

Electronic Supplementary Information for

Biodegradable chito-beads replacing non-biodegradable microplastics for cosmetics

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Supplementary Tables

Table S1. Comparison of the hardness of indentation in this study with previous reports on natural nutshell, synthetic polymers and extracted skin exfoliators.

Synthetic polymer			Natural polymer		
Material	Hardness of indentation (MPa)	Ref.	Material	Hardness of indentation (MPa)	Ref.
UHMWPE	73.1	1	Walnut shell	290	2
PVC	86.9	1	Walnut	450	2
PVA	39.2	1	Pistachio	360	2
PS	167.5	1	Pecan	560	2
PMMA	164.5	3	Paranut	330	2
PMMA	187.1	1	Macadamia	540	2
PE	122	4	Hazelnut	330	2
PC	127.2	1	Beechnut	130	2
PAA	244.8	1	Apricot shell	244	4
Nylon 6	157.9	1	CB-H-1	128.1	This work
LDPE	24	5	CB-M-1	113.3	This work
LDPE	19.9	6	CB-L-1	129.7	This work
LDPE	22.4	1	Chitosan	82.9	This work
HDPE	37.9	6			
HDPE	61.8	1			

UHMWPE: Ultra-high molecular weight polyethylene; PVC: Polyvinyl chloride; PVA: Polyvinyl alcohol; PS: Polystyrene; PMMA: Polymethyl methacrylate; PE: Polyethylene; PC: Polycarbonate; PAA: Polyacrylic acid; LDPE: Low-density polyethylene; HDPE: High-density polyethylene.

Table S2. Components of liquid soap used for cleansing tests.

Chemical name	Function	Wt%
Sodium laureth sulfate	Surfactant	10
Cocamide diethanolamine	Thickener	4
Disodium lauryl sulfosuccinate	Surfactant	6
Lauryl glucosides	Surfactant	3
Glycerin	Humectant	2
Citric acid	pH controller	0.1
Sodium Chloride	Thickener	0.1
Purified water		74.6
Sodium Hyaluronate	Skin conditioner	0.1
Centella asiatica	Skin conditioner	0.1

Table S3. Effects of different Chito-beads concentrations on germination rate, shoot length, root length, dry weight, and seedling vigor index of *Avena sativa* L.

	Control (0 mg/kg)	100 mg/kg	1000 mg/kg
Shoot length (cm)	28.7 (± 4.4)	26.3 (± 9.4)	28.7 (± 4.8)
Root length (cm)	18.0 (± 8.0)	18.4 (± 7.1)	18.2 (± 5.3)
Germination rate (%)^a	100 (± 0)	100 (± 0)	90 (± 4.71)
Dry weight (g)^b	0.13 (± 0.013)	0.145 (± 0.002)	0.153 (± 0.019)
SVI - I	4678 (± 162)	4471 (± 312)	4442 (± 337)
SVI - II	13.0 (± 1.3)	14.5 (± 0.2)	13.8 (± 1.8)

^aPercentage of plants grown after 14 days divided by the total seed planted. ^bTotal dry mass divided by the number of samples. Data are the mean \pm standard error.

Table S4. Effects of different Chito-beads concentrations on germination rate, shoot length, root length, dry weight, and seedling vigor index of *Brassica napus L.*

	Control (0 mg/kg)	100 mg/kg	1000 mg/kg
Shoot length (cm)	11.9 (± 1.7)	10.5 (± 1.6)	11.0 (± 1.6)
Root length (cm)	12.8 (± 8.1)	16.3 (± 5.1)	16.3 (± 3.5)
Germination rate (%)^a	80 (± 0)	70 (± 5.34)	90 (± 4.71)
Dry weight (g)^b	0.162 (± 0.025)	0.22 (± 0.003)	0.175 (± 0.014)
SVI - I	2085 (± 214)	1876 (± 210)	2447 (± 161)
SVI - II	13.0 (± 2.0)	15.4 (± 1.2)	15.8 (± 1.5)

^aPercentage of plants grown after 14 days divided by the total seed planted. ^bTotal dry mass divided by the number of samples. Data are the mean \pm standard error.

