Electronic Supporting Information for

Bioplastics from vegetable waste via an eco-friendly water-based

process.

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Experimental

<u>Thermal properties</u>: Thermal gravimetric analysis (TGA) was done with a Q500 TGA (TA Instruments). Measurements were performed on 15 - 30 mg samples, under inert (N_2) atmosphere with a flow rate of 50 mL/min. The temperature range that was investigated was from 30 to 600°C, using a heating rate of 5°C/min. The weight loss and its first derivative were recorded simultaneously as a function of time/temperature.

<u>FTIR characterization</u>: Infrared spectra were measured in Attenuated Total Reflectance (ATR) configuration coupling a MIRacle ATR (PIKE Technologies) to a Fourier Transform Infrared (FTIR) spectrometer (Equinox 70 FT-IR, Bruker). All spectra were recorded in the range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹, accumulating 64 scans.

Bioplastic composition: the evaluation of the bioplastic composition was performed using the ¹³C CPMAS NMR spectra reported in Figure S5. Since many of the signals are an overlap of different contributions, the spectra have been deconvoluted applying a line fitting routine. The assignments of the peaks are done in accordance with Komatsu et al¹ and Simmons et al² for hemicellulose and with Sinitsya et al³ for pectin. To obtain a tentative estimation of films' composition, some assumptions were used: 1) pectin is approximated as polygalacturonic acid; 2) the amount of O-COCH₃ groups is given by the intensity of the signal at 23.6 ppm; 3) the aliphatic polyesters are approximated as polyaleurate (poly 9,10,16 tryhydroxydecanoic acid); 4) the hemicellulose is approximated as 50:50 mixture of C6 and C5 sugars. The consistency of this method was confirmed using a film with known amount of MCC, pectin, sugar similar to the one shown in Figure 5.

Food contact migration: to characterize the possible migration of molecules from the bioplastics to the food, Tenax[®] was used as a food simulant. Tenax[®] was cleaned before the experiment following a previously published protocol.^{4, 5} The characterization of the overall migration was done following the EU *Technical guidelines for compliance testing in the framework of the plastic FCM Regulation (EU) No*

10/2011. Briefly, for all bioplastics a round sample of 2.5 cm in diameter was cut from a bioplastic film, the sample was put in a clean glass dish with 80 mg of Tenax[®] (40 mg below and 40 mg above the sample), as a control sample 80 mg of Tenax[®] with no bioplastic were used. The *OM3* condition of the technical guidelines was followed for the thermal treatment: the samples were stored in the oven for 2 hours at 70 °C. The overall migration was obtained by calculating the mass difference of Tenax[®] before and after the treatment. The mass of the materials was measured using a scale with 0.01 mg precision and the test was run in triplicate times for each bioplastic.



Figure S1: SEM images of the bioplastic films obtained with our fabrication protocol. A) carrot bioplastic, B) parsley bioplastic, C) radicchio bioplastic, D) Cauliflower bioplastic. The bioplastics seem to be made of a matrix in which fibrous-like and powder-like particles are dispersed.

Sample	Young Modulus (MPa)	Elongation at break (mm/mm)	UTS (MPa)
Carrot	1300 ± 200	0.058 ± 0.008	38 ± 5
Parsley	180 ± 50	0.10 ±0.02	8.0 ± 0.4
Radicchio	230 ± 40	0.05 ±0.01	4.4 ± 0.4
Cauliflower	470 ± 80	0.04 ± 0.01	10.0 ± 0.9

Table S1: Summary of the mechanical properties of vegetables-derived bioplastic films.



Figure S2: comparison of the mechanical properties of bioplastics films obtained with the water-based HCl hydrolysis described in the present paper (label HCl) and the with the TFA-process described by Bayer et al⁶ (label TFA).

Sample	Young Modulus (MPa)	Tensile Strain at maximum Load (mm/mm)	Tensile stress at Maximum Load (MPa)
Carrot – no dialysis	300 ± 150	0.15 ± 0.05	9.5 ± 3.5
Carrot – dialysis	1300 ± 200	0.058 ± 0.008	38 ± 5

Table S2: comparison between carrot bioplastic films obtained with or without the dialysis step.



Figure S3: Thermal gravimetric analysis of the vegetable waste powder and the bioplastic films obtained with our conversion process. A) carrot, B) parsley, C) radicchio, D) cauliflower. The bioplastic films showed a degradation similar to the original waste powder. In all cases but radicchio films, the onset of the degradation was shifted at higher temperatures few tens of degrees.



Figure S4: FTIR spectra of the bioplastic films obtained with our fabrication protocol and the original waste powder as obtained. A) carrot, B) parsley, C) radicchio, D) cauliflower. The bioplastic films showed spectra that are very similar to the ones of the original waste powders.



Figure S5: Films obtained by casting A) MCC, pectin, sugar, salts and B) pure MCC after processing using the conversion protocol used for vegetable bioplastics.



Figure S6: mechanical properties of the MCC-pectin-sugar-salt sample and the carrot bioplastic.

Sample	Young Modulus (MPa)	Tensile Strain at maximum Load (mm/mm)	Tensile stress at Maximum Load (MPa)
Carrot	1300 ± 200	0.058 ± 0.008	38 ± 5
MCC	-	-	-
MCC-pectin-sugar	2200 ± 100	0.01 ±0.003	14 ± 1

 Table S3:
 Summary of the mechanical properties of MCC-pectin-sugar-salts sample and the carrot bioplastic



Figure S7: ¹³C CPMAS NMR spectra of the bioplastics films obtained for the four different vegetables: carrot, parsley, radicchio and cauliflower.



Figure S8: water contact angle on a MCC film similar to the one shown in Figure S4B. The water contact angle was of 127 °, showing a strong hydrophobic behaviour.

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