

Supporting Information

Boric acid-crosslinked poly(vinyl alcohol): biodegradable, biocompatible, robust, and high-barrier paper coating

Shinhyeong Choe,^a Seulki You,^b Kitae Park,^c Youngju Kim,^{a,b} Jehee Park,^a Yongjun Cho,^a Jongchul Seo,^c Hanseul Yang,^b and Jaewook Myung*^a

correspondence to: jjaimyung@kaist.ac.kr

^a. Department of Civil and Environmental Engineering, KAIST, Daejeon, 34141, Republic of Korea

^b. Department of Biological Sciences, KAIST, Daejeon, 34141, Republic of Korea

^c. Department of Packaging & Logistics, Yonsei University, 1 Yonseidae-gil, Wonju-si, Gangwon-do 26493, Republic of Korea

This supporting information file includes:

Text S1 to S3

Table S1 to S3

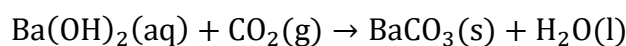
Fig. S1 to S6

Text S1. Calculation for mineralization levels.

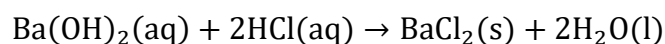
The biodegradation behavior of coated papers (KP-P, KP-PB, and KP-PBH) was assessed by the degree of carbon mineralization into CO₂, employing a systematically designed respirometer, as previously stated.¹ The total carbon content (%) of each sample was determined as an average of 3 respective measurements through a FLASH 2000 series elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Theoretical CO₂ amount as a result of complete mineralization (CO_{2,th}) was then calculated by multiplying the sample weight (W_s) by the carbon content.

$$\text{CO}_{2,\text{th}}(\text{mg}) = W_s (\text{mg}) \times C (\%) \times \frac{44 \text{ mg CO}_2}{12 \text{ mg C}}$$

When the respired CO₂ passes through the 100 mL of 12.5 mM Ba(OH)₂ solution, a precipitate (BaCO₃) forms.



Periodically, the change of buffer capacity in Ba(OH)₂ was evaluated *via* Orion Star T900 automatic titrator (Thermo Fisher Scientific, MA, USA), using 50 mM HCl as a titrant.



Accordingly, 1 mole of produced CO₂ is equivalent to 2 moles of consumed HCl. The Ba(OH)₂ solution was filtered with a 0.45 μm cellulose acetate filter to remove BaCO₃ precipitates and a 30 mL aliquot was titrated. The produced CO₂ is calculated as follows:

$$\text{CO}_2 (\text{mmol}) = \text{Ba}(\text{OH})_{2,\text{i}} (\text{mmol}) - \frac{\text{HCl} (\text{mmol})}{2} \times \frac{\text{Ba}(\text{OH})_{2,\text{o}} (\text{mL})}{\text{Ba}(\text{OH})_{2,\text{a}} (\text{mL})}$$

where CO₂ is the respired CO₂ from a bioreactor, and Ba(OH)_{2,i} is the initial concentration of Ba(OH)₂ solution (12.5 mM). HCl is the concentration of titrant (50 mM). Ba(OH)_{2,o} indicates the final volume of Ba(OH)₂ at the time of titration. Ba(OH)_{2,a} is the aliquot volume used for titration (30 mL). The difference in respired CO₂ between the blank (containing only inoculum) and samples is considered as a net CO₂ production pertaining to the biodegradation, as follows:

$$\text{mineralization} (\%) = \frac{(\text{CO}_{2,\text{s}} (\text{mg}) - \text{CO}_{2,\text{b}} (\text{mg}))}{\text{CO}_{2,\text{th}} (\text{mg})} \times 100$$

where CO_{2,s} and CO_{2,b} are the average of produced CO₂ from the sample and blank bioreactors in milligrams, respectively.

Text S2. Calculation for *E* factor.