Table S5. Characterization of base soil used for phytotoxicity test according to fertilizer quality inspection of rural development administration, Korea.

Parameters	Base soil
Nitrogen (mg/kg)	1226.1
pH	6.75
Soil water (%)	21.47
Bulk density (g/cm ³)	0.58
Electrical conductivity (dS/m)	0.42
<i>Listeria monocytogenes</i>	Not detected
Arsenic (mg/kg)	2.09
Cadmium (mg/kg)	0.26
Mercury (mg/kg)	0.0075
Lead (mg/kg)	11.25
Copper (mg/kg)	28.96
Nickel (mg/kg)	35.72
Zinc (mg/kg)	60.94

Supplementary Figures

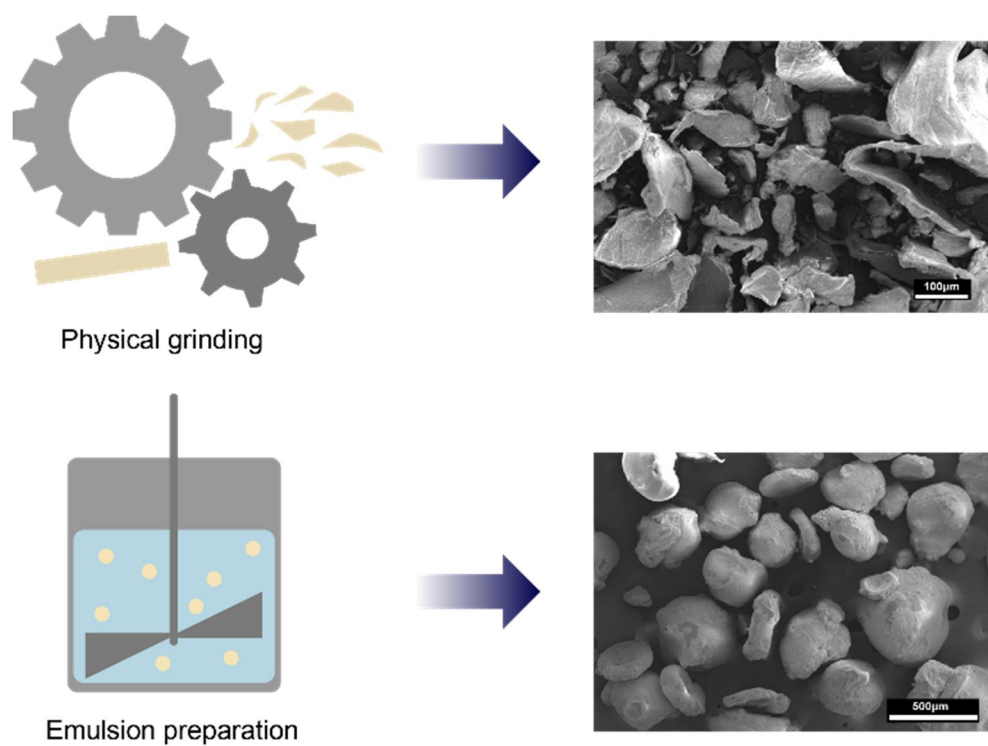


Fig. S1. Differences in particle morphology according to the preparation methods.

