Electronic Supplementary Material (ESI) for Green Chemistry.

Direct transformation of industrial vegetable waste into bioplastic composites intended for agricultural mulch films

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SUPPORTING INFORMATION

SI.1 Procedure for CP-MAS analysis

Spectral fitting routines for bioplastics materials have been established based on assignments reported in literature, however in some cases resonance positions cited in the literature may vary significantly from ours, due to different chemical shift referencing. It is reasonable to assume that the linewidths of the various resonances should be quite similar. In fact, considering that spin-diffusion is effective in strongly coupled systems, for a single-phase carbohydrates material a single T_2 value can be envisaged. The absence of very mobile systems, as confirmed by HPDEC, makes the assumption of very similar linewidths even more reasonable. On the other hand, inhomogeneous broadening of the resonances ca be caused by small variation of chemical environment of the same entity in complex systems, (i.e., the carboxylic groups of pectin can interact with other pectin chains but can also be quite close to cellulose chains in specific zone of the sample). Thus, we decided not to use Lorentzian lines for the fitting but a mixed lorentzian/gaussian (1:1) line-shape with full width at half maximum (FWHM) from 300 to 600 Hz. Applying this approach all the spectra have been full deconvoluted and the calculated spectrum was compared with the experimental one. In **Fig. S.1** an example of deconvolution is report for the spinach stems. The grey line represent the simulated spectrum built with the calculated resonances, the Chemical shifts and intensities of all the peaks are reported in **Table S.1**.

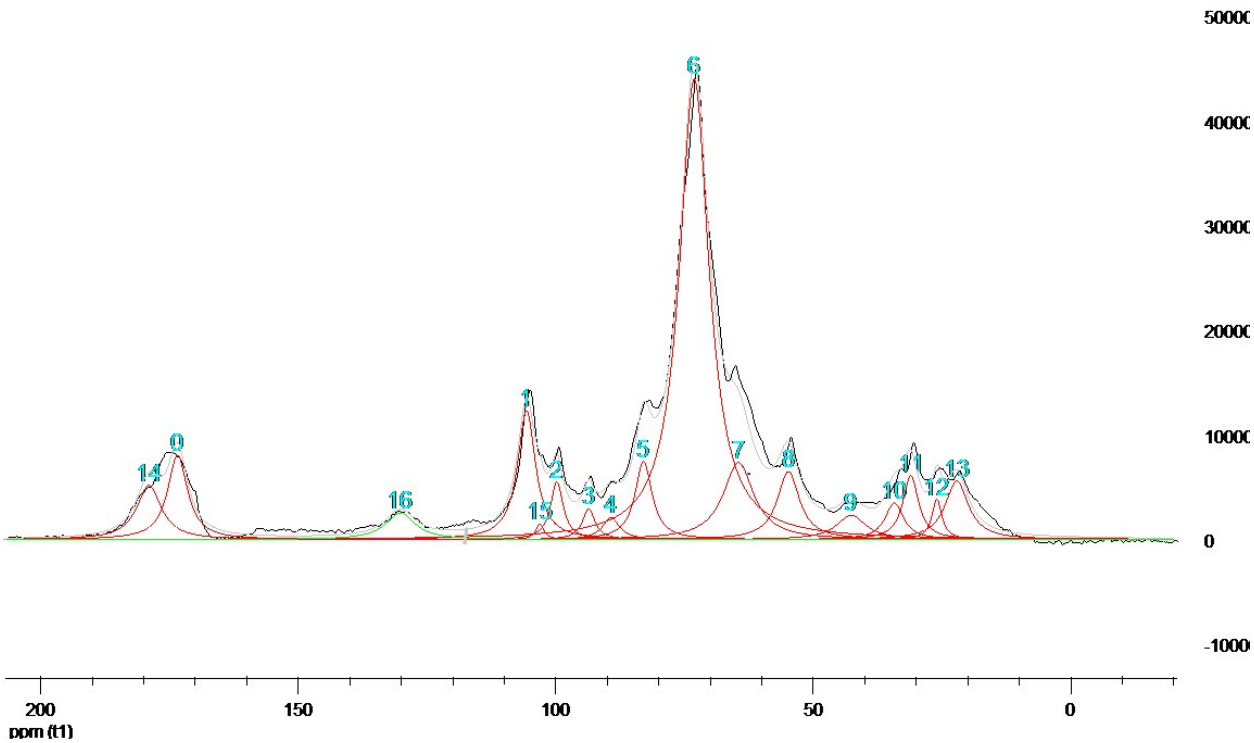

Fig. S.1 ^{13}C CPMAS NMR Spectrum of Spinach Stems (black line) together with the calculate spectrum (grey line) and deconvoluted resonance (red lines).

