Electronic Supplementary Information

Biodegradable nanocomposite of poly(ester-*co*-carbonate) and cellulose nanocrystals for tough tear-resistant disposable bags

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Experimental section

Materials

Dimethyl carbonate (DMC, ≥99%), 1,4-butanediol (BD, ≥99%), citric acid (CA, ≥99.5%), and titanium(IV) butoxide (Sigma–Aldrich, USA), dimethyl succinate (DMS, ≥99%) (Alfa Aesar, USA), and cellulose nanocrystals (CNCs, spray-dried, 0.85 wt% sulfur on dry CNCs sodium form) (Process Development Center of the University of Maine, USA) were used as received. Commercial low-density polyethylene (LDPE) and commercial biodegradable bags (PBAT/PLA blend film) were purchased from Kwangjin F&T (Korea) and Sejong Green Pack (Korea), respectively (thickness: 0.02 mm, each). The general procedure for producing CNCs was as follows: strip-cut pulp was hydrolyzed in 64 wt% sulfuric acid for 60 min at 45 °C in an oxygen-free atmosphere. Following hydrolysis, the solution was diluted with water, and sodium chlorite was added to remove color. Finally, the acid was neutralized with sodium hydroxide. The material was fractionated, concentrated with 20 μm membranes, and obtained as a spray-dried powder.[S1, S2]

Synthesis of poly(butylene succinate) (PBS)

PBS was prepared by polymerization as described in a previous report.[S3]

M_n: 72,300 g/mol, M_w: 141,500 g/mol, PDI: 1.95. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.15-4.05 (d), 2.66-2.56 (br), 1.74-1.64 (tr). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.28, 64.17, 29.02, 25.22.

Synthesis of poly(butylene succinate-*co*-butylene carbonate) (PBS-1C)

DMS (75.99 g, 0.52 mol), DMC (70.26 g, 0.78 mol), and BD (97.32 g, 1.08 mol) were loaded into a flat-bottomed glass reactor equipped with a mechanical stirrer and condenser (20 cm long, 55 °C) and purged with nitrogen for 1 h. The feed molar ratio of the acid derivatives (ester and carbonate sources) per alcohol group was 1.2. The temperature was raised to 80 °C for the esterification step, after which titanium(IV) butoxide (0.132 g, 0.39 mmol) was added to the reactor. The reaction mixture was gradually heated from 80 to 150 °C for 9 h at 5 °C min^{-1} to obtain the intermediate esterified product. For the second polycondensation step, the intermediate product was transferred to a round-bottomed glass reactor equipped with a mechanical stirrer, an outlet connected to a vacuum pump, and a nitrogen inlet. The reaction mixture was heated from 150 to 200 °C for 13 h at 5 °C min^{-1} as the pressure was gradually reduced to below 100 mTorr to effectively extract byproducts. The stirring rate was decreased from 100 to 30 rpm as the viscosity of the reactant increased. The final product was removed from the reactor, quenched in water, and dried in a vacuum oven for 48 h at 60 °C.

M_n: 97,500 g/mol, M_w: 158,000 g/mol, PDI: 1.62. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.24-3.98 (d), 2.65-2.54 (br), 1.79-1.50 (tr). ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 172.27, 155.17, 67.34, 64.16, 29.02, 25.21.

Synthesis of poly(butylene succinate-*co*-butylene carbonate-*co*-butylene citrate) (PBS-2C)

PBS-2C was prepared in an identical manner to PBC-1C, with the exception that DMS (75.99 g, 0.52 mol), DMC (70.26 g, 0.78 mol), BD (97.32 g, 1.08 mol), and CA (0.1 g, 0.520 mmol) were used as the initial feed monomers.

M_n: 78,400 g/mol, M_w: 142,600 g/mol, PDI: 1.81. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.19-4.00 (d), 2.65-2.50 (br), 1.77-1.62 (tr). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.27, 155.18, 67.34, 64.16, 29.02, 25.21.

Synthesis of CNC/poly(butylene succinate-*co*-butylene carbonate-*co*-butylene citrate) composite by the *in situ* method (PBS-3C)

PBS-3C was prepared in an identical manner to PBC-1C with the following exceptions: 1) DMS (75.99 g, 0.52 mol), DMC (70.26 g, 0.78 mol), BD (97.32 g, 1.08 mol), CA (0.1 g, 0.520 mmol), and CNC (0.097g; 0.10 wt% relative to the BD input) were used as the initial feed monomers. 2) CNC was pre-dispersed in the BD by probe-tip sonication (VCX 750, 750W, 20kHz; Sonics & Materials, USA) for 25 min (2 s in action and 1 s rest).

M_n: 78,800 g/mol, M_w: 142,800 g/mol, PDI: 1.81. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.20-4.00 (d), 2.70-2.50 (br), 1.77-1.62 (tr). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.25, 155.16, 67.32, 64.15, 29.01, 25.20.

Chemical, physical, mechanical, and morphological characterization

The morphologies and sizes of the CNCs were examined using an atomic force microscope (Multimode V, Veeco, USA) and a Nano ZS Zetasizer (Malvern, UK).