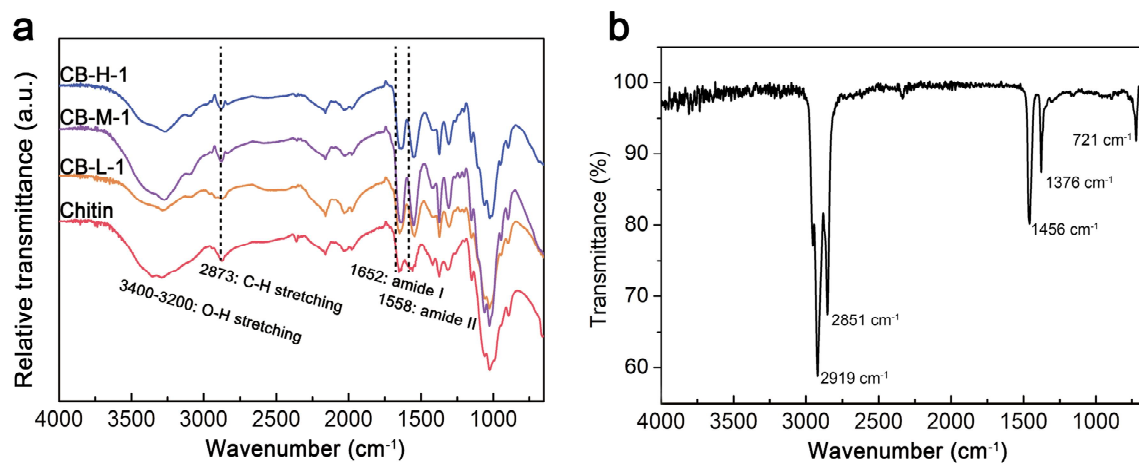


Fig. S2. (a) FTIR spectra of chito-beads compared with commercial chitin powder. (b) FTIR spectra of paraffin oil used in the continuous phase. 2851 cm^{-1} and 2919 cm^{-1} (C–H stretching), 1456 cm^{-1} (C–H bending), and 721 cm^{-1} (CH_2 rocking)⁷.

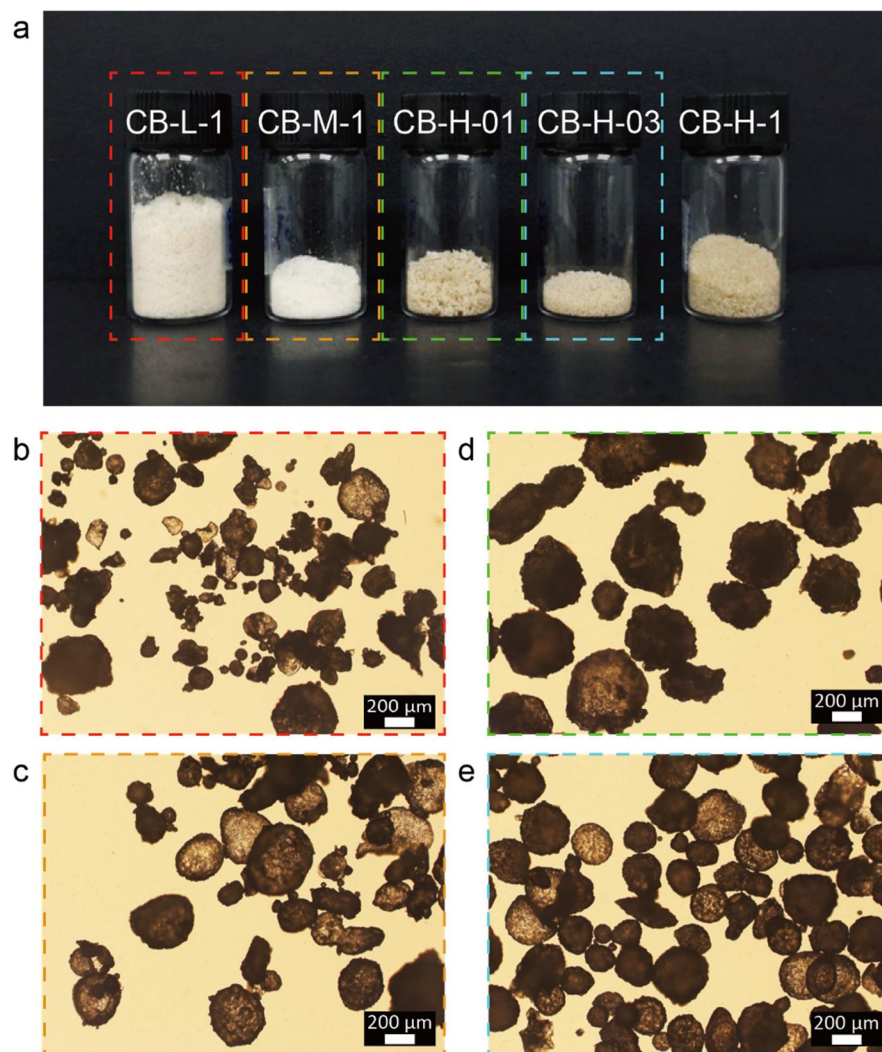


Fig. S3. (a) Photograph of acetylated chitosan microbeads differing molecular weight and degree of acetylation. Optical microscope images of: (b) CB-L-1, (c) CB-M-1, (d) CB-H-01, and (e) CB-H-03.

