Supporting Information for

All-water-based fabrication of biodegradable mulch films from dead leaves via complex hydrogen-bonded networks

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Characterization methods

Chemical composition of samples

The percentages of cellulose and hemicellulose were determined following a previously reported method.[1] Briefly, 1 g of leaf powder was mixed with 8 mL of sodium chlorite solution (5 wt%) and 2 mL of acetic acid, then heated at 90 °C for 5 h under continuous stirring. The resulting solid was collected by centrifugation, thoroughly washed with deionized water, and oven-dried at 60 °C for 24 h. The dried solid mass was recorded as the holocellulose content. To determine the cellulose content, the obtained holocellulose was treated with 20 mL of sodium hydroxide solution (10 wt%) at 80 °C for 5 h, followed by washing and drying at 60 °C. The difference in mass between the holocellulose and cellulose fractions was used to calculate the hemicellulose content.

The Klason lignin content was determined according to the ASTM D1106-21 standard with minor modification. In brief, 1 g of leaf powder was hydrolyzed with 20 mL of sulfuric acid (72 wt%) for 2 h at room temperature. The mixture was then diluted to a 3 vol% acid concentration with 750 mL of DI and heated at 100 °C for 4 h. The resulting acid-insoluble residue, corresponding to the lignin fraction, was filtered, washed, and weighed.

Supplementary tables

Table S1. Detailed main chemical compositions of virgin leaf and LCNF powders

Samples	**Cellulose (wt%)**	**Hemicellulose (wt%)**	**Lignin (wt%)**
Raw leaves	32.4 ± 0.8	23.6 ± 0.4	25.3 ± 0.5
LCNF	40.3 ± 1.1	4.9 ± 0.3	30.6 ± 0.9

Table S2. Carbon content and theoretical CO_2 production of the samples

Samples	**Sample weight (mg)**	**Carbon content (%)**	**ThCO_2 (mg)**
LANC	10000	44.51	16319
LANC50PVA50	10000	47.79	17523
α-Cellulose	10000	41.97	15389
LDPE	10000	84.84	31108

Table S3. Bulk and skeletal densities, and porosity of LCNF/CNC and LANC/PVA films

Samples	**Bulk density (g/cm^3)**	**Skeletal density (g/cm^3)**	**Porosity (%)**
PVA	1.3429	1.3437	0.06
LANC25PVA75	0.9133	0.9344	2.25
LANC50PVA50	0.9267	1.0277	9.83
LANC75PVA25	0.9333	1.1606	19.58
LANC	0.9067	1.1969	24.25
LCNF	0.6743	1.3103	48.54
CNC	1.4294	1.4456	1.12

Table S4. Thermal properties of the LANC/PVA films

Samples	**T_{onset} (°C)**	**T_{max} (°C)**	**Residues (%) at 600 °C**
PVA	245	285	2.6
LANC25PVA75	310	369	16.7
LANC50PVA50	298	362	19.0
LANC75PVA25	285	335	23.9
LANC	268	312	22.4

Table S5. Mechanical properties of the LCNF/CNC and LANC/PVA films

Samples	Tensile strength (MPa)	Strain at break (%)	Young's modulus (MPa)
PVA	17.6	279.07	310.8
LANC25PVA75	24.32	17.92	848.9
LANC50PVA50	22.65	15.92	852.8
LANC75PVA25	20.5	9.92	914.4
LANC[a]	11.96	5.26	796.1
CNC	22.56	3.59	1878.2
LCNF30CNC70	14.99	4.59	1062.1
LCNF50CNC50	11.96	5.26	796.1
LCNF70CNC30	9.21	4.59	581.3
LCNF	0.76	2.26	57.8

[a] LANC is equal to LCNF50CNC50

Table S6. Water Vapor Permeability of Lignin/Cellulose/Polymer Nanocomposites.

Materials	WVP[a]	Conditions
LCNF (from dead leaves)/PVA[2]	1.93–5.74	23 °C, 50/0 %
Kraft lignin-grafted CNF (from paper mill sludge)/PVA[3]	43.2	23 °C, 50/0 %
Sunflower protein isolates/Bacterial nanocellulose (BNC) films[4]	20.7	23 °C, 50/0 %
Poly(hydroxyhexadecanoate) (PHHA, from leaf cuticle)	1.1	23 °C, 50/0 %
PPLA/spinach stems mulch film[5]	10.4	23 °C, 100/0 %
LCNF (from willow bark)/PVA[6]	7.1	23 °C, 75/0 %
LCNF (from corncob residues) films[7]	1.72	23 °C, 50/0 %
CNF (from bleached softwood pulp)/$CaCO_3$/gluconolactone films[8]	51.8	25 °C, 50/0 %
Pure PLA[9]	3.02	23 °C, 50/0 %
CNF (from bleached kraft pulp)/tannin films[10]	2.35	23 °C, 50/0 %
Potato starch/MXene nanocomposite films[11]	20.6	23 °C, 75/0 %
Cassava starch/PVA[12]	1.68	23 °C, 42/0 %

[a] WVP unit (g μm (m^2 day Pa)$^{-1}$).