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired using a QNP probe on a Bruker AVANCE II instrument (USA) at 500 MHz and 125 MHz, respectively. Samples were dissolved in $CDCl_3$ containing 0.03 vol% tetramethylsilane (TMS). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI = M_w/M_n) were measured by gel permeation chromatography (GPC) with an ACQUITY APC XT column (Waters Corp., USA) and a refractive index detector, using chloroform as the mobile phase. The system was universally calibrated using polystyrene standards.

Specimens of PBS-series for tensile and tear testing were prepared by hot-pressing at 180 °C for 10 min. The dumbbell-shaped specimens for tensile testing followed ASTM D638-5 standard and were 63 × 26 × 0.5 mm in dimensions. Tensile properties were examined using a universal testing machine (UTM, Instron 5943, UK) at 100 mm min^{-1} with a 1 kN load cell. Tensile toughness was calculated by integrating the area under the tensile stress–strain curve. The angle type specimens for tear testing followed KS M 6518 standard (10.2.1, type B) and were 100 × 20 × 0.1 mm in dimensions. A 1 mm long notch was formed at the mid-point of the specimen. Tear properties were examined using the UTM at 500 mm min^{-1} with a 1 kN load cell. Tear toughness was calculated by integrating the area under the tear strength–extension curve.

The morphologies of the fractured surfaces of the specimens were examined by field-emission scanning electron microscopy (FE-SEM; Tescan MIRA3, Brno, Czech Republic). The specimens were sputter-coated with a thin platinum layer to reduce charge effects prior to FE-

SEM (150 mA, 90 s). Differential scanning calorimetry (DSC) (DSC 25, TA Instruments, USA) was performed from −70 °C to 150 °C at heating and cooling rates of 10 °C min^{-1}.

Rheology

The rheological properties of the PBS series were evaluated by dynamic oscillation testing using a rotational rheometer (MCR 302, Anton Paar, Austria), with a parallel-plate geometry with a 25-mm diameter adopted during dynamic frequency sweep testing. The plate gap and strain level were 1 mm and 10%, respectively. Disc-shaped specimens were prepared by the hot-press procedure, after which rheological testing was conducted at 140 °C in the 0.05−500 rad s^{-1} angular frequency range.

Bio-decomposition testing under enzymatic and composting conditions

The enzymatic degradation of the PBS-carbonate series was examined using lipases from *Pseudomonas cepacia* (PS) and *Thermomyces lanuginosus* (TL), which were purchased from Sigma–Aldrich. The polymer films were placed in a 5-mL vial containing 4 mL of PS or TL lipase solution (5 mg/mL of enzyme in 100 mM phosphate buffer; pH 6.5 and pH 7.0, respectively) and incubated at 50 °C in a shaking water bath (80 rpm). The film specimens were prepared in accordance with the KS M ISO 37-4 standard size and 30–40 mg weight. The film specimens were recovered every 24 h from the vial, washed with ethanol and deionized water, and then dried for 24 h in a vacuum oven at 60 °C. Enzymatic degradability was determined by the ratio of the change in film weight to the initial weight.

In order to investigate biotic environmental degradation, 250 mL Erlenmeyer flasks filled with 50 g of compost mixture and three replicates of each hot-pressed film (10 × 10 mm, 80–100 μm thick) were buried between a 25-g lower layer and a 25-g upper layer. To improve the moisture-holding capacity and facilitate airflow, a commercial garden soil/compost mixture (5:5, w/w) was employed. Flasks were incubated at 50 °C for two weeks and periodically recovered after incubation. The specimens were washed with ethanol and distilled water and then dried in a vacuum oven at room temperature for 24 h.

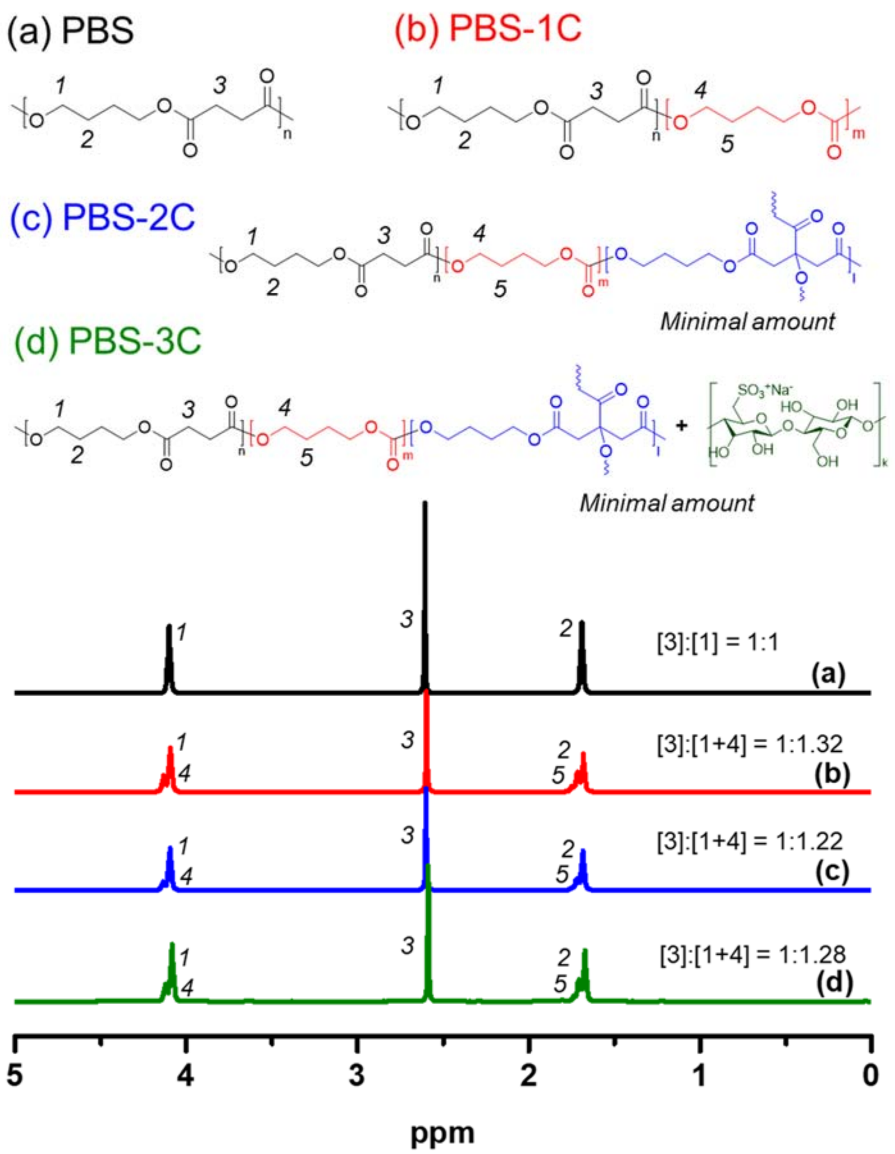
Germination index (GI)