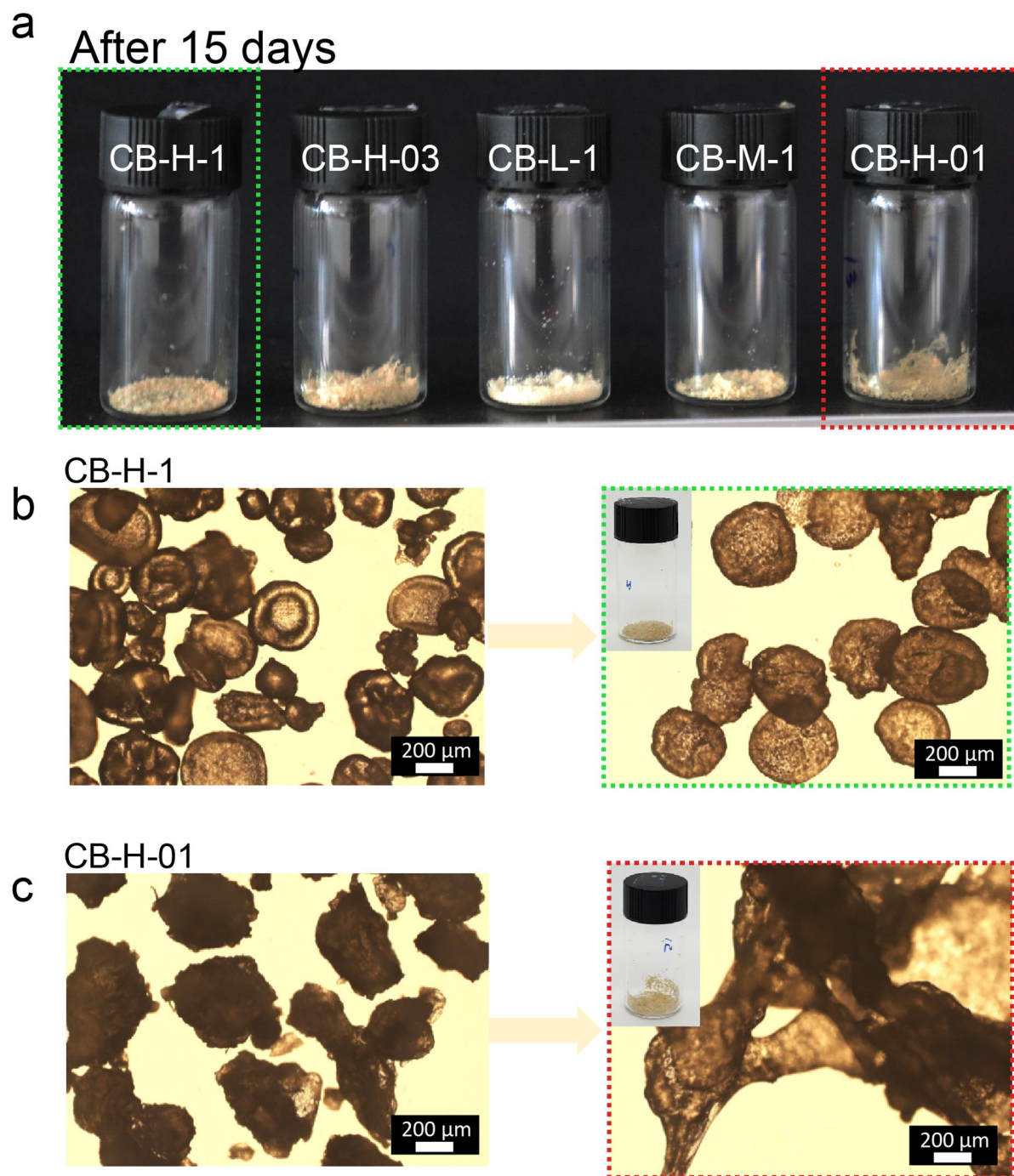


Fig. S4. (a) Photograph of acetylated chitosan particles soaking in deionized (DI) water for 2 weeks; (b) optical microscope image of CB-H-1 particles maintaining its shape after 2 weeks in DI water; and (c) optical microscope image of CB-H-01 particles deformed its shape after 2 weeks in DI water.