Table S.1 Chemical Shifts assignments and relative intensities.

	Spinach Stems	
	C.S. (ppm)	Intensity
O-*C*OCH$_3$ **R-*C*OO-R'** **Pectin COO$^-$**	176.1	0.07
Pectin COOH **Pectin *C*OOCH$_3$**	173.27	0.08
C$_1$ Cellulose	105.65	0.17
C$_1$ Hemicellulose (xylan)	103.06	0.01
C$_1$ Pectin	99.76	0.05
C$_4$ Crystalline cellulose	89.26	0.03
C$_4$ Amorphous cellulose **C$_4$ Pectin**	82.9	0.10
C$_{2,3,5}$ Cellulose **C$_{2,3,5}$ Hemicellulose (xyloglucan)** **C $_{2,3,4}$ hemicellulose (xylan)** **C$_{2,3,5}$ pectin**	73.09	1
C$_6$ Cellulose **C$_6$ Hemicellulose (xyloglucan)** **C$_5$ Hemicellulose (xilose)**	64.5	0.17
COO*C*H$_3$ pectin	54.8	0.05
CH$_2$ aliphatic polyester	34.2 31.1 25.9	0.15 0.09 0.05 0.1
O-CO*C*H$_3$	25.9	0.03
CH$_3$	22.1	0.10

The calculation of the composition of the samples has been carried out identifying all the signals univocally due to a single component (as an example the crystalline C1 of cellulose around 105 ppm) and applying simple necessary stoichiometric rules for the mixed signals. The signal at 176.1 ppm that can be generated by the COO- group of pectin but also by an acetate group and the carboxylic group of polyesters. However, the acetate group has also a signal at 25.9 ppm, its methyl group, thus we can subtract the same intensity of this signal to the signal at 176. 1 ppm and we remove the contribution of the acetate. To remove the contribution of polyesters we do the same calculation once identified a pure polyester peak. Since hemicellulose has just one resonance univocally assigned, the anomeric peak 103 ppm, its quantification is more prone to large variations, due to fact in the fitting routine, for the samples studied, the signal was always overlapped with cellulose C1 and pectin C1.

Uncertainty on composition is around 2%; i. e. 15% of polyester in spinach stems should be read as 15 ± 1 %.

SI.2 XRD analysis.