Table S7. Obtained parameters of fitted first-order and Hill-like kinetic models for samples and references

Kinetic models	Unit	LANC	LANC50PVA50	α-Cellulose	LDPE
1. First order					
Bm	%	46.34 ± 0.02	32.78 ± 0.01	77.25 ± 0.03	4.42 ± 0.01
k	d^{-1}	0.061 ± 1.2x10^{-4}	0.073 ± 1.5x10^{-4}	0.051 ± 7.3x10^{-5}	0.018 ± 4.8x10^{-5}
adj-R^2	-	0.9808	0.9756	0.9913	0.9896
χ^2	-	2.04	1.23	3.01	0.01
2. Hill-Like					
a	%	51.55 ± 0.03	36.44 ± 0.02	83.92 ± 0.06	4.81 ± 0.01
b	d	11.99 ± 0.02	11.00 ± 0.02	14.39 ± 0.02	43.61 ± 0.20
c	-	1.13 ± 2.0x10^{-3}	1.11 ± 2.1x10^{-3}	1.30 ± 2.0x10^{-3}	1.38 ± 4.9x10^{-3}
adj-R^2	-	0.9961	0.9955	0.9974	0.9905
χ^2	-	0.41	0.23	0.91	0.01

Table S8. Detailed information about biodegradable plastics and commercial mulch film

Classification	Material (main components)	Trade name (producer)
Biodegradable film	LANC50PVA50	-
	PCL[13]	CAPA 6500 (Perstorp)
	PHO[13]	Bioplastech R (Bioplastech, Ireland)
	PBS[14]	Novamont, Italy
	PHB[14]	Mirel™ P5001 (Metabolix, USA)
Commercial mulch film	Bio360 (PBAT)[13]	Mater-Bi® grade EF04P (Novamont, Italy)
	Organix (PBAT)[13]	Ecovio® grade M2351 (BASF, Germany)
	Naturecycle (copolyester)[13]	Copolyester (Custom Bioplastics, USA)
	Ecoflex (PBAT)[14]	Ecoflex® F BX 7011 (BASF, Germany)
	Ingeo (PLA)[14]	Ingeo 4042D (NatureWorks, USA)
	Biomulch[15]	3M Company, USA

Table S9. Estimated energy consumption of DES treatment for an experimental batch (12 g of leave powder, 300 mL DES solvent was heated at 100 °C for 3 h).

Equipment[a]	**Power (W)**	**Uptime (h)**	**Workload (%)**	**Capacity (L)**	**Energy demand (Wh)**
Blender	700	0.1	80	0.012	0.5
Hot plate	650	3	25	0.3	36.6
Ultrasonicator	1000	1	80	0.2	80
Drying	800	48	25	0.012	3.5
Total	282 Wh				
Estimated cost[b]	54 KRW (or 0.037 USD) per 0.23 m^2				

[a] LU multi blender (LT2-BL3M-E) with maximum capacity of 1.5 L; Digital hotplate stirrer (Evo HS1) with maximum capacity of 4 L at 400 °C; Ultrasonic Homogenizer (UH-1000Z) with maximum capacity of 2 L; Dry heat sterilizer (JSON-030S) with maximum capacity of 33 L at 250 °C are used.

[b] Industrial electricity cost in Korea was set to 190.4 KRW Kwh^{-1} (as of December 2025). Under our casting conditions, 1 g of raw leaves yields approximately 190.85 cm^2 of LANC50PVA50 film.

Table S10. Estimated screening cost for producing 100 m^2 of LANC50PVA50 film.

1. Components[a]	**Quantity**	**Unit**	**Unit cost (KRW $unit^{-1}$)**	**Cost (KRW)**
Raw leaves (dry)	5.2	kg	0	0
Choline chloride	10.8	kg	800	8645
Citric acid	32.4	kg	600	19452
Water (DES)	10.8	L	0.8	9
CNC	2.4	kg	6943	16371
PVA	2.4	kg	2140	5046
Glycerol	1.5	kg	1330	1976
Process water	26.2	L	0.8	21

2. Equipment[b]	**Power (W)**	**Uptime (h)**	**Workload (%)**	**Capacity (L)**	**Energy demand**[c] **(Kwh)**
Blender	2000	0.1	80	5.2	0.01
Reactor	8000	3	100	131	15.7
Ultrasonicator	6000	1	20	78.6	0.6
Drying	3000	48	20	5.2	0.5
Estimated total cost[d] (1+2)	548 (KRW m^{-2}) or 0.37 (USD m^{-2})				

[a] Raw leaves were collected as a waste biomass feedstock; therefore, the cost was assumed to be "0". The cost of all other chemicals (except water) is inquired about bulk unit prices, noting that prices may vary by supplier, purchase volume, and location. DES recycling was assumed to be 70% by volume. Cleaning water demand was as 5 L per kg leaves.

[b] Consider industrial blender (1403 industrial grinder) with maximum capacity of 130 kg/h; Reactor (Ai 200L ReactorHeater) with maximum capacity of 200 L at 200 °C; Ultrasonicator (UIP6000hdT) with maximum capacity of 150 L; and industrial oven (GP 220A) with maximum capacity of 330 L at 300 °C are used.

