otoni: caio.otoni@ufscar.br; Claro: pedrocunhaclaro@ymail.com)

^dDepartment of Physics and Chemistry, FEIS, São Paulo State University – Av. Brasil 56, Ilha Solteira, SP 15385-000, Brazil (de Moura: marcia.aouada@unesp.br)

*Corresponding Authors:

Caio Gomide Otoni
caio.otoni@ufscar.br

^cPPG-CEM, Department of Materials Engineering, Federal University of São Carlos – Rodovia Washington Luís km 235, São Carlos, SP 13566-905, Brazil

Marcos Vinicius Lorevice
marcos.lorevice@lnnano.cnpem.br

Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, São Paulo, Brazil

¹Present address: *Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970 Campinas, São Paulo, Brazil*

A. Complementary Dynamic Light Scattering Data

Table S1: Average size, PDI, and zeta potential of poly(ϵ -caprolactone) nanoparticles in three repetitions of the same synthesis protocol.

Repetition	Size (nm)	Polydispersity index	Zeta potential (mV)
1	144 ± 7^b	0.13 ± 0.01^a	-18 ± 1^a
2	126 ± 6^{ab}	0.12 ± 0.02^a	-17.1 ± 0.5^a
3	124 ± 2^a	0.10 ± 0.01^a	-17.2 ± 0.5^a

^{ab} Mean values \pm standard deviations followed by the same lowercase superscript letters within a column are not different ($p > 0.05$).

B. Complementary FT-IR analysis

Table S2: Infrared spectroscopy of poly(ϵ -caprolactone) (PCL), Tween 80, and poly(ϵ -caprolactone) nanoparticles (PCLNP).

PCL (cm ⁻¹)	Tween 80 (cm ⁻¹)	PCLNP (cm ⁻¹)	Vibration
-	3489	3431	(-OH)
2954	2923	2932	(C-H) asymmetrical
2862	2860	2866	(C-H) symmetrical
1729	1735	1725	(-C=O)
1235	1249	1240	(-C-O-C-) asymmetrical
1163	1102	1173	(-C-O-C-) symmetrical

C. Complementary spectroscopy analysis

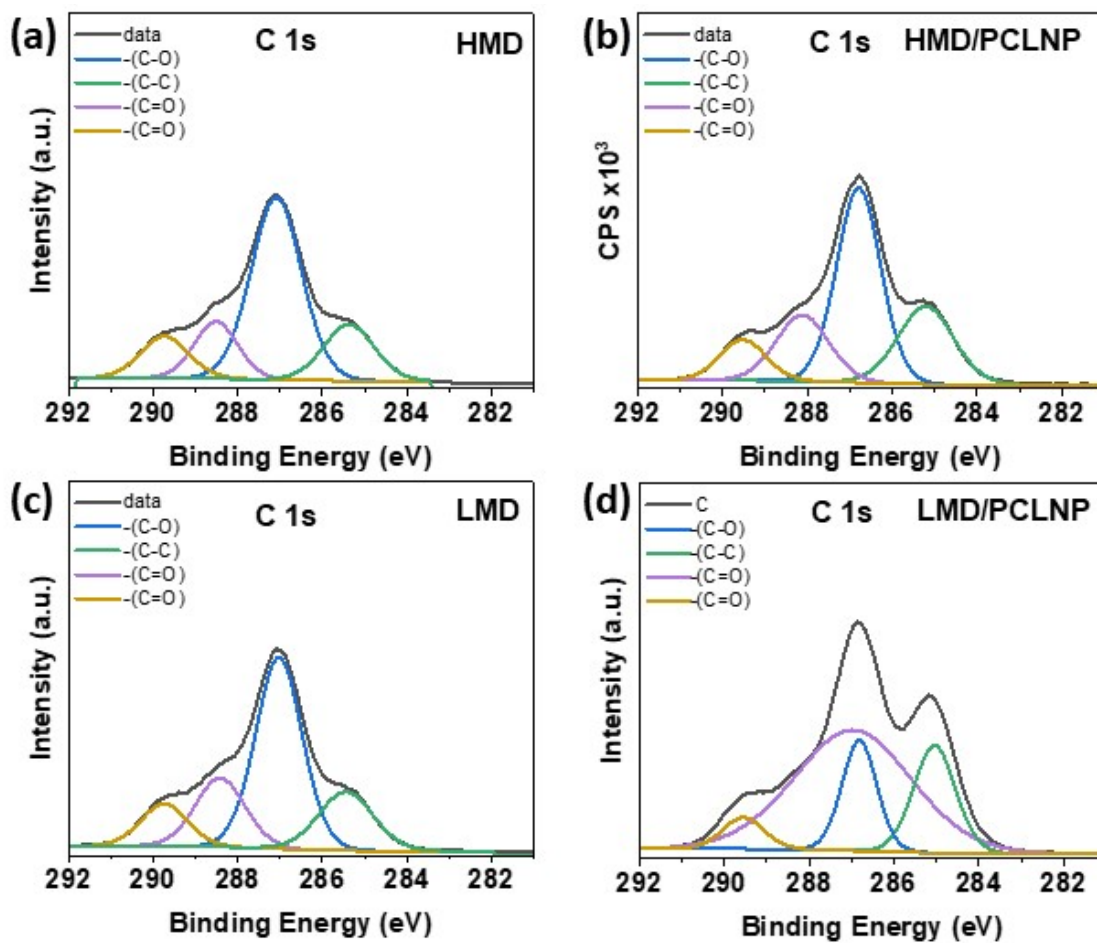


Figure S1. High-resolution XPS spectra of C1s for (a) HMD, (b) HMD/PCLNP, (c) LMD, and (d) LMD/PCLNP pectin-based films.