The *E* factor (Environmental factor) is defined as the mass ratio of total waste to total product during the manufacturing process. The *E* factor can be expressed as:

$$E \text{ factor} = \frac{\text{total waste (g)}}{\text{total product (g)}}$$

To evaluate the *E* factor of coated papers, the mass of chemicals used in the fabrication process (*i.e.*, BA, HCl, ECH solutions) was used for the calculation (Table S1). The primary assumption applied for the calculations is that 90% of chemicals are recycled and the density of solutions is 1 g/mL. For instance, the *E* factor of KP-PBH is calculated as follows:

$$E \text{ factor} = \frac{0.1[(10 + 100) + (0.5 + 25) + (0.5) + (1 + 99)]}{x} = 23.6/x$$

Where:

- Mass of PVA solution in grams (10 g PVA in 100 ml water)
- Mass of BA solution in grams (0.5 g BA in 25 ml water)
- Mass of HCl solution in grams (0.5 g)
- Mass of ECH solution in grams (100 g)
- Mass of desired product in grams (*x*)

We fabricated twenty A4-sized ($W0.21 \times H0.297$ m) KP-PBH using the chemical solutions. Subsequently, the mass of the product (KP-PBH) can be calculated by multiplying the total area by its basic weight (g/m^2), utilizing the density of KP-PBH reported in an earlier study (110 g/m^2).²

$$\text{Total area} = 20 \times (0.21 \text{ m} \times 0.297 \text{ m}) = 1.25 \text{ m}^2$$

$$\text{Total mass} = \frac{110 \text{ g}}{\text{m}^2} \times 1.25 \text{ m}^2 = 137.5 \text{ g}$$

Accordingly, the *E* factor of KP-PBH is 0.17.

Text S3. Scanning electron microscopy (SEM).

The coated papers (KP-P, KP-PB, and KP-PBH) strips immersed in seawater/sediment mixture were retrieved after 60 d of the microcosm experiment. The samples were transferred into a freshly prepared 2.5% paraformaldehyde-glutaraldehyde fixing solution buffered with 0.1 M phosphate buffer (pH 7.2) for 2 h and washed with the same buffer for 10 min. The samples were postfixed in 1% osmium tetroxide in the 0.1 M phosphate buffer at 25 °C for 1 h. The samples were then dehydrated with a series of increasing concentrations of ethanol/isoamyl acetate solutions (30, 50, 70, 80, 98, and 100% for 10 min, respectively), followed by critical point drying in liquid CO₂ *via* EM CPD300 (Leica, Germany). Finally, the samples were sputtered with gold in a sputter coater SC502 (POLARON, Canada) and observed using the scanning electron microscope FEI Quanta 250 FEG (FEI, USA) at a magnification of 2500–10000×. The surface morphology of both sides (*i.e.*, coated and uncoated) was observed in order to discriminate the microbial colonization patterns.

Table S1. Oxygen transmission rate (OTR), water vapor transmission rate (WVTR), oil resistance, tensile strength, and fracture load of the coated papers (KP-P, KP-PB, and KP-PBH). OTR: oxygen transmission rate. WVTR: water vapor transmission rate. RH: relative humidity. N.A.: not applicable.

Sample	Barrier properties			Mechanical properties		
	OTR (cc/m ² ·d)	WVTR (g/m ² ·d)	Oil resistance (Kit No.)	Tensile strength (0% RH, MPa)	Tensile strength (80% RH, MPa)	Fracture load (50% RH, kPa)
KP	N.A.	N.A.	1	31.4 ± 3.2	26.1 ± 3.5	199.4 ± 3.1
KP-P	5.30 ± 0.50	50.7 ± 4.0	12	40.3 ± 2.1	24.2 ± 3.9	319.7 ± 12.7
KP-PB	1.92 ± 0.04	28.0 ± 3.6	12	45.1 ± 1.7	38.8 ± 2.5	361.8 ± 10.1
KP-PBH	0.89 ± 0.03	5.2 ± 0.4	12	53.0 ± 4.8	51.9 ± 1.2	462.6 ± 42.2

Table S2. Biodegradation test results. The values were calculated on 111 d of the marine biodegradation test. The values are the averages of duplicates. The rate constant (k , d^{-1}) was assessed assuming that the biodegradation behavior of the coated papers follows the first-order decay model³⁻⁵.