[c] The energy demand was calculated as literature[16]: $power \times uptime \times workload \times \frac{batch\ size}{max\ capacity}$

[d] Estimated production cost is the summary cost of (1) and (2). Current industrial electricity cost in Korea is 190.4 KRW Kwh^{-1} (as of December 2025).

Table S11. Indicative market prices of commercial mulch films.

Product	Price per area (USD m^{-2})
LANC50PVA50	0.38
Bio360 biodegradable mulch[a]	0.78–0.86
Cornstarch lightweight biodegradable mulch film[b]	0.72
Non-biodegradable PE mulch film[c]	0.29

[a-c] The references are embedded accordingly (accessed January 2026).

Supplementary figures

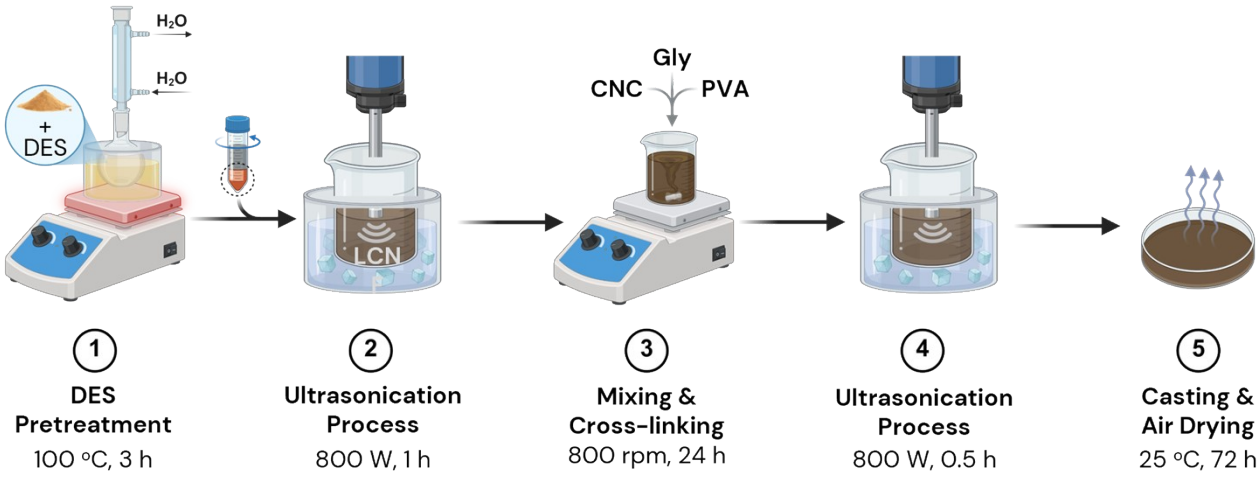

Fig. S1. Schematic illustration of BDM film fabrication process

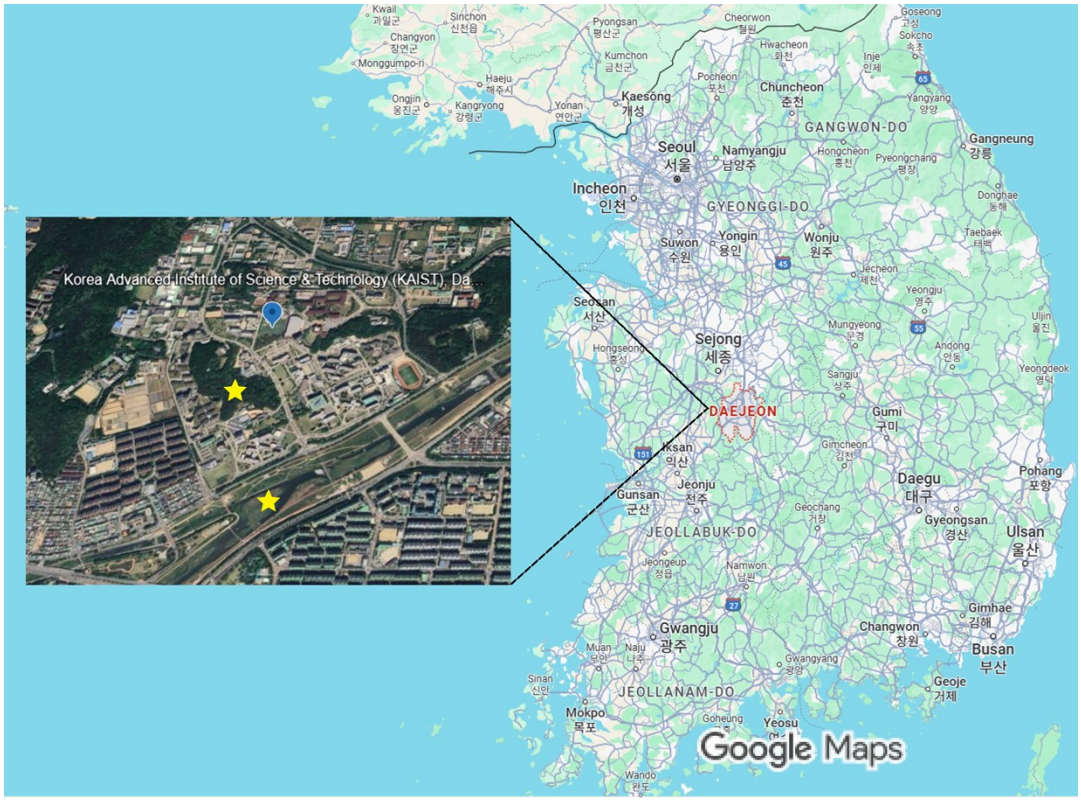

Fig. S2. Map of two sampling sites (Eoeun-dongsan 36°22'09"N/127°21'31"E; Gapcheon river 36°21'48"N/127°21'42"E) for collecting soil used for biodegradation test. The maps were captured from Google Maps and Google Earth.