At the end of the plastic bio-decomposition experiments, the used mixed soil was incubated at 50 °C for an additional two months to complete the biodegradation process and produce CO_2. To extract the soil, the soil sample (5.5 g) and distilled water (100 mL) was sealed and placed in a water bath at 70 °C for 2 h. After paper filtration, the filtrate (5 mL; soil extractant) was placed in a Petri dish with clean filter paper. Thirty *Lactuca sativa L.* seeds were placed on the plate, and the dish was sealed. The seeds were incubated at 23 °C for 5 d without light. The number of germinations was counted and root lengths were measured. An extension of the root from the junction of the plumule and radicle of over 2 cm was considered as germinated.

$$(1)\quad \text{Relative (\%)} = \frac{\text{Sample elongation}}{\text{Control elongation}} \times 100$$

$$(2)\quad \text{Germination rate (\%)} = \frac{\text{Sample germination}}{\text{Control germination}} \times 100$$

$$(3)\quad \text{GI} = \frac{(\text{Germination rate}) \times (\text{Relative})}{100}$$



PBS-1C

$$[\text{DMC}]\ \text{content}\ (\%) = \left(1 - \frac{[\text{DMS}]}{[\text{DMC}]+[\text{DMS}]}\right) \text{X}\ 100$$

$$= \left(1 - \frac{[\text{DMS}]}{[\text{BD}]}\right) \text{X}\ 100 = \left(1 - \frac{1}{1.32}\right) \text{X}\ 100 = 24\%$$

Figure S1. ^{1}H NMR spectra of the PBS-series, and calculating the carbonate contents (500 MHz, $CDCl_3$).