Test material	Carbon content (%)	Theoretical CO₂ (mg)	Respired CO₂ (mg)	Mineralization (%)	k (d^{-1})
Blank	-	-	38.7 ± 2.40	-	-
KP	40.65 ± 0.08	33.99 ± 0.07	66.7 ± 3.32	94.4 ± 14.4	0.029
KP-P	45.47 ± 0.11	43.09 ± 0.10	72.70 ± 7.64	81.6 ± 17.0	0.015
KP-PB	46.73 ± 0.19	39.41 ± 0.16	61.93 ± 6.33	59.2 ± 27.7	0.008
KP-PBH	46.09 ± 0.08	34.13 ± 0.06	58.18 ± 6.62	60.5 ± 18.4	0.008

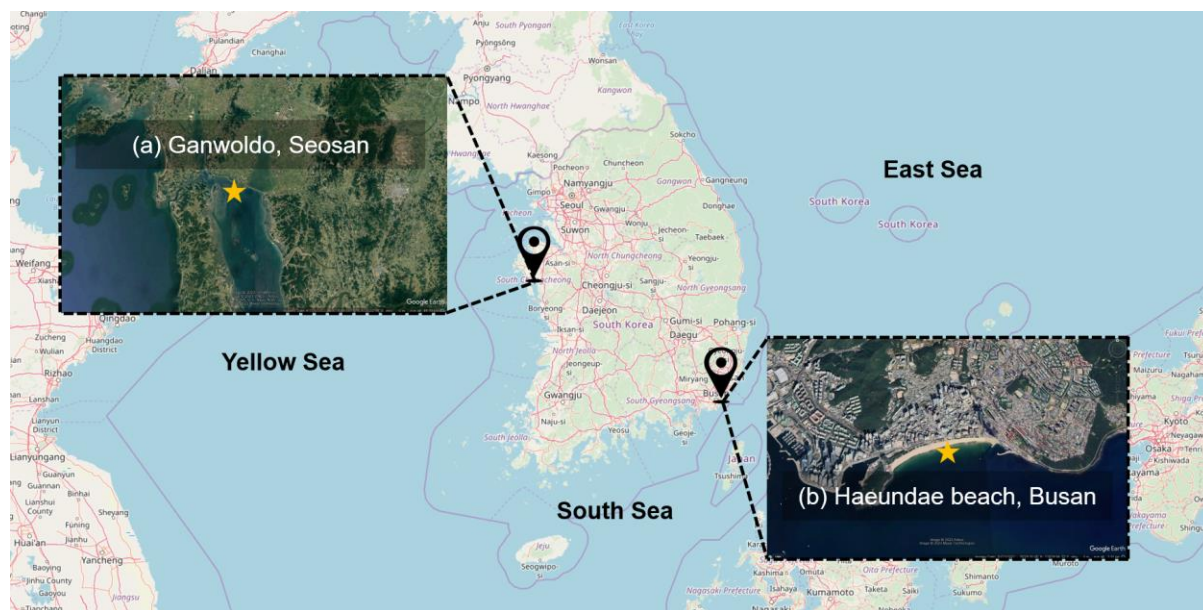


Fig. S1. Map of two sampling sites for collecting seawater and sediment (*i.e.*, inoculum) used for marine biodegradation test. (a) Ganwoldo, Seosan, South Korea ($36^{\circ}36'09''\text{N}$, $126^{\circ}24'42''\text{E}$), (b) Haeundae Beach, Busan, South Korea ($35^{\circ}09'30''\text{N}$, $129^{\circ}09'45''\text{E}$). Geologically distinct sites (Yellow and South Sea) were selected as sampling points for microbial heterogeneity. The map was created using OpenStreetMap, and image screenshots were taken from Google Earth.