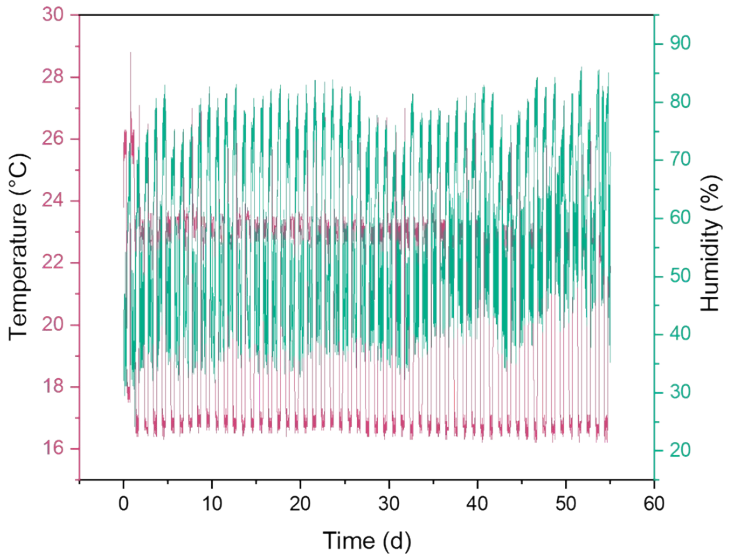

Fig. S3. Temperature and relative humidity profile during the ecotoxicity and anti-drought behavior experiments.

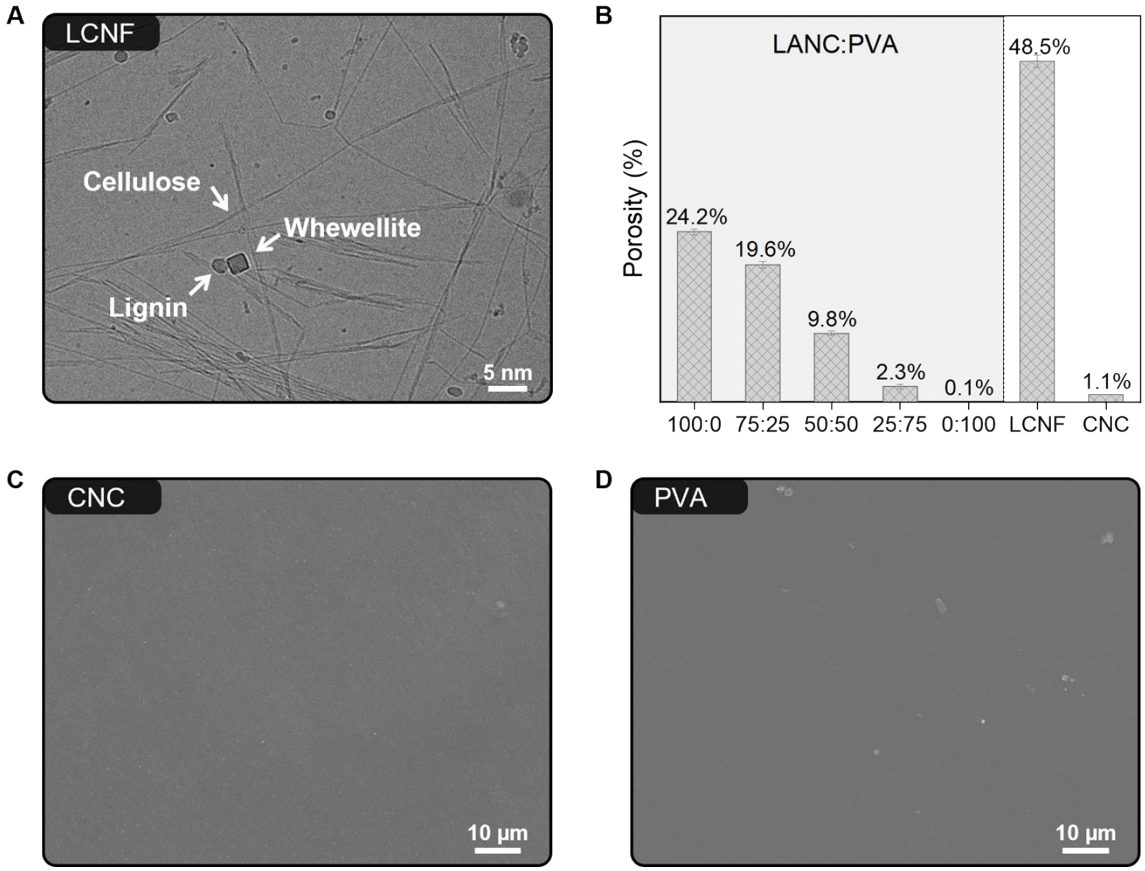

Fig. S4. (A) TEM image of LCNF suspension. (B) Porosity of all samples. (C), (D) SEM images of CNC and PVA