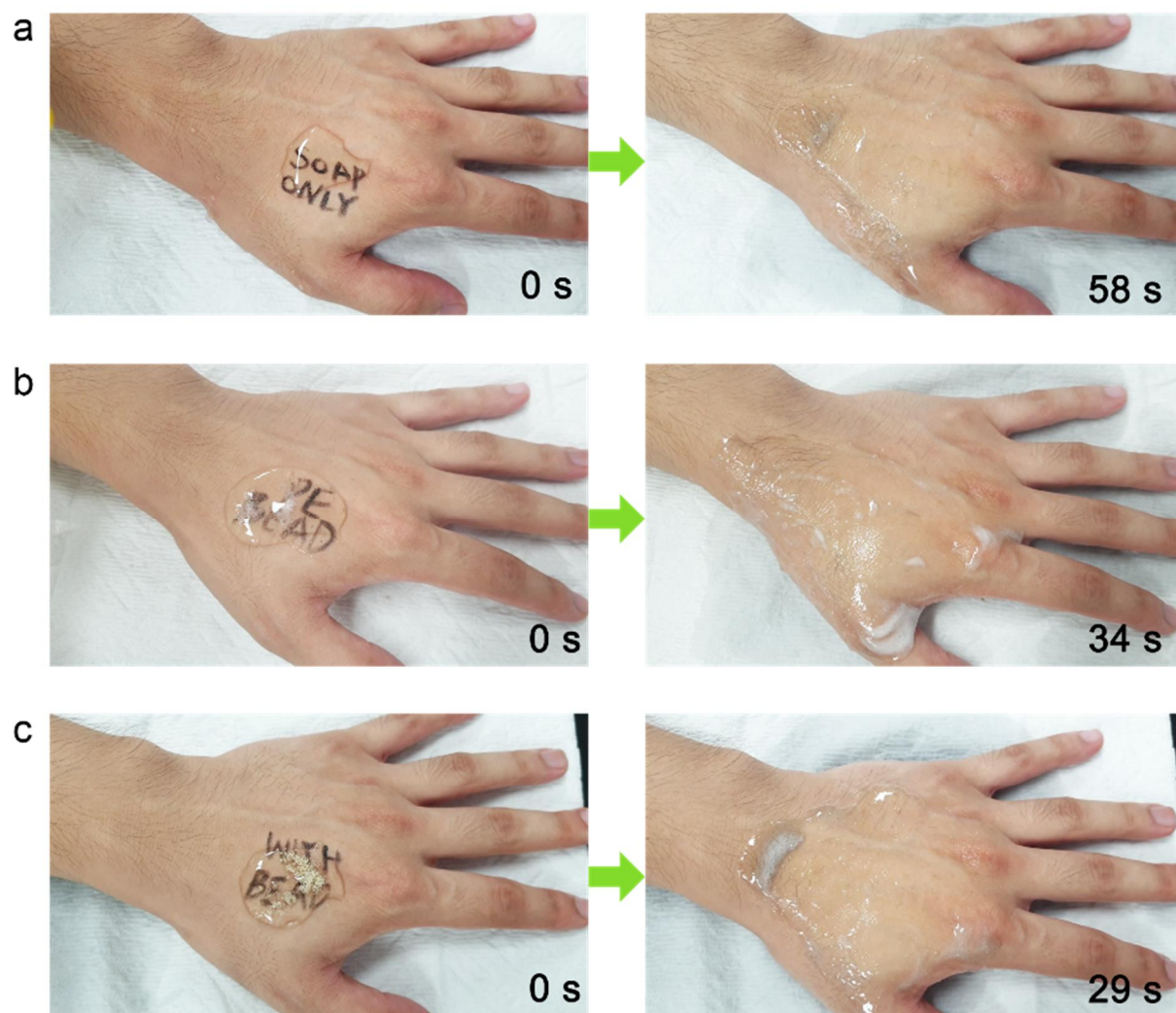


Fig. S5. Comparison of cleansing efficiency using: (a) Liquid soap; (b) soap with polyethylene (PE) beads; and (c) soap with CB-H-1 on the skin.