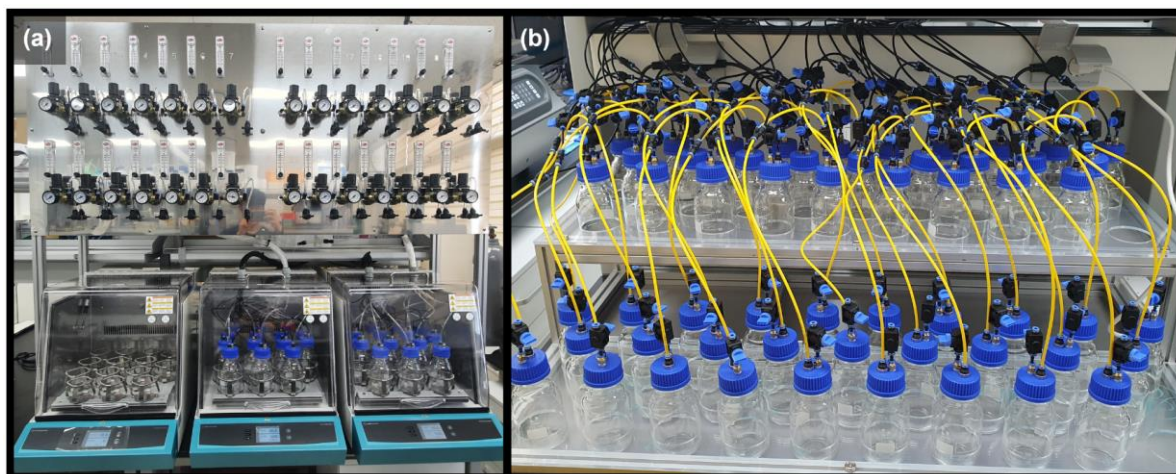


Fig. S2. Biodegradation respirometer employed in this study. (a) Gas flow control system and bioreactors in incubators. (b) CO₂ trapping system. The respired CO₂ resulting from the biodegradation was constantly captured in two stages of Ba(OH)₂ solutions and quantified using titration. The detailed scheme of the respirometer can be found in our previous study ¹.

