

Abbreviations

^mCPBA, m-chloroperoxybenzoic acid

CALB, Immobilized lipase from *Candida antarctica*

TF, Transforming factor, ratio of oxidized functional groups

EA, Ethyl acetate

M6, *T. fusca* cutinase mutant, D204C/E253C/H184S/Q92G/F209I/I213K

LDPE, Low-density polyethylene

_{UV}PE, LDPE irradiated by UVC for 8 d

EA-_{UV}PE, _{UV}PE soaked in ethyl acetate for 1 d

CALB-_{UV}PE, Using CALB-EA-H₂O₂ catalysis system to treat _{UV}PE for 1 d

CALB-_{UV}PE-M6, Using *T. fusca* cutinase M6 hydrolysis system to treat CALB-_{UV}PE for 7 d

_{CPBA}PE, Using ^mCPBA catalysis system to treat LDPE

_{CPBA}PE-M6, Using *T. fusca* cutinase M6 hydrolysis system to treat _{CPBA}PE for 7 d

EA-_{CPBA}PE, _{CPBA}PE soaked in ethyl acetate for 1 d

CALB-_{CPBA}PE, Using CALB-EA-H₂O₂ catalysis system to treat _{CPBA}PE for 1 d

CALB-_{CPBA}PE-M6, Using *T. fusca* cutinase M6 hydrolysis system to treat CALB-_{CPBA}PE for 7 d