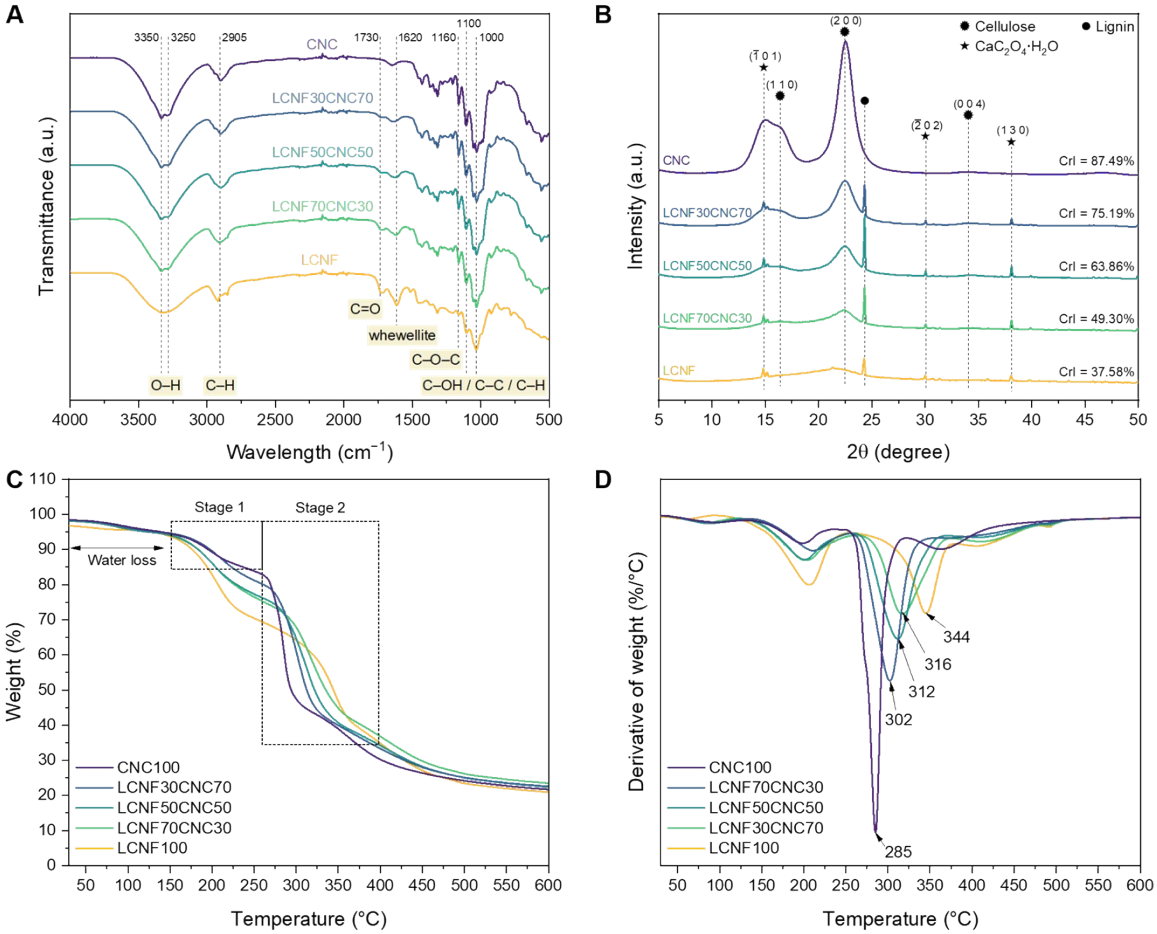

Fig. S5. (A) FTIR spectra, (B) XRD plots, (C) TGA curves, and (D) DTG curves of the LANC/PVA films at different ratio.