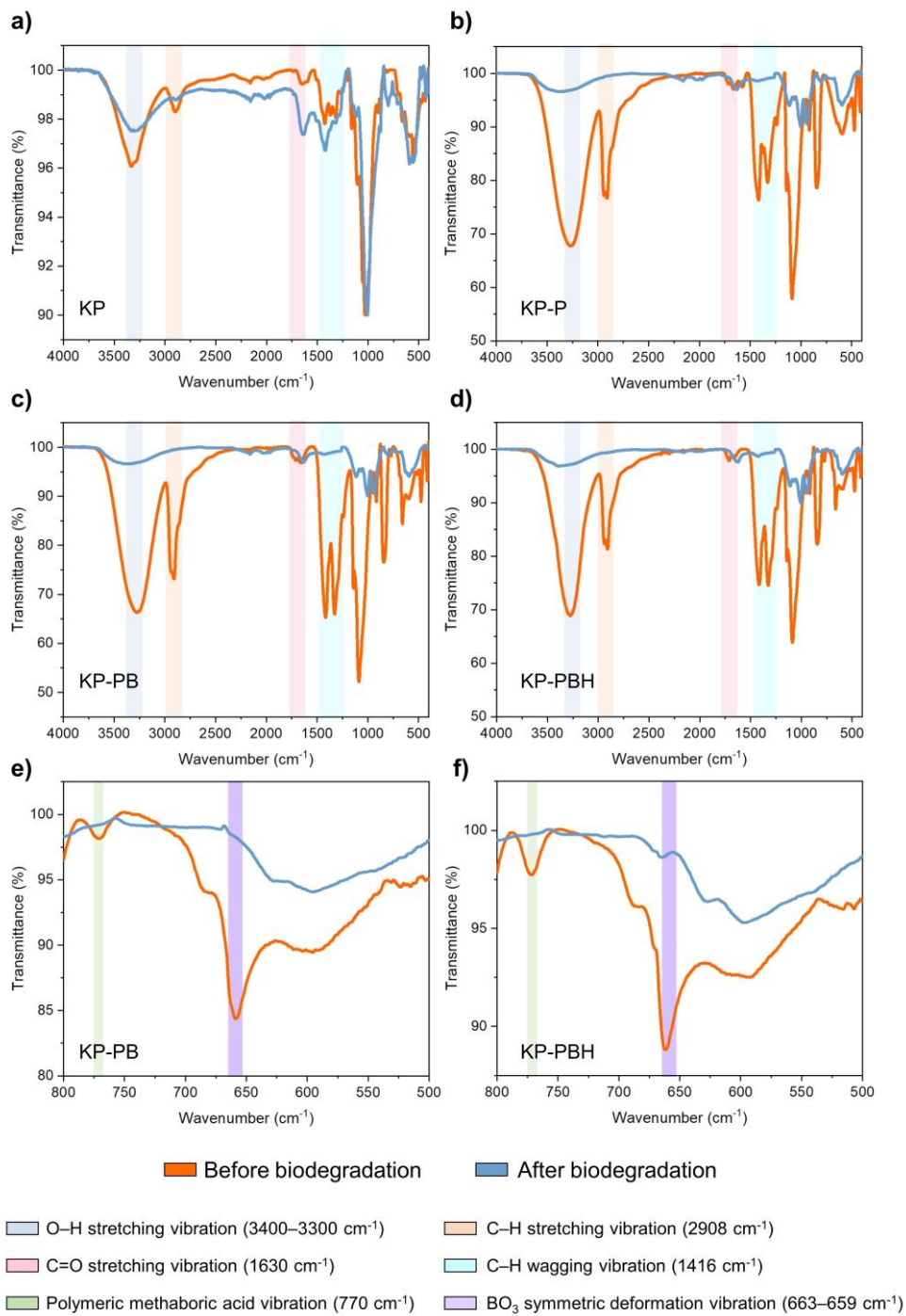


Fig. S3. FT-IR graphs of (a) KP, (b) KP-P, (c,e) KP-PB, (d,f) KP-PBH before and after biodegradation test. The shaded regions indicate the characteristic peaks of molecular bonds in the samples.