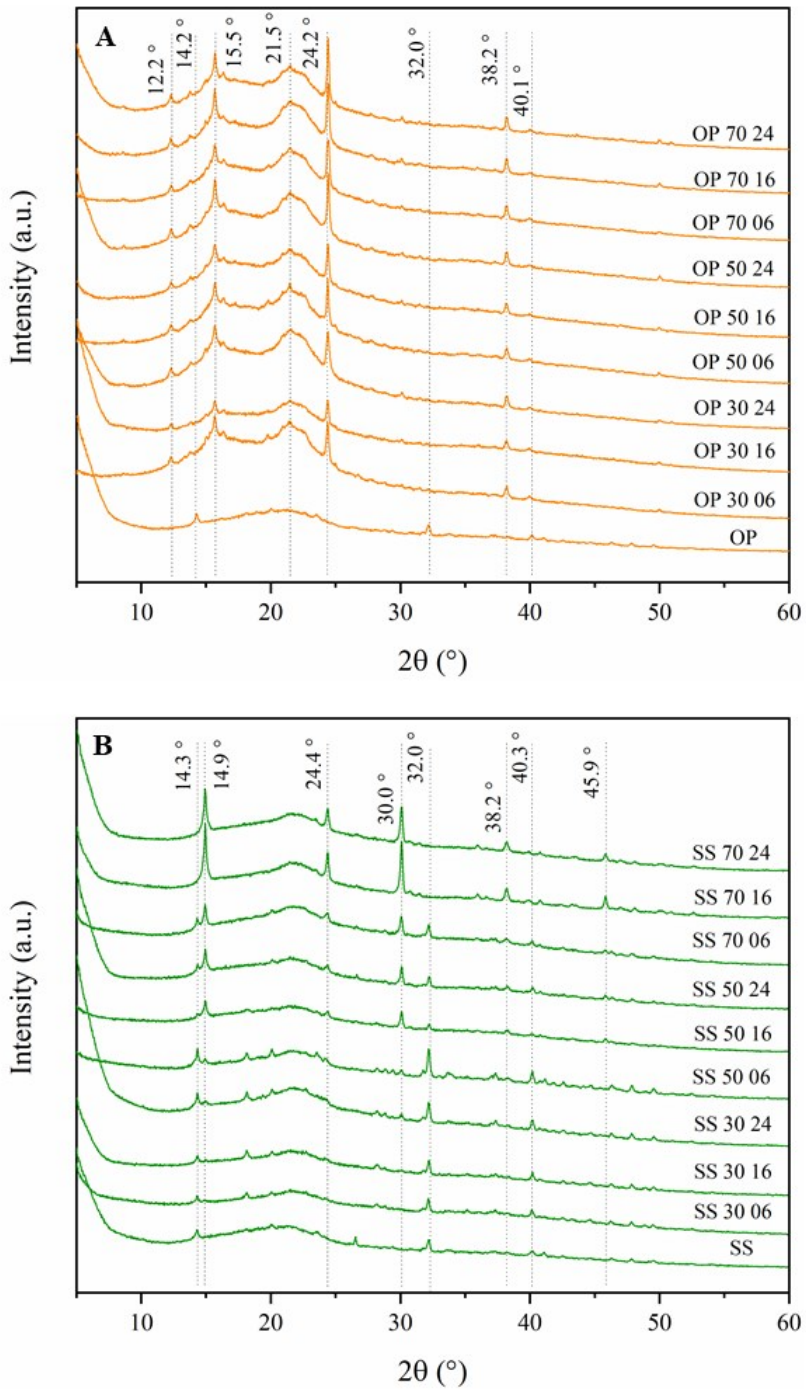

Fig. S.2 X-Ray diffraction patterns of **A**: OP powder and OP-based films obtained in different hydrolytic conditions and, **B**: SS powder and SS-based films also obtained in different hydrolytic conditions.

SI.3 ATR-FTIR spectra.