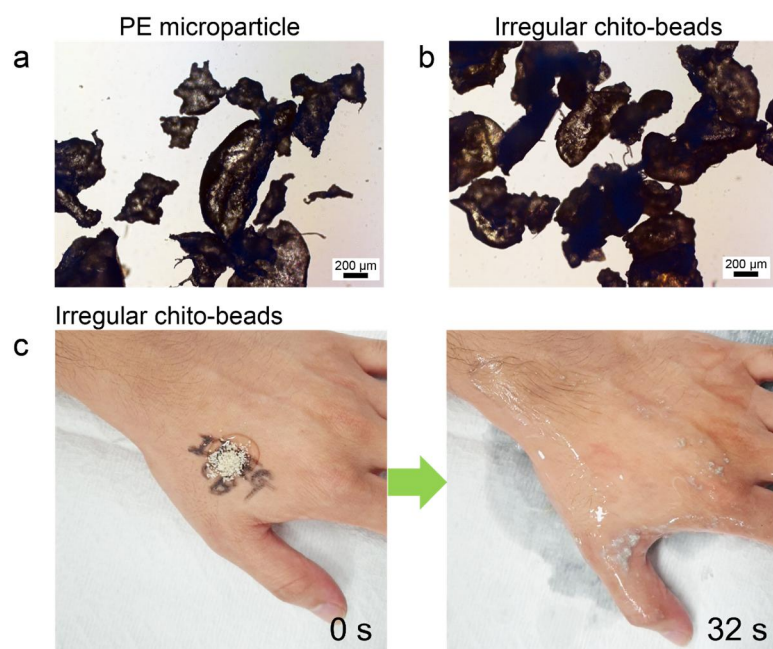


Fig. S6. Optical microscope image of (a) PE microparticle, (b) irregular chito-beads; (c) Cleansing efficiency using soap with irregular CB-H-1 on skin.

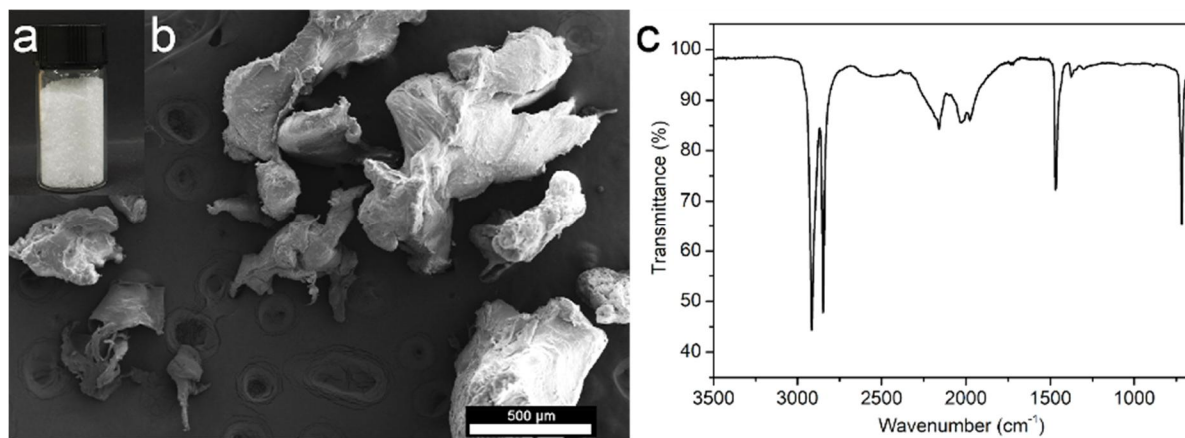


Fig. S7. (a) Photograph and (b) SEM image of polyethylene (PE) microbeads extracted from commercial body scrub; and (c) FTIR spectra.