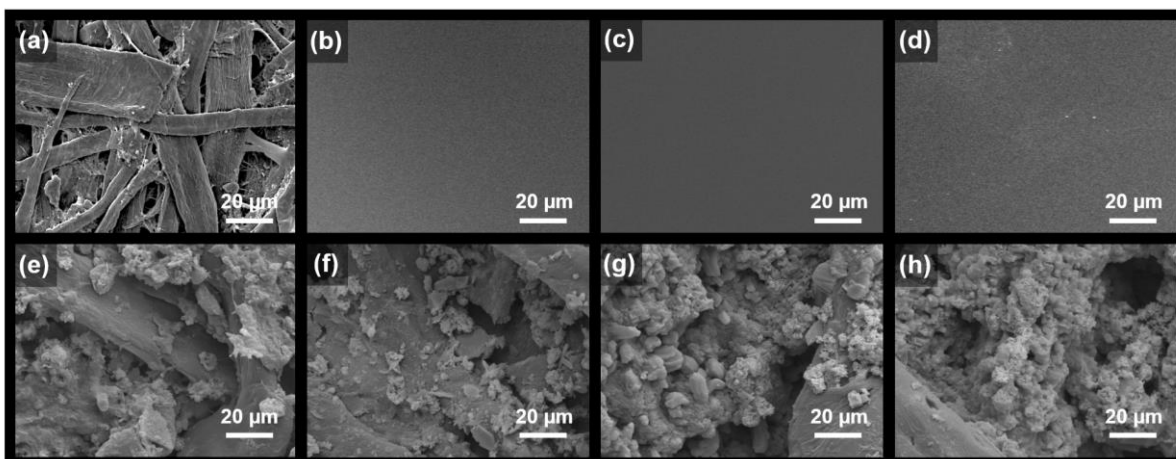


Fig. S4. SEM images after biodegradation test. (a and e) KP, (b and f) KP-P, (c and g) KP-PB, and (d and h) KP-PBH. (a and d) Initial samples, (e and h) Residue collected after marine biodegradation test performed for 111 d.