Changes to the morphology of polyethylene under different oxidation treatments

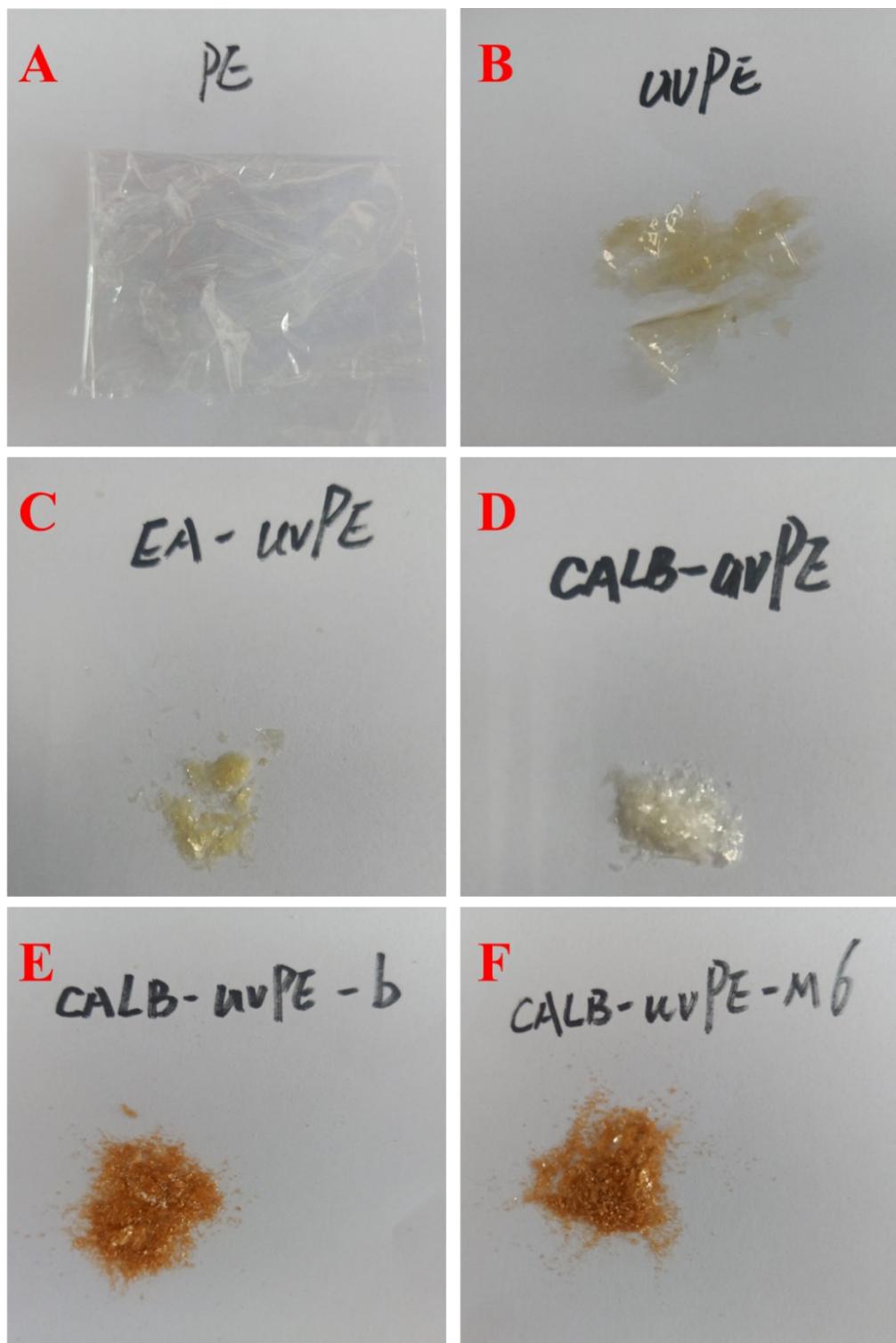


Fig. S1 Changes in polyethylene morphology during the treatment of LDPE by the CALB-EA-H₂O₂ catalytic system and *T. fusca* cutinase M6 hydrolysis system (pathway I).

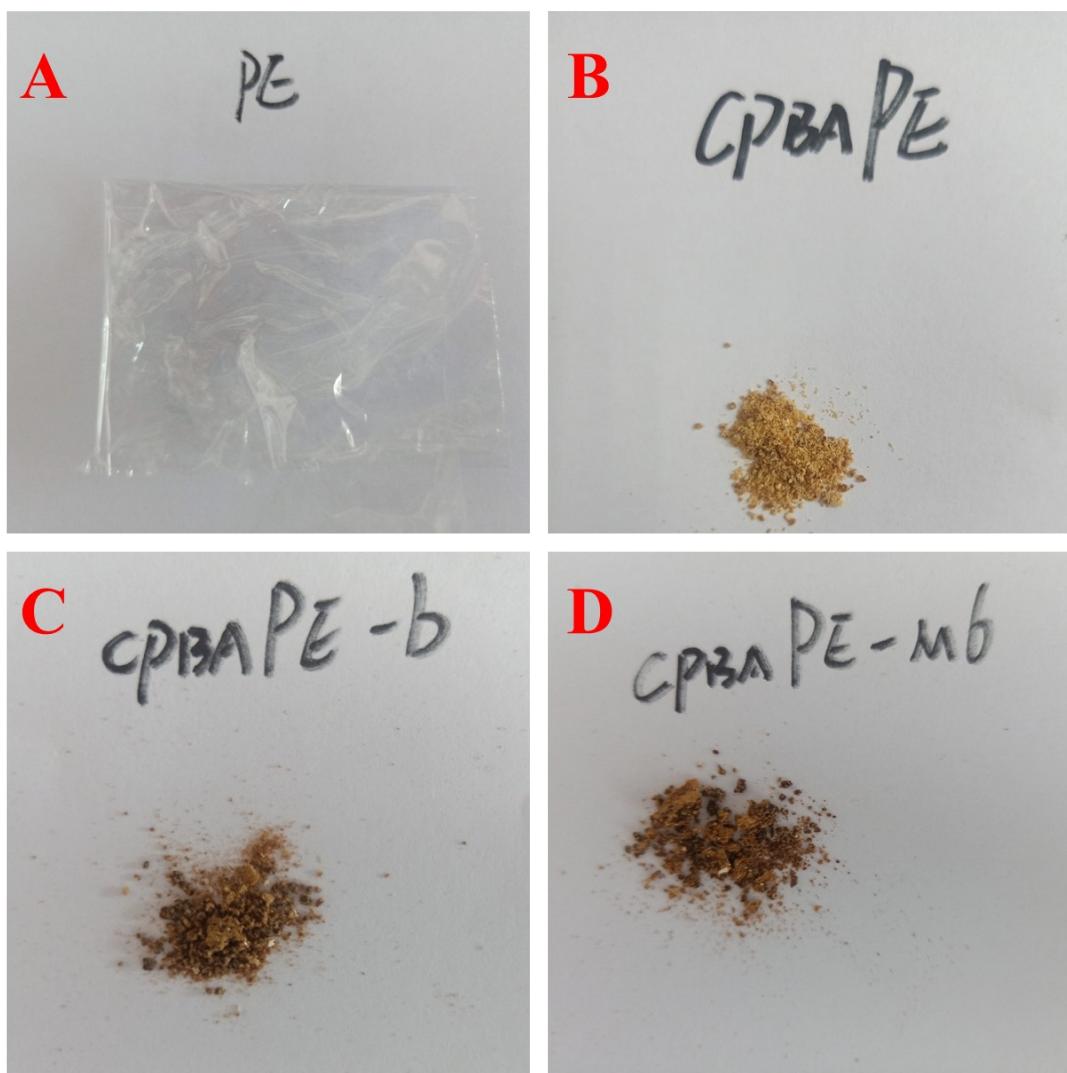


Fig. S2 ^mCPBA catalytic system and *T. fusca* cutinase M6 hydrolysis system.
polyethylene morphology changes during the treatment of LDPE. (Pathway II)