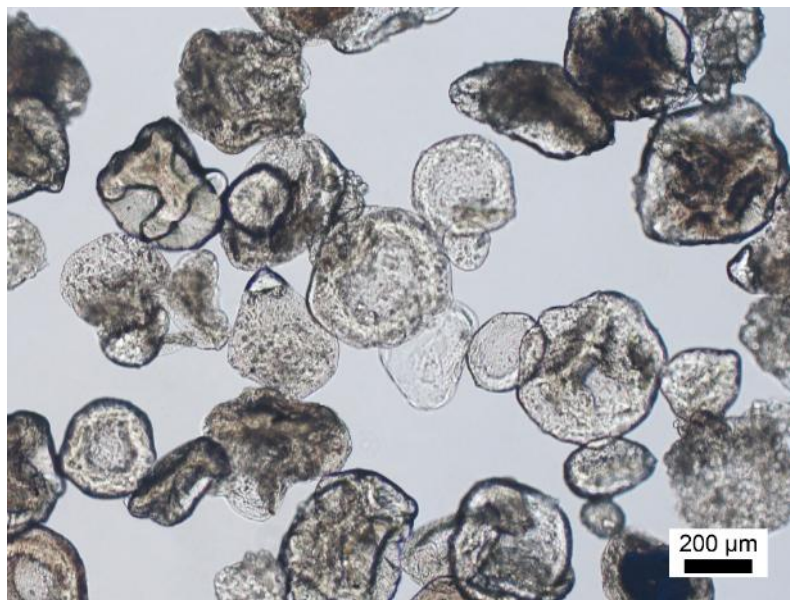


Fig. S8. Optical microscope image of CB-H-1 stored in paraffin oil for 15 days.

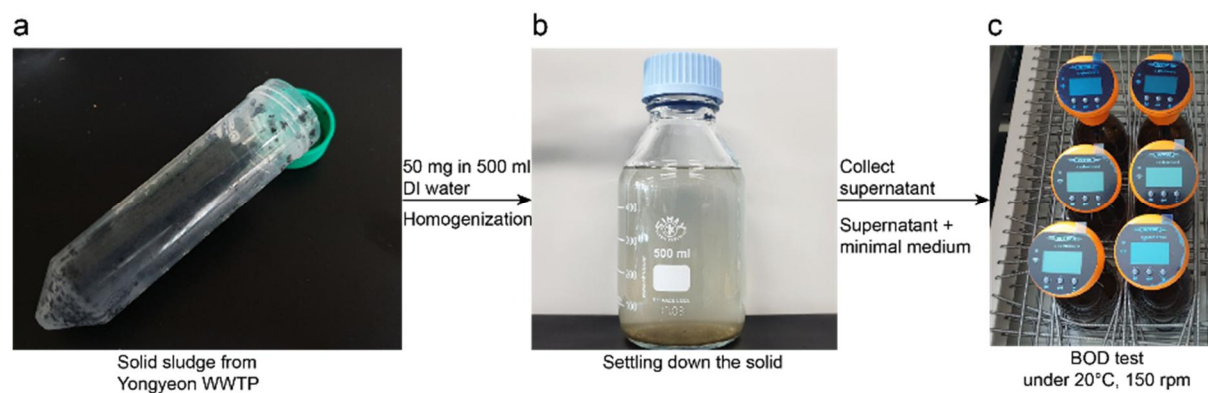


Fig. S9. Photographs of: (a) Obtained solid sludge; (b) homogenized and settling down; and (c) incubating for 15 days at 20 °C and 150 rpm in the dark condition.