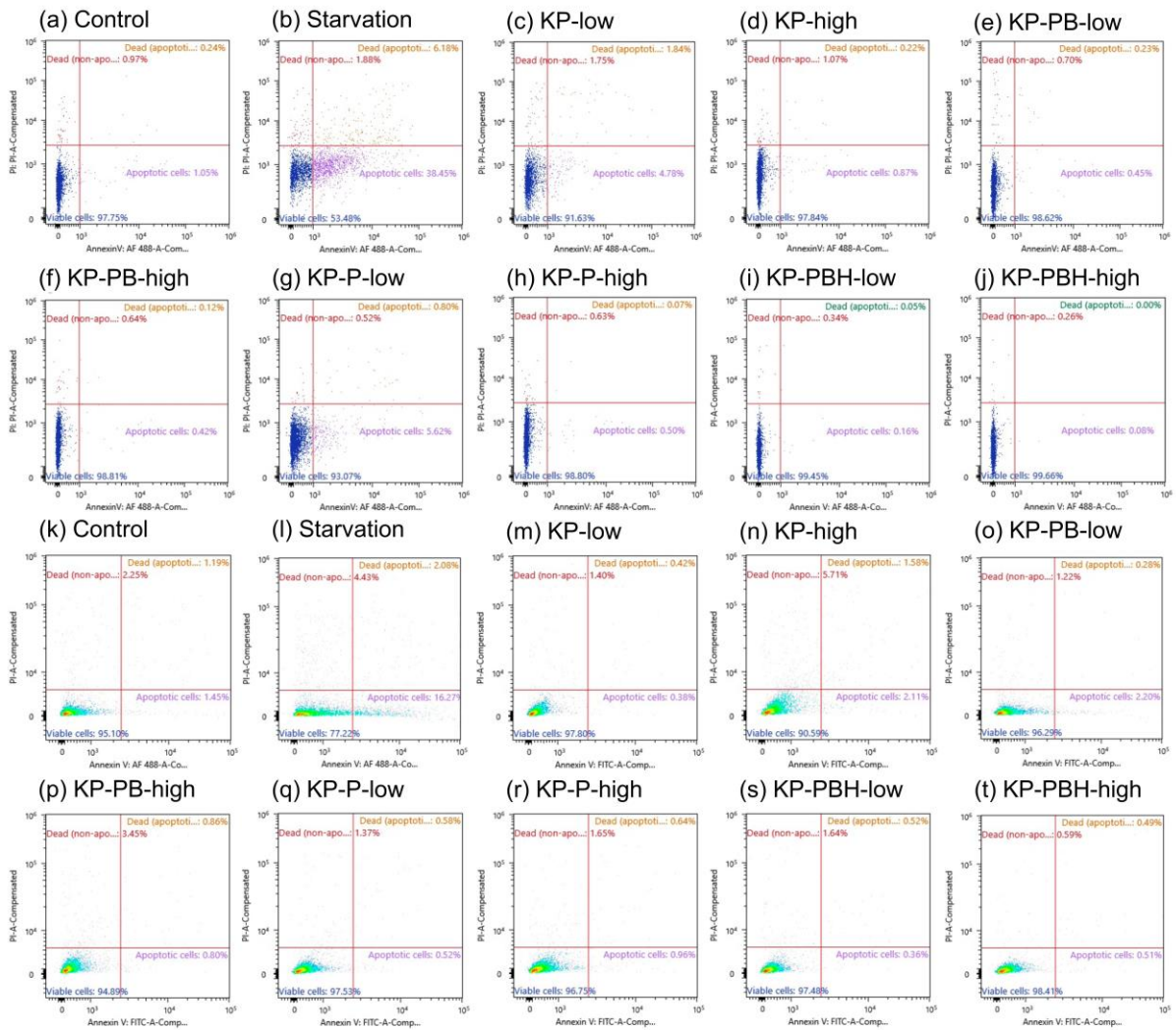


Fig. S5. *In vitro* biocompatibility analysis results of coated papers (KP-P, KP-PB, and KP-PBH) with (a-j) Mouse embryonic fibroblast (MEF) and (k-t) Human embryonic kidney (HEK293) cells. Sample concentrations of 0.05 and 0.2 mg/mL are denoted as low and high, respectively.

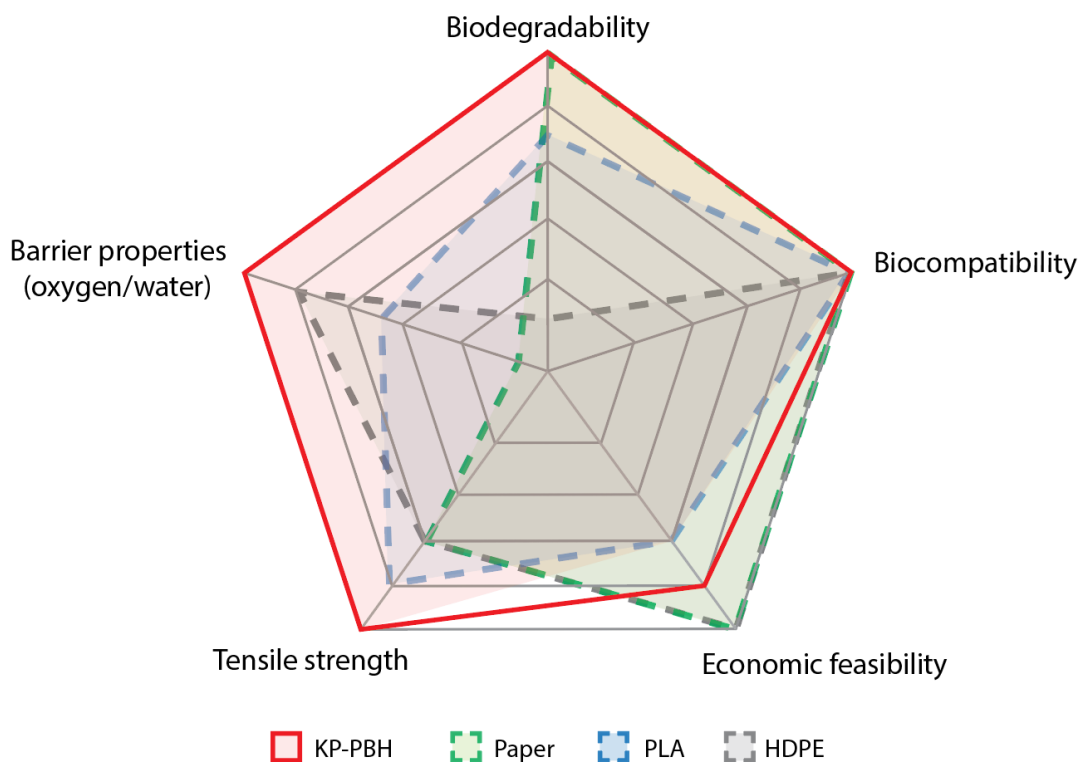


Fig. S6. Comparative versatility of KP-PBH compared to other plastics used for hard packaging applications such as Kraft paper, high-density polyethylene (HDPE), and poly(lactic acid) (PLA).