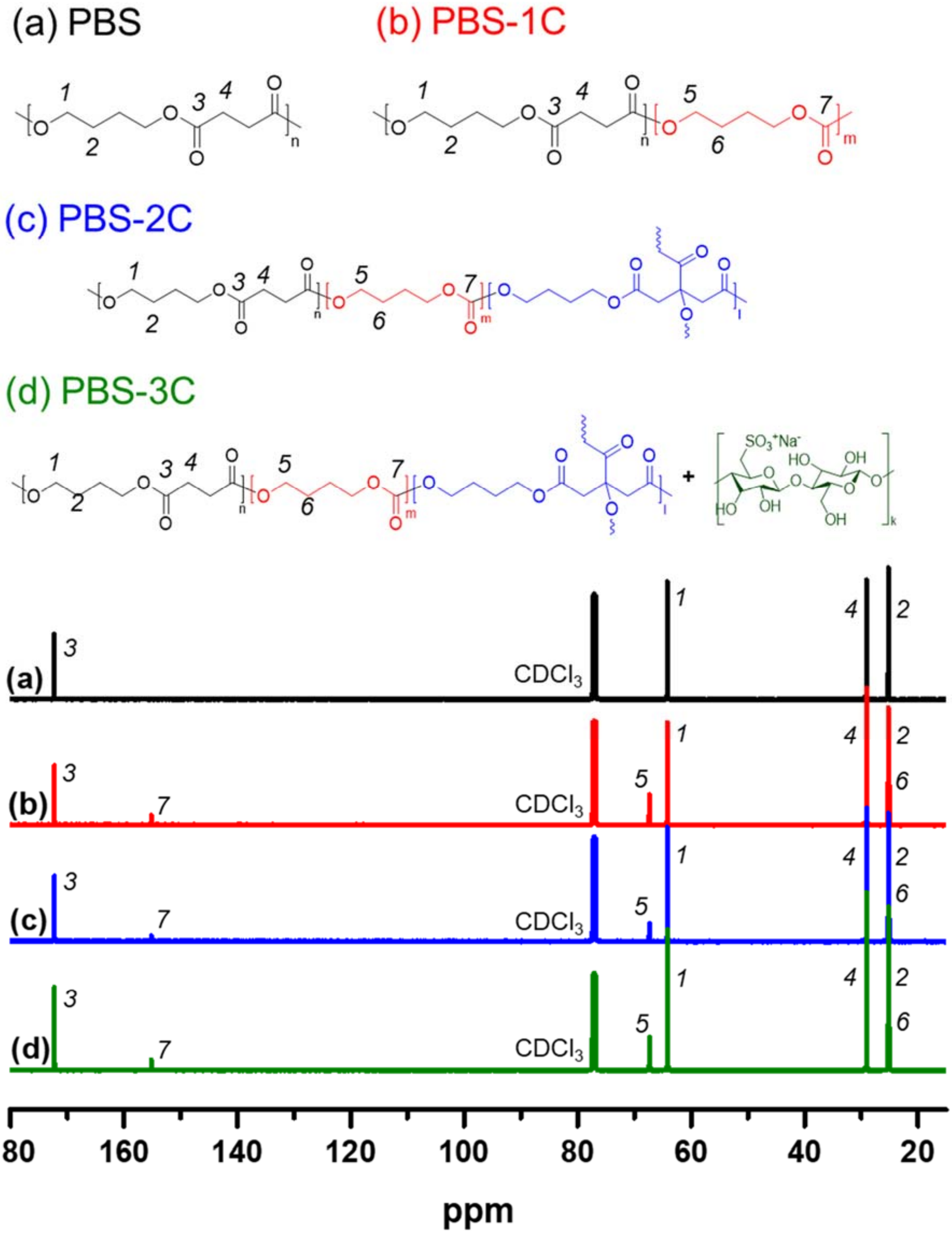


Figure S2. ^{13}C NMR spectra of the PBS-series (125 MHz, CDCl$_3$).

Table S1. Polymerization data.

Code	Incorporated ratio[a] ([DMS]:[DMC] unit)	Additives	M_n[b] (kg mol^{-1})	M_w[b] (kg mol^{-1})	PDI[b]	T_g[c] (°C)	T_c[d] (°C)	T_m[c] (°C)	$\triangle H_m$[c] (J g^{-1})
PBS	1:0	-	72.3	141.5	1.95	−32	69	113	76
PBS-1C	0.73:0.24	-	97.5	158.0	1.62	−40	ND[e]	85	44
PBS-2C	0.85:0.18	CA	78.4	142.6	1.81	−35	37	100	58
PBS-3C	0.78:0.22	CA, CNC	78.8	142.8	1.81	−37	28	90	46

[a] Calculated by ^{1}H NMR peak integration.

[b] Determined by chloroform-GPC (polystyrene standard).

[c] Measured by differential scanning calorimetry (DSC), 10 °C min^{-1} (2nd heating).

[d] Measured by DSC, 10 °C min^{-1} (1st cooling).

[e] The cold crystallization temperature was measured by DSC (2nd heating) to be 1.6 °C.

Table S2. Tensile and tear data.

Code	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Tensile toughness (MJ m^{-3})	Ultimate tear strength (N cm^{-1})	Extension at break (mm)	Tear toughness[b] (J cm^{-1})
PBS	711 ± 6	41±1	228 ± 6	70.6 ± 1.0	1,134 ± 61	10 ± 4	8.85 ± 4
PBS-1C	399 ± 8	37 ± 1	555 ± 12	130.6 ± 0.8	1,441 ± 122	35 ± 1	37.96 ± 2
PBS-2C	538 ± 3	54 ± 1	602 ± 14	203.2 ± 3.8	1,203 ± 14	30 ± 1	26.68 ± 1
PBS-3C	345 ± 31	64 ± 1	690 ± 13	254.6 ± 5.2	1,363 ± 30	31 ± 1	31.99 ± 1
Commercial LDPE (MD[a])	254 ± 11	31 ± 1	580 ± 5	111.5 ± 1.6	1,293 ± 46	16 ± 1	15.86 ± 1
Commercial biodegradable bag (MD)	1,007 ± 32	25 ± 1	148 ± 3	28.6 ± 1.0	901 ± 112	15 ± 3	13.36 ± 2

[a] The tear direction is along the machine direction (MD) of the blown film.

[b] Tear toughness was calculated by integrating the area under the tear strength–extension curves.