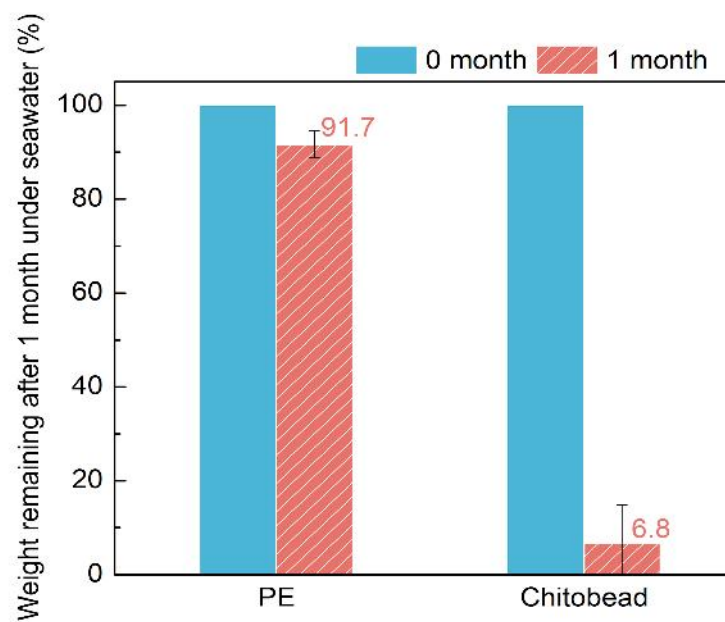


Fig. S10. Weight (%) of polyethylene (PE) microparticles and Chito-beads remaining after 1 month in seawater. Error bars represent the standard deviation.

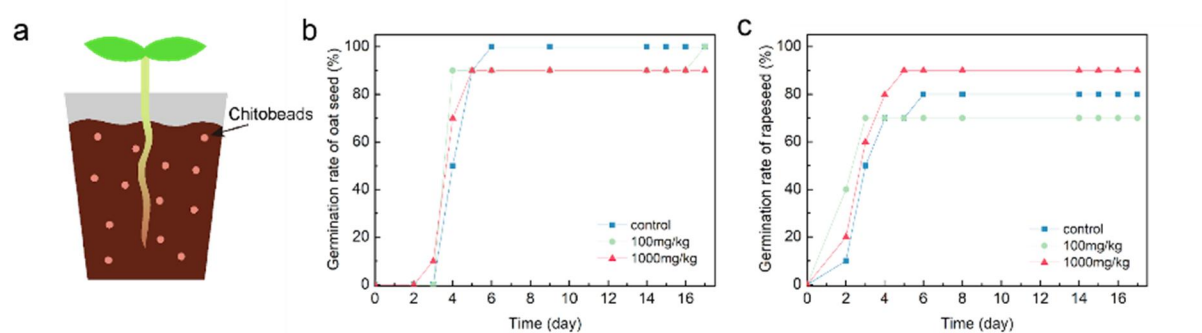


Fig. S11. Phytotoxicity test of Chito-beads in soils. (a) Illustration of plants growing in soils mixed with Chito-beads. Germination rates of: (b) oat (*Avena sativa* L.) and (c) rapeseed (*Brassica napus* L.) for 17 days.

Supplementary References

- 1 A.-Y. Jee and M. Lee, *Polym. Test.*, 2010, **29**, 95-99.
- 2 G. Kaupp and M. R. Naimi-Jamal, *J. Mater. Chem.*, 2011, **21**, 8389-8400.
- 3 Y. Yang, C.-E. He, W. Tang, C. P. Tsui, D. Shi, Z. Sun, T. Jiang and X. Xie, *J. Mater. Chem. A*, 2014, **2**, 20038-20047.
- 4 W. Li, Z. H. Zhai, Q. Pang, L. Kong and Z. R. Zhou, *Wear*, 2013, **301**, 353-361.
- 5 P. Nikaeen, D. Depan and A. Khattab, *Nanomaterials*, 2019, **9**, 1357.
- 6 D. Manas, M. Ovsik, A. Mizera, M. Manas, L. Hylova, M. Bednarik and M. Stanek, *Polymers*, 2018, **10**, 158.
- 7 Amit, R. Jamwal, S. Kumari, A. S. Dhaulaniya, B. Balan and D. K. Singh, *LWT*, 2020, **118**, 108754.