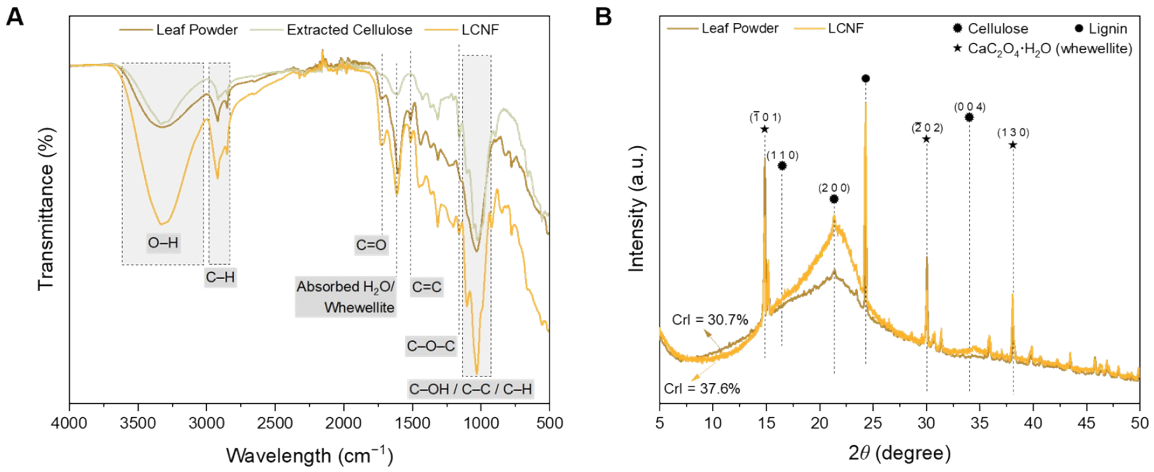

Fig. S6. (A) FTIR spectra, (B) XRD plots of raw leaves

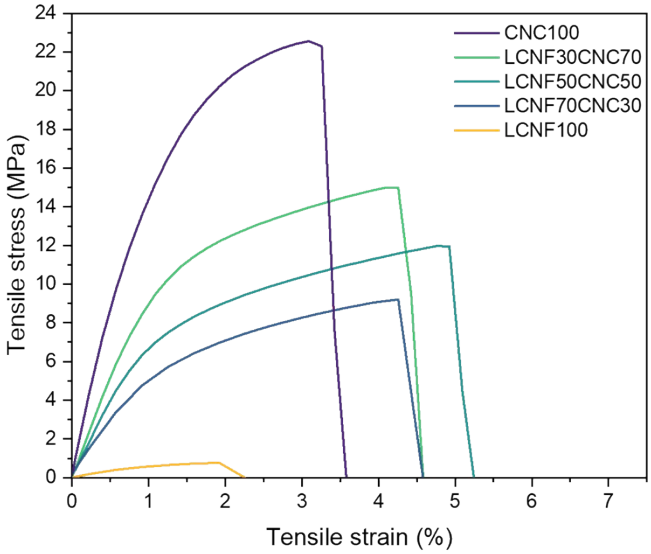

Fig. S7. Typical stress–strain curves of LCNF/CNC films.