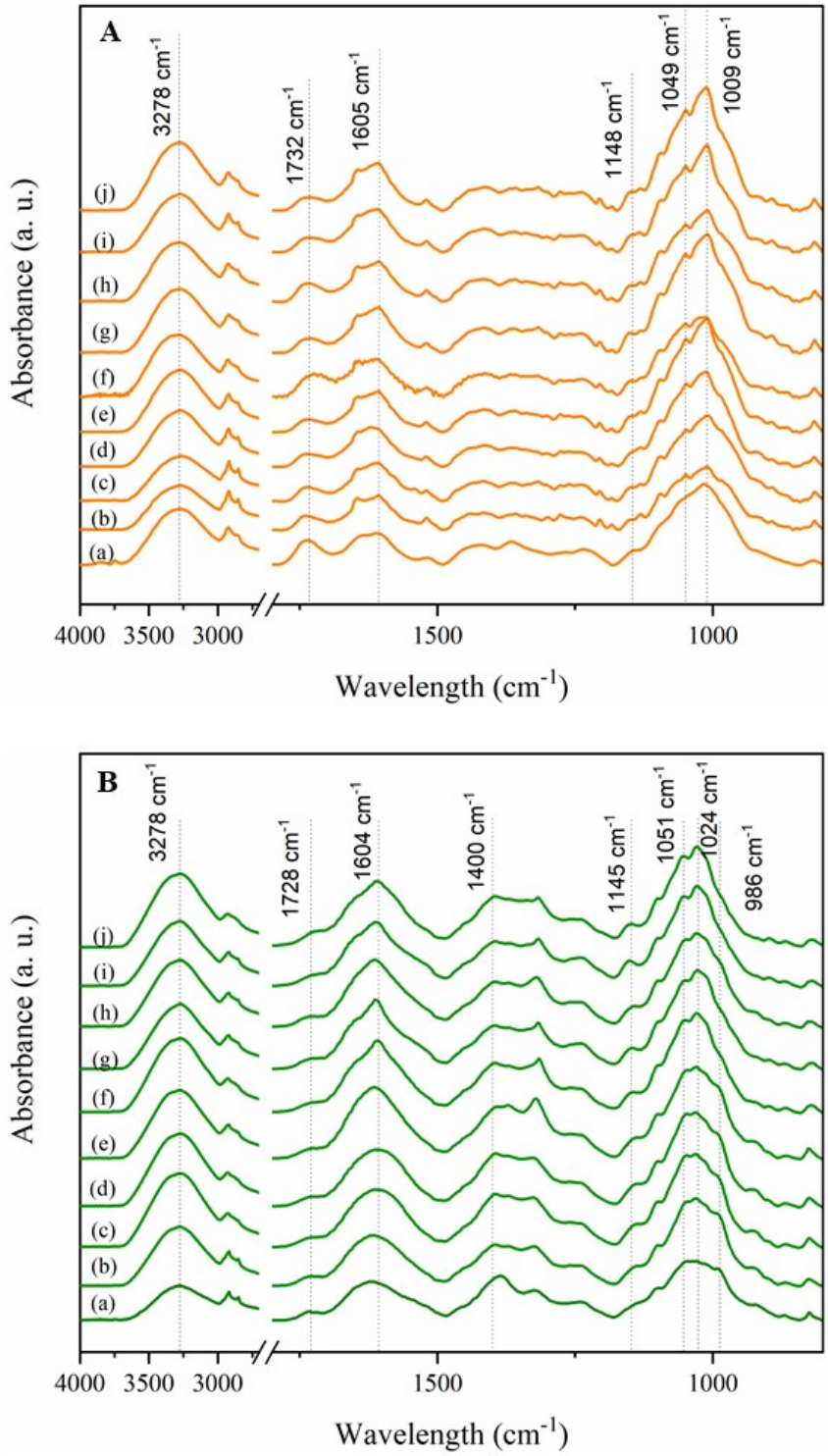

Fig. S.3 ATR-FTIR spectra. **A**: OP (a) and OP-based bioplastics: (b) OP 30 06, (c) OP 30 16, (d) OP 30 24, (e) OP 50 06, (f) OP 50 16, (g) OP 50 24, (h) OP 70 06, (i) OP 70 16, (j) OP 70 24. **B**: SS (a) and SS-based plastics: (b) SS 30 06, (c) SS 30 16, (d) SS 30 24, (e) SS 50 06, (f) SS 50 16, (g) SS 50 24, (h) SS 70 06, (i) SS 70 16, and (j) SS 70 24.

SI.4 DTGA curves of vegetable cell wall polymers

Materials: High-purity microcrystalline cellulose (MCC) from cotton linter pulp, lignin (alkali, with low sulfonate content) from the Kraft pulping process, and Pectin from citrus peel (83 wt. % galacturonic acid units and 7.7 wt. % methoxyl groups) were acquired from Sigma-Aldrich. Xylan (from corn core, product number X0078, 75.0% minimum xylose content) was purchased from TCI Europe.

Results:

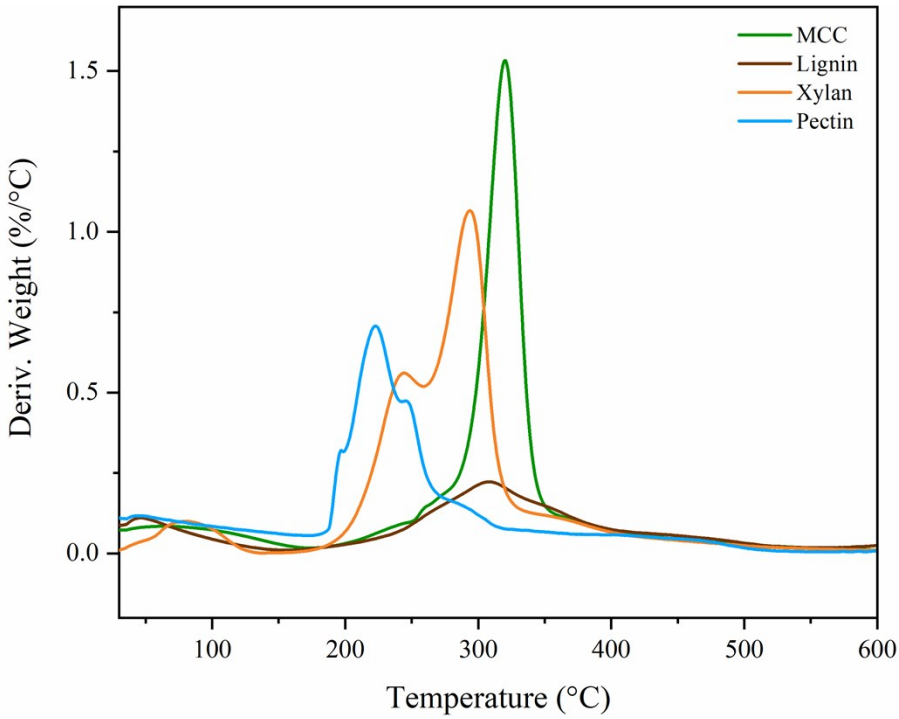

Fig. S.4 DTGA curves of commercial MCC, Lignin, Xylan and Pectin.