Table S3. Key properties and economic feasibility of KP-PBH, Kraft paper (KP), High-density polyethylene (HDPE), and poly(lactic acid). OTR: oxygen transmission rate. WVTR: water vapor transmission rate. PVA: poly(vinyl alcohol)

Properties	KP-PBH	Kraft paper	High-density Polyethylene (HDPE)	Poly(lactic acid) (PLA)
Biodegradability	Biodegradable in marine environment	Biodegradable in marine environment	Non-biodegradable ⁶	Biodegradable only in industrial composting ^{3, 6, 7}
Biocompatibility	Biocompatible <i>in vitro</i> and <i>in vivo</i>	Biocompatible <i>in vitro</i> and <i>in vivo</i>	Biocompatible <i>in vitro</i> and <i>in vivo</i>	Biocompatible <i>in vitro</i> and <i>in vivo</i>
Tensile strength (MPa)	80	25.6	24–32 ⁸	44–65 ³
Barrier properties	OTR (cc/m ² ·d)	0.87 ⁹	15780	49.2 ¹⁰
	WVTR (g/m ² ·d)	4.0 ⁹	790	0.76 ¹⁰
Economic feasibility (USD \$/kg)	KP: 0.1–1.0 ¹² PVA: 1.2 ¹³	0.1–1.0 ¹²	0.95–1.18 ⁸	3.31–3.53 ⁸

Reference List

1. S. Choe, Y. Kim, G. Park, D. H. Lee, J. Park, A. T. Mossisa, S. Lee and J. Myung, *ACS Appl. Polym. Mater.*, 2022, **4**, 5077-5090.
2. K. Park, S. Choe, K. Sadeghi, P. K. Panda, J. Myung, D. Kim and J. Seo, *Food Chem.*, 2024, **445**, 138772.
3. G. X. Wang, D. Huang, J. H. Ji, C. Völker and F. R. Wurm, *Adv. Sci.*, 2021, **8**, 2001121.
4. S. Chinaglia, M. Tosin and F. Degli-Innocenti, *Polym. Degrad. Stab.*, 2018, **147**, 237-244.
5. F. Ruggero, R. Gori and C. Lubello, *Waste Manag. Res.*, 2019, **37**, 959-975.
6. O. García-Depraect, R. Lebrero, S. Rodríguez-Vega, S. Bordel, F. Santos-Beneit, L. J. Martínez-Mendoza, R. A. Börner, T. Börner and R. Muñoz, *Bioresour. Technol.*, 2022, **344**, 126265.
7. E. L. Eronen-Rasimus, P. P. Nakki and H. P. Kaartokallio, *Environ. Sci. Technol.*, 2022, **56**, 15760-15769.
8. X. Zhao, K. Cornish and Y. Vodovotz, *Environ. Sci. Technol.*, 2020, **54**, 4712-4732.
9. K. Park, Y. Oh, P. K. Panda and J. Seo, *Prog. Org. Coat.*, 2022, **173**, 107186.
10. M. Sun, S. Zhu, C. Zhang, A. Olah, E. Baer and D. A. Schiraldi, *ACS Appl. Polym. Mater.*, 2019, **1**, 259-266.
11. Y. B. Tee, R. A. Talib, K. Abdan, N. L. Chin, R. K. Basha and K. F. M. Yunus, *BioResources*, 2016, **11**, 1518-1540.
12. Fastmarket, Drop in Unbleached Kraft Paper Prices, <https://www.fastmarkets.com/insights/drop-in-unbleached-kraft-paper-prices>). (accessed April 2023).
13. M. S. Islam, i *Industrial Applications of Biopolymers and their Environmental Impact*, CRC Press, 2020, pp. 135-152.