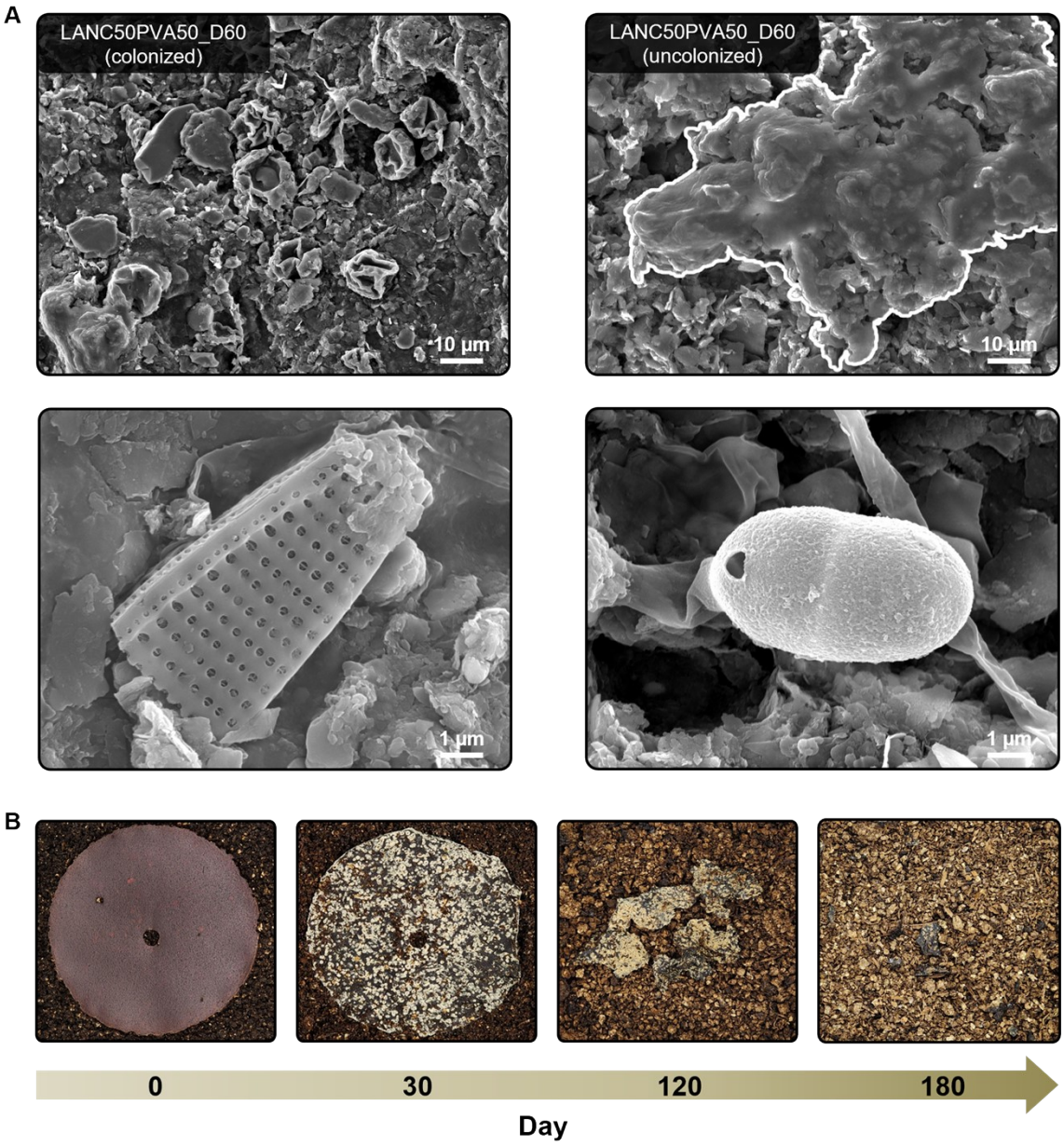

Fig. S8. (A) SEM images showing the top surface of samples in areas colonized and uncolonized by microorganisms, as well as additional detected unicellular organisms, after 60 days of soil burial. (B) Digital images of LANC50PVA50 film biodegradation under controlled composting conditions, as specified in ISO 14855-1:2012 (58 °C and 55% RH). Compost was supplied by the Institute of Agricultural Science, Chungnam National University (Republic of Korea) with the following composition: ash (15%), volatile solids (22%), total bacteria (6 x 10^9 CFU g^{-1}). The film degraded by over 90% after 180 days.

Fig. S9. Current methods for collecting dead leaves in Korea.

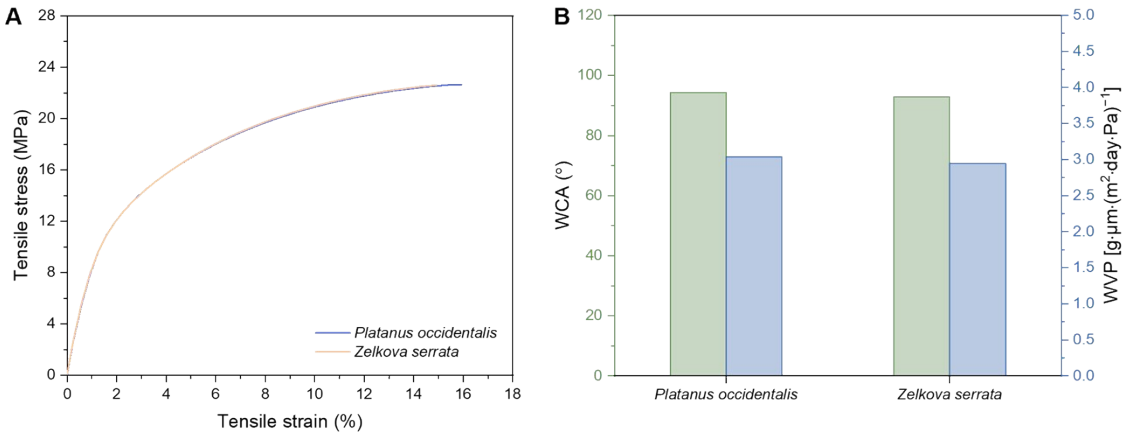

Fig. S10. (A) Typical stress–strain curves, and (B) WCA and WVP of LANC50PVA50 film films fabricated from two dead leaf types.