SI.5 Optical properties of OP and SS-based bioplastics

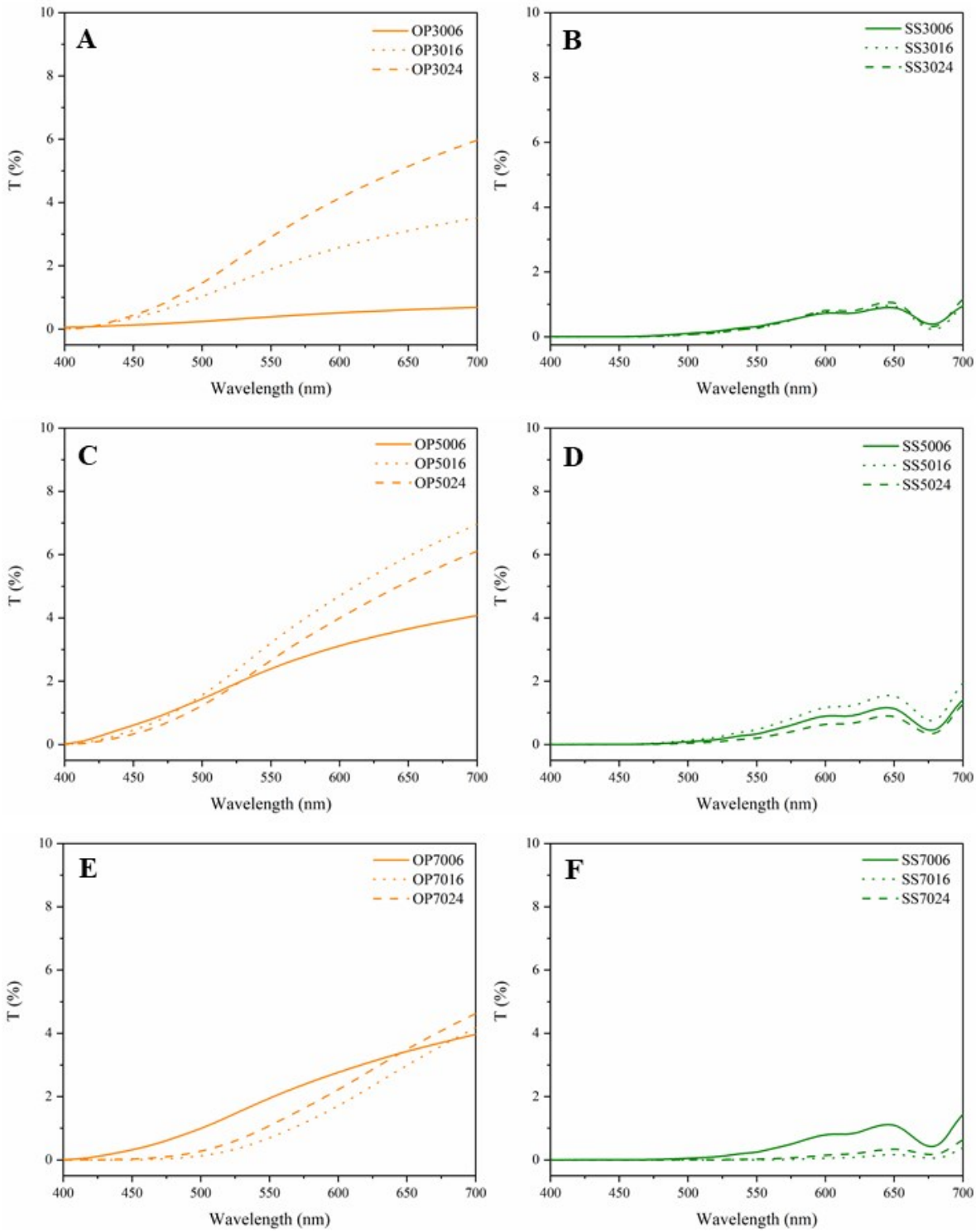

Fig. S.5 UV-Vis spectra in the PAR region (400-700 nm) for **A**: OP3006, OP3016, and OP3024; **B**: OP5006, OP5016, and OP5024; **C**: OP7006, OP7016, and OP7024; **D**: SS3006, SS3016, and SS3024; **E**: SS5006, SS5016, and SS5024; and **F**: SS7006, SS7016, and SS7024.

SI.6 Scratch test. Coefficients of friction.

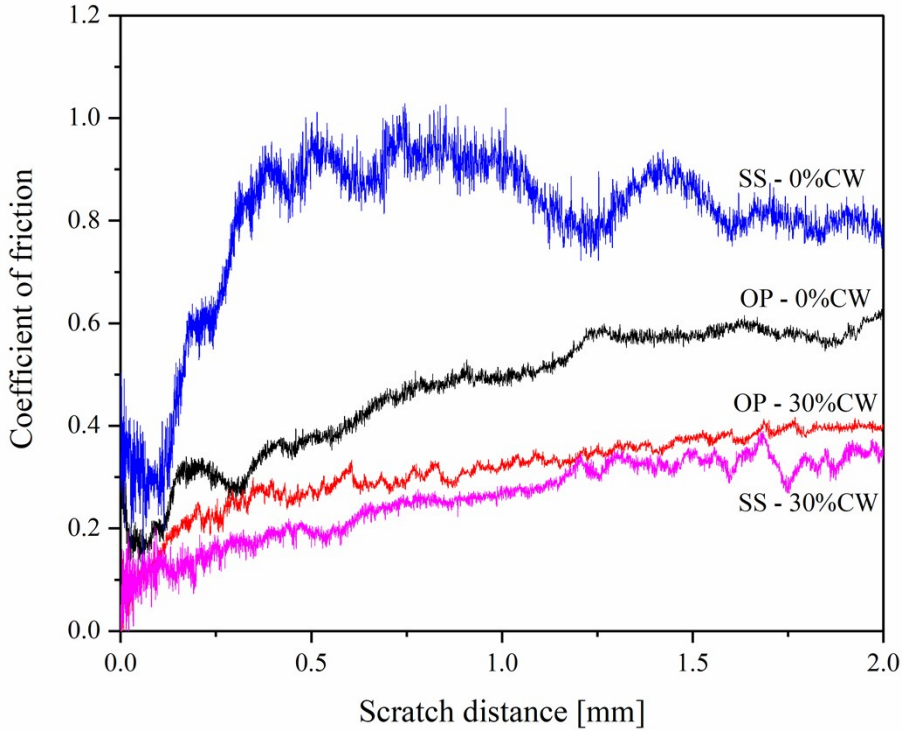

Fig. S. 6 Coefficient of friction as function of the scratch distance (mm).

SI. 7 Scratch test. Microscope images.