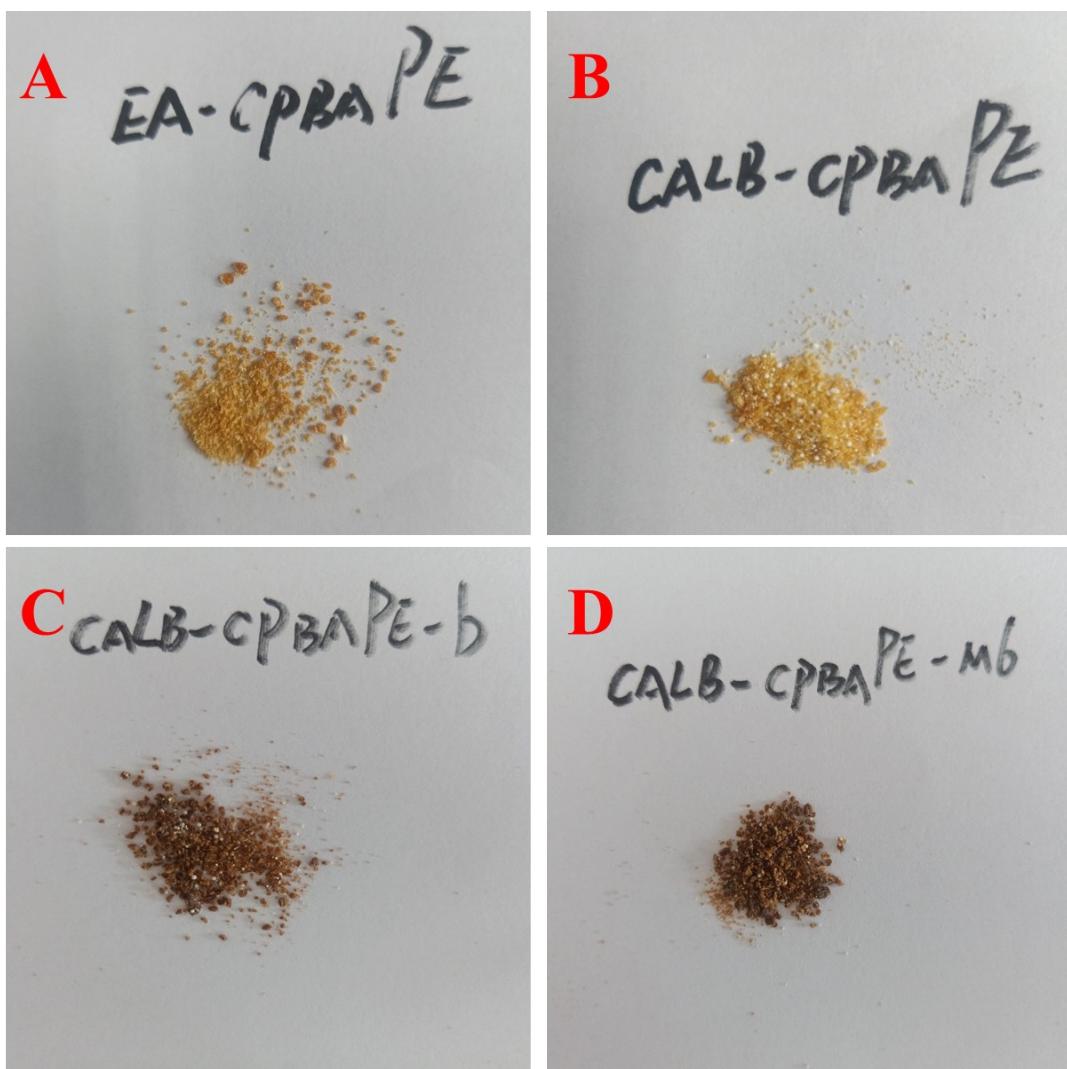


Fig. S3 Changes in polyethylene morphology during the treatment of CPBA PE by the CALB-EA- H_2O_2 catalytic system and *T. fusca* cutinase M6 hydrolysis system (pathway III).

NMR Data

NMR Data for _{uv}PE: ¹H NMR (700 MHz, C6D4Cl2) δ 5.73 (td, J = 16.9, 6.7 Hz), 4.90 (dd, J = 43.5, 13.7 Hz,), 3.55 – 3.48 (m, CH₂-OH), 2.21 (dt, J = 15.3, 7.7 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.78 – 0.69 (m, CH₂-CH₂-CH₂).

NMR Data for _{CALB-UV}PE: ¹H NMR (700 MHz, C6D4Cl2) δ 