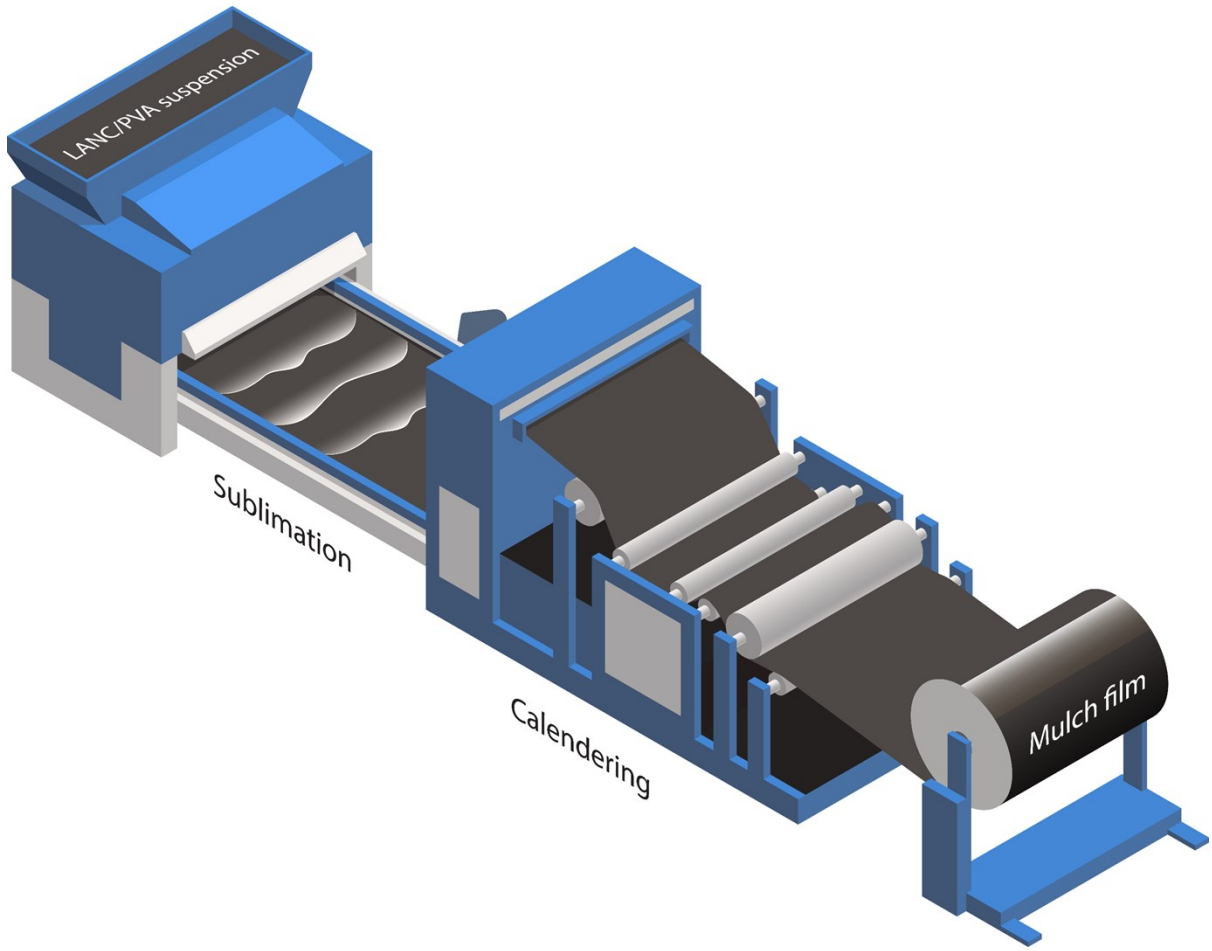

Fig. S11. Proposed schematic illustration of the large-scale production of LANC/PVA mulch films.

References

1. Q. Xia, C. Chen, Y. Yao, J. Li, S. He, Y. Zhou, T. Li, X. Pan, Y. Yao and L. Hu, *Nat. Sustain.*, 2021, **4**, 627-635.
2. M. Parit, H. Du, X. Zhang and Z. Jiang, *ACS Appl. Polym. Mater.*, 2022, **4**, 3587-3597.
3. M.-N. Efthymiou, E. Tsouko, A. Papagiannopoulos, I.-G. Athanasoulia, M. Georgiadou, S. Pispas, D. Briassoulis, T. Tsironi and A. Koutinas, *Sci. Rep.*, 2022, **12**, 6935.
4. S. Singha, V. Gowda and M. S. Hedenqvist, *ACS Appl. Polym. Mater.*, 2021, **3**, 4088-4100.
5. D. Merino, A. Zych and A. Athanassiou, *ACS Appl. Mater. Interfaces*, 2022, **14**, 46920-46931.
6. J. Dou, T. Vuorinen, H. Koivula, N. Forsman, M. Sipponen and S. Hietala, *ACS Appl. Nano Mater.*, 2021, **4**, 2921-2929.
7. J. Luo, Y. Su, J. Chen, X. Wang and J. Liu, *Cellulose*, 2021, **28**, 4671-4684.
8. Q. Han, Y. Wang, H. Wang, T. Zhou, Z. Song, D. Yu, X. Liu, W. Liu and S. Ge, *ACS Sustain. Chem. Eng.*, 2024, **12**, 2120-2129.
9. M. Cvek, U. C. Paul, J. Zia, G. Mancini, V. Sedlarik and A. Athanassiou, *ACS Appl. Mater. Interfaces*, 2022, **14**, 14654-14667.
10. A. L. Missio, B. D. Mattos, C. G. Otoni, M. Gentil, R. Coldebella, A. Khakalo, D. A. Gatto and O. J. Rojas, *Biomacromolecules*, 2020, **21**, 1865-1874.
11. M. Dong, G. Mastroianni, E. Bilotti, H. Zhang and D. G. Papageorgiou, *ACS Sustain. Chem. Eng.*, 2024, **12**, 11056-11066.
12. J. S. A. Friedrichsen, A. R. S. Bruni, E. S. Alves, B. H. F. Saqueti, A. L. Figueiredo, P. R. d. Souza, J. M. G. Mikcha, M. R. S. Scapim, E. G. Bonafe and O. O. Santos, *ACS Food Sci. Technol.*, 2024, **4**, 365-372.
13. M. B. Anunciado, D. G. Hayes, A. F. Astner, L. C. Wadsworth, C. D. Cowan-Banker, J. E. L. y. Gonzalez and J. M. DeBruyn, *J. Polym. Environ.*, 2021, **29**, 2916-2931.
14. P. A. Palsikowski, C. N. Kuchnier, I. F. Pinheiro and A. R. Morales, *J. Polym. Environ.*, 2018, **26**, 330-341.
15. A. A. Thompson, M. B. Samuelson, I. Kadoma, E. Soto-Cantu, R. Drijber and S. E. Wortman, *J. Polym. Environ.*, 2019, **27**, 498-509.
16. J. D. Estrada-Sotomayor, Ł. Łopusiewicz, E. Lizundia, S. Guenther and D. Merino, *Green Chem.*, 2025, **27**, 4587-4602.