Table S3: Binding energy of pectin-based nanocomposites determined by C1s XPS deconvolution.

Samples	Peak Binding Energy (eV)			
	C-C/C-H	C-O	O-C-O/C-O-H	O-C=O
HMD	285.4	287.0	288.4	289.7
LMD	285.4	287.0	288.4	289.7
HMD/PCLNP film	285.3	286.9	288.2	289.6
LMD/PCLNP film	285.1	287.1	286.8	289.6

Table S4: Surface composition of pectin-based nanocomposites determined by C1s XPS deconvolution.

Samples	C1s XPS deconvolution (%)			
	C-C/C-H	C-O	O-C-O/C-O-H	O-C=O
HMD	14.3 ± 3	56.0 ± 1	16.9 ± 1	12.8 ± 1
LMD	16.0 ± 2	51.9 ± 1	20.1 ± 1	12.0 ± 1
HMD/PCLNP film	23.2 ± 1	47.1 ± 1	19.3 ± 1	10.4 ± 1
LMD/PCLNP film	15.7 ± 1	59.5 ± 1	19.0 ± 3	5.8 ± 1

D. Complementary mechanical analysis

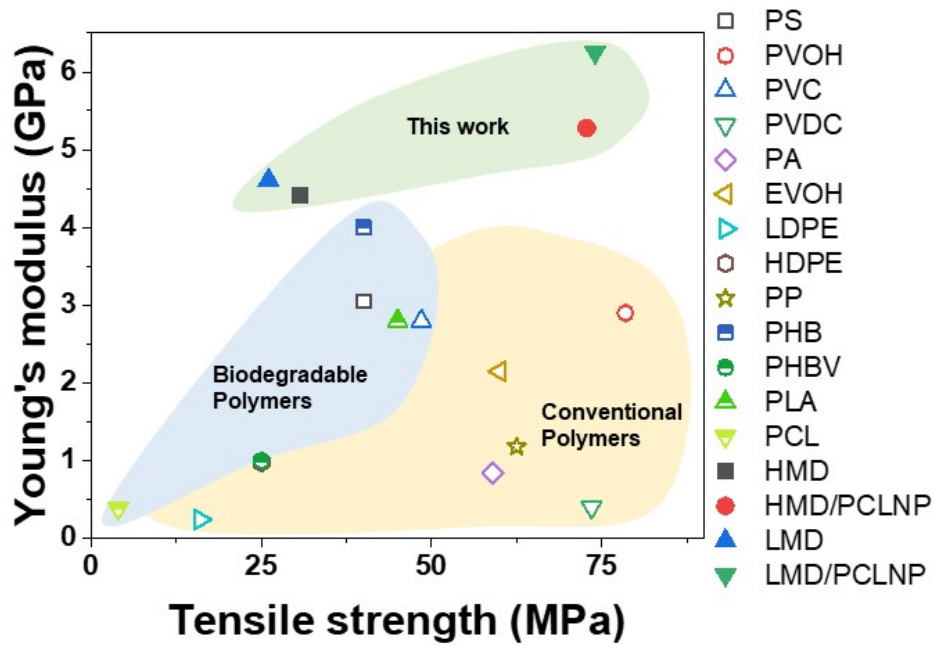


Figure S2. Young's modulus vs. Tensile strength for petroleum-based polymeric and nanocomposites films. The polymer acronyms meaning from up to bottom are: PS – *polystyrene*; PVOH - *polyvinyl alcohol*; PVC - *polyvinylchloride*; PVDC - *poly(vinylidene chloride)*; PA - *Polyamide (nylon)*; EVOH - *ethylene–vinyl alcohol copolymer*; LDPE - *low-density polyethylene*; HDPE - *high-density polyethylene*; PP – *polypropylene*; PHB - *Poly 3-hydroxybutyrate*; PHBV - *Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)*; ; PLA - *poly(lactic acid)*; PCL - *poly(ϵ -caprolactone)*; HMD - *high-methoxyl-degree of pectin*; LMD - *low-methoxyl-degree of pectin*. The highlighted areas in blue, yellow and green have no physical meaning. They indicate, respectively, the biodegradable, conventional and the nanocomposites-BASED polymers compared. Data adapted from ^{1,2}.

E. References

- 1 L. Bastarrachea, S. Dhawan and S. S. Sablani. *Food Engineering Reviews*. 2011. 3. 79–93.
- 2 R. A. Gross and B. Kalra. *AIChE (Am. Inst. Chem. Eng.) J.* 2002. **297**. 803–807.