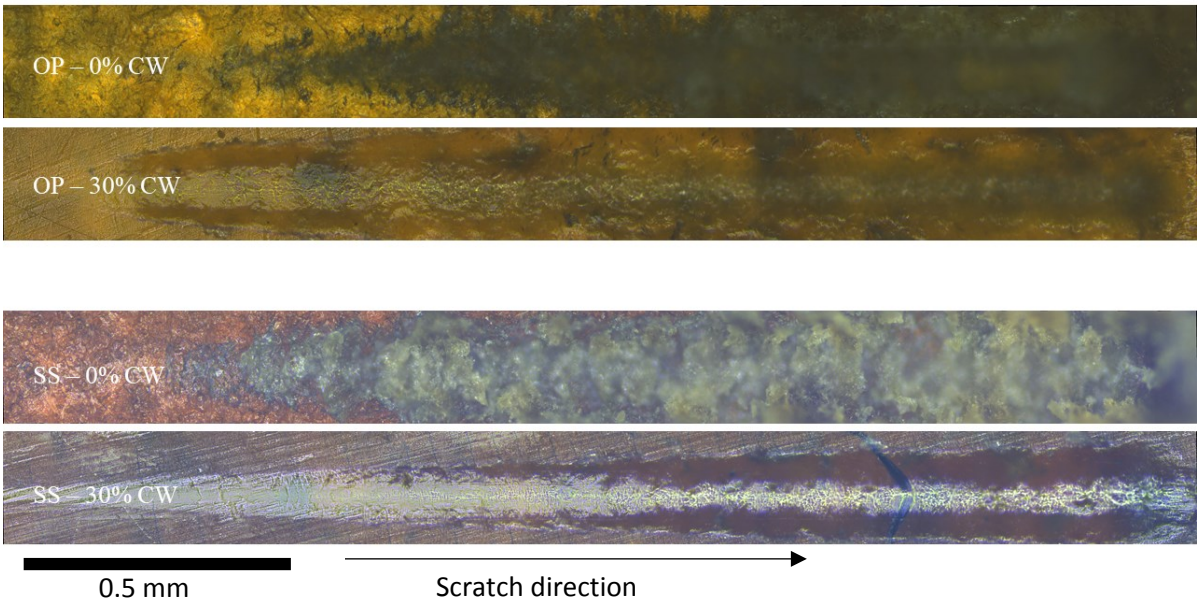

Fig. S.7 Microscope images of the surface of OP – 30%CW and SS – 30%CW with their respective controls, OP – 0%CW and SS – 0%CW.

SI. 8 Assessment of OP and SS-based films biodegradability in soil.

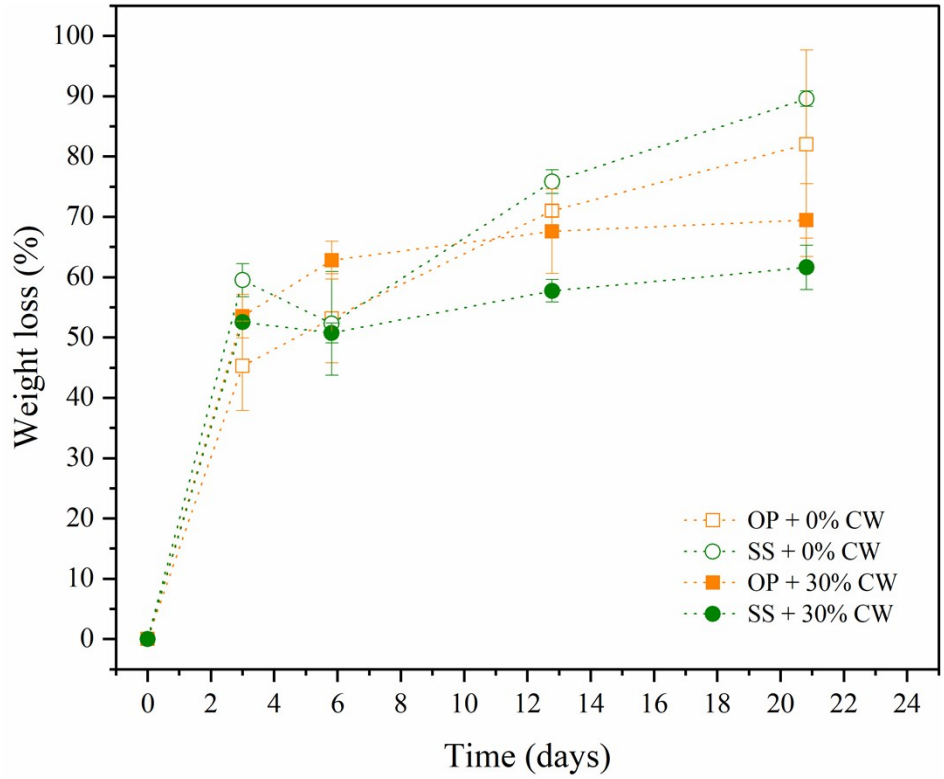

Fig. S. 8 Weight loss (%) of buried films as function of time (days) during the experiment of biodegradation in soil.