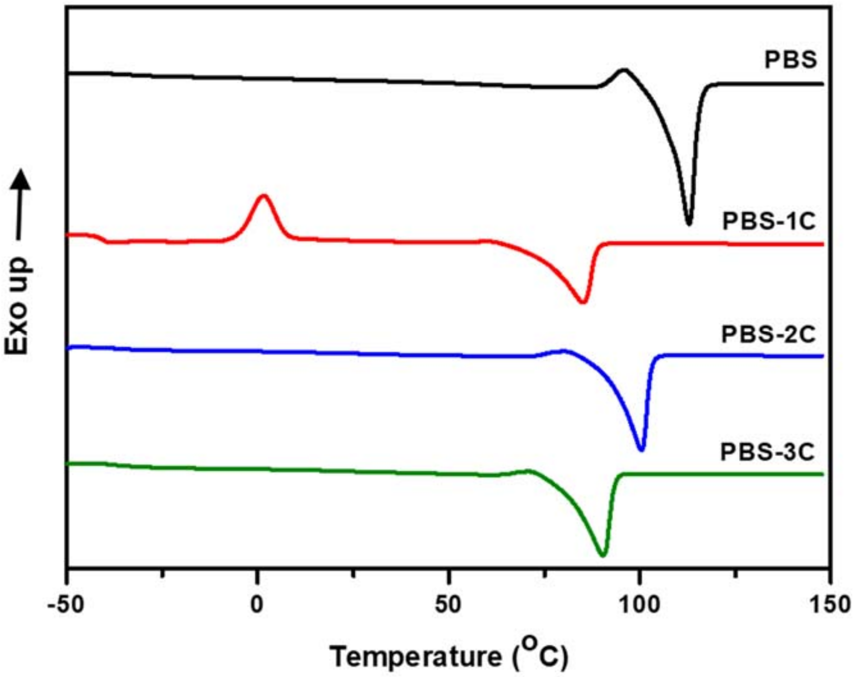


Figure S3. DSC curves of the PBS-series (second heating scan, 10 °C min^{-1}).

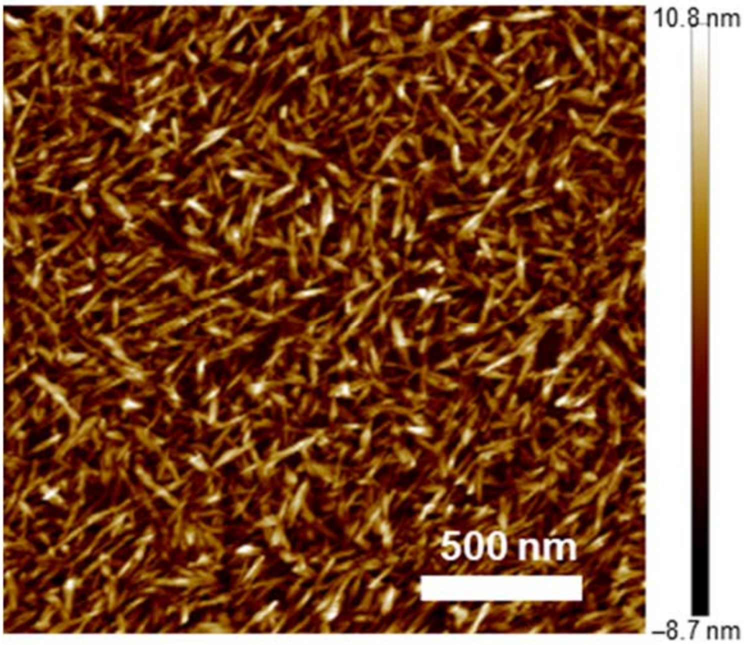


Figure S4. AFM image of CNCs (spray-dried, sourced from the University of Maine, USA).

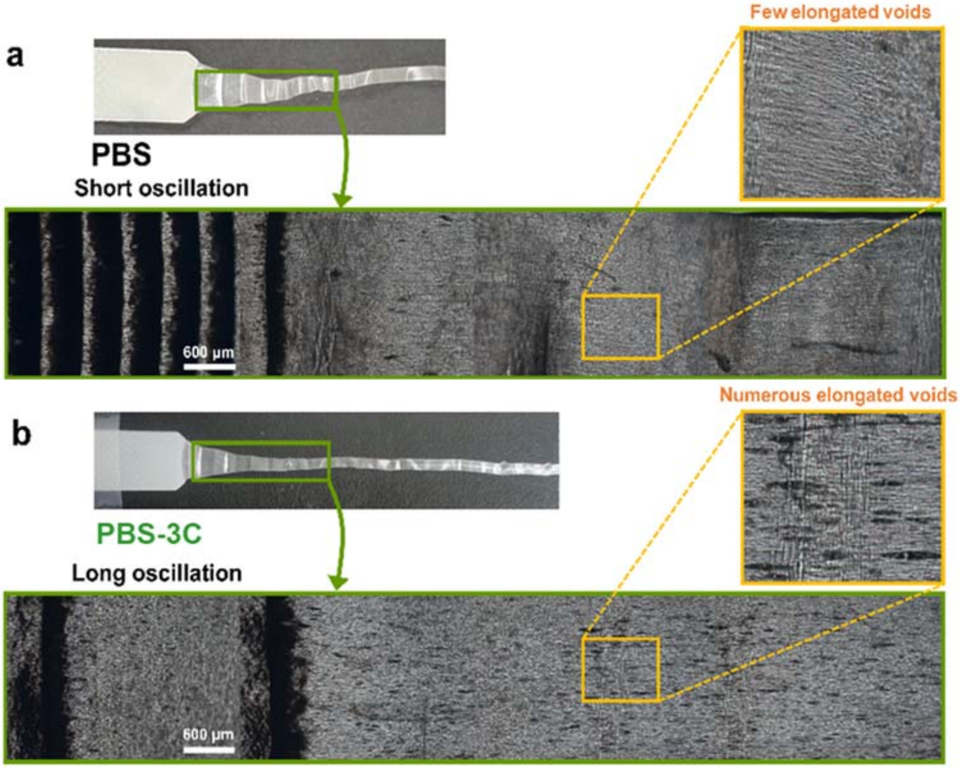


Figure S5. OM images of the surface morphologies of tensile-tested specimens: (a) PBS and (b) PBS-3C.

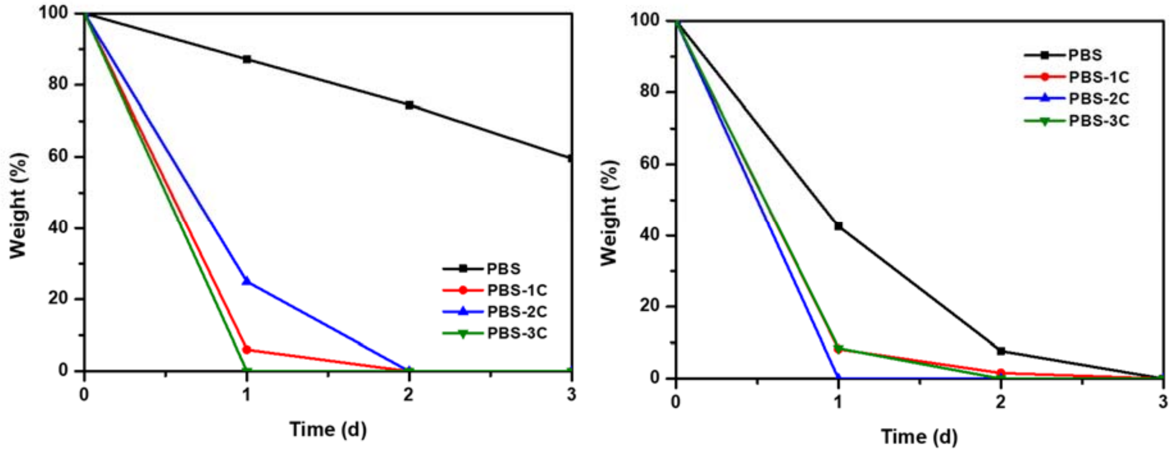


Figure S6. Time-dependent enzymatic weight-degradation data using lipases from *Pseudomonas cepacia* (PS) and *Thermomyces lanuginosus* (TL).

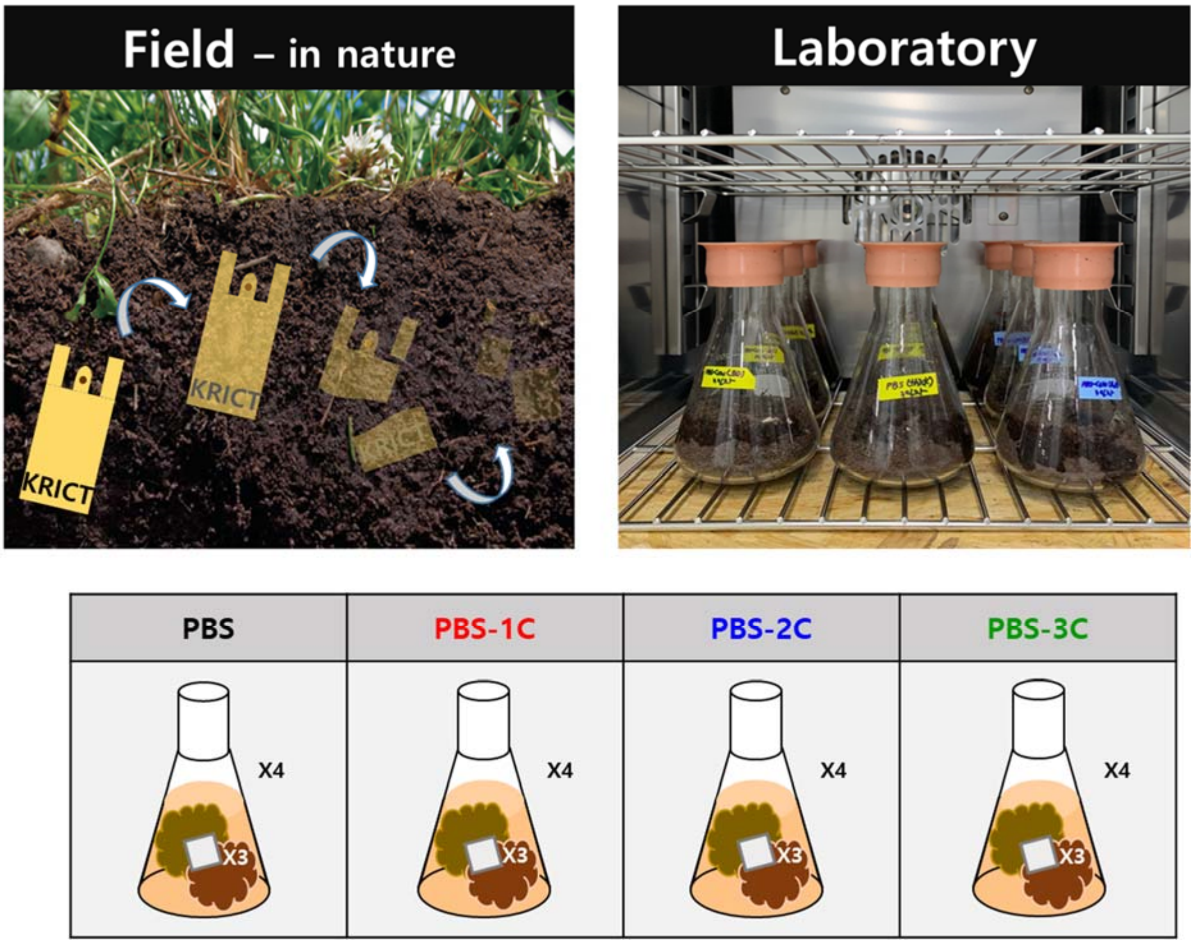


Figure S7. Laboratory bio-decomposition experiments in composting soil that mimic real biodegradation in the field.

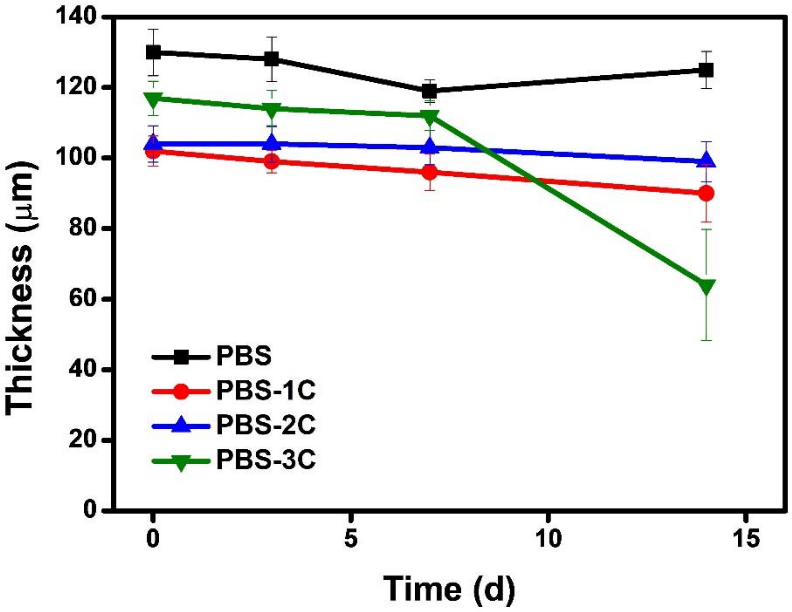


Figure S8. Bio-decomposition (film thickness change) of the PBS series in composting soil.

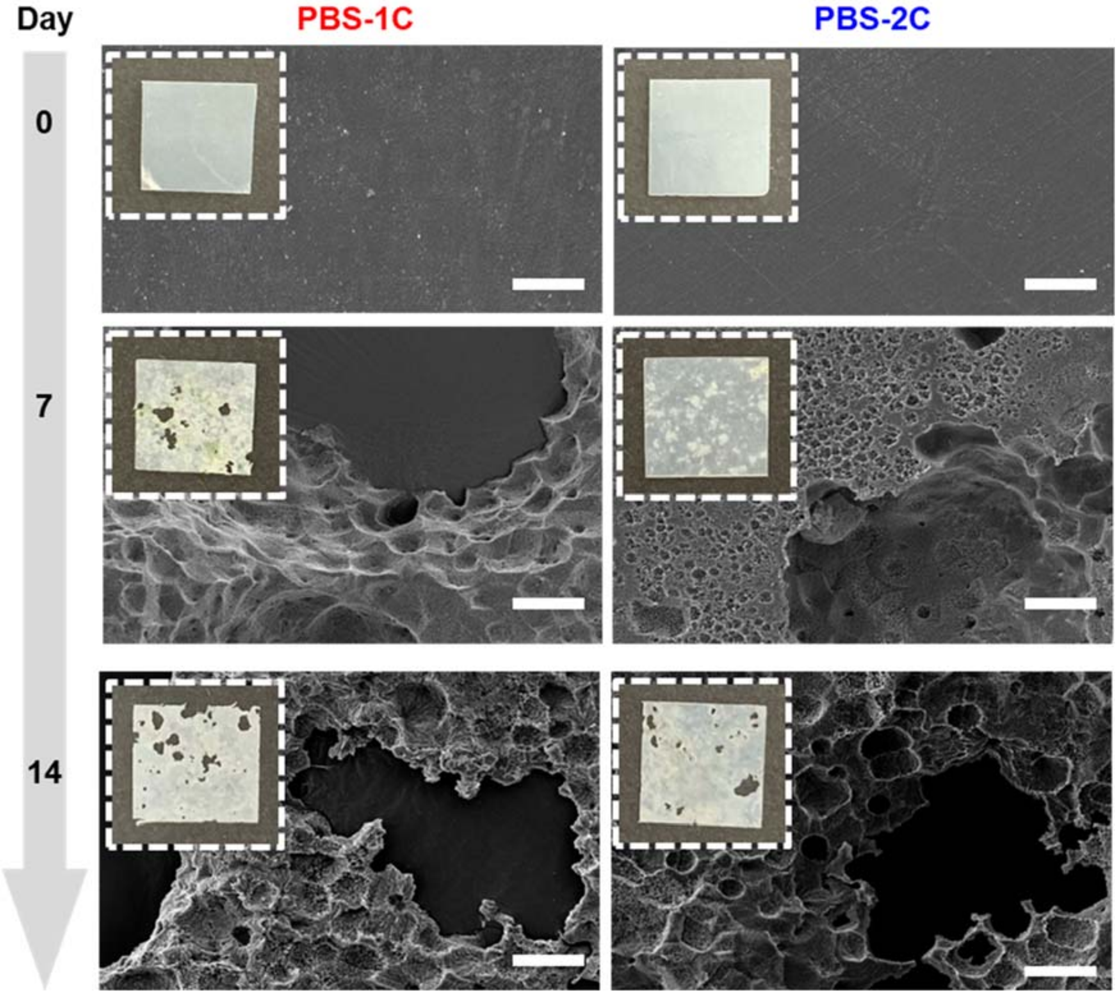


Figure S9. Optical and SEM images of the surfaces of PBS-1C and PBS-2C films before and after decomposition in the composting soil (film sizes: 10 × 10 mm, scale bar: 10 μm).

Table S3. Germination numbers and average root lengths.

	Germination number	Average root length (cm)
Negative control[a]	26	2.8
PBS	28	2.7
PBS-1C	25	2.8
PBS-2C	27	2.8
PBS-3C	25	2.8

[a] Based on distilled water

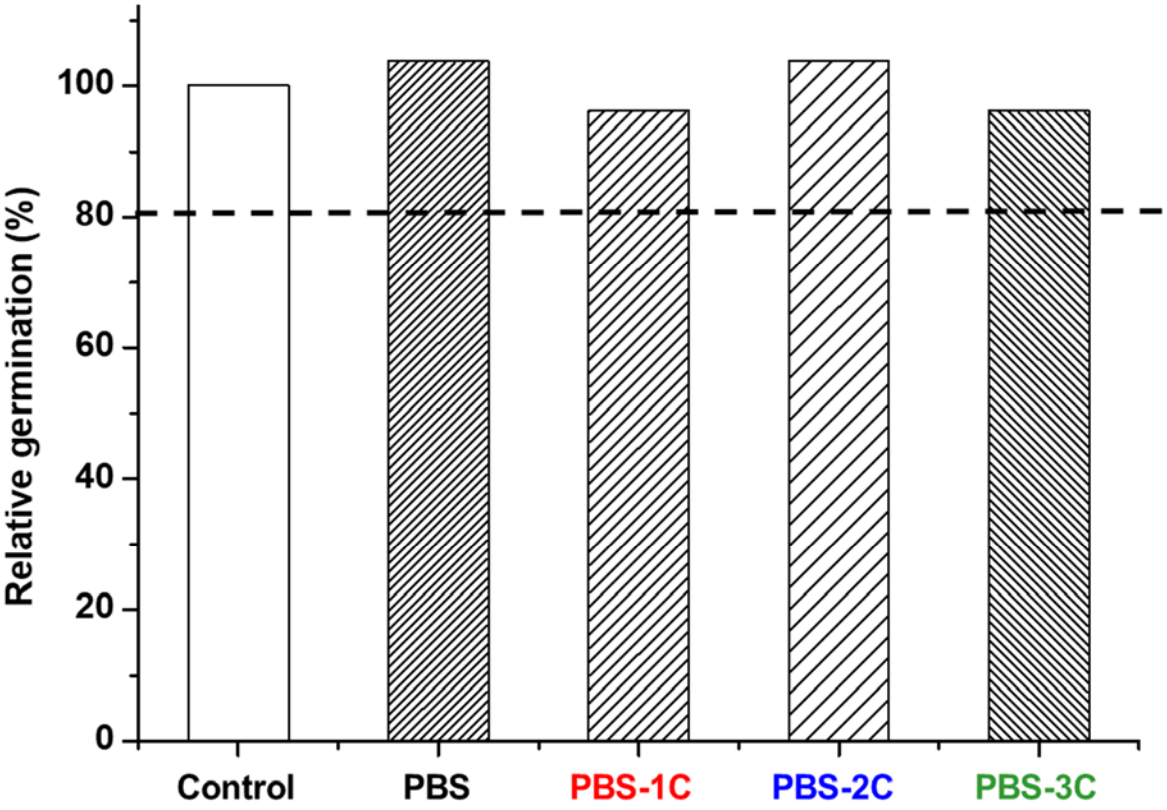


Figure S10. Relative germinate rates of aqueous soil extracts after plastic bio-decomposition experiments.

Movie S1. Tensile experiments: (a) LDPE, (b) PBS, and (c) PBS-3C (5× speed).

Movie S2. Tear experiments: (a) LDPE, (b) PBS, and (c) PBS-3C (5× speed).

Supporting references

[S1] M. S. Reid, M. Villalobos and E. D. Cranston, *Langmuir*, 2017, **33**, 1583-1598.

[S2] Cellulose nanocrystals (CNC) - Product Specification. https://umaine.edu/pdc/wp-content/uploads/sites/398/2016/03/Specs-CNC.pdf (accessed Jan, 2021)..

[S3] T. Kim, H. Jeon, J. Jegal, J. H. Kim, H. Yang, J. Park, D. X. Oh and S. Y. Hwang, *RSC Adv*., 2018, **8**, 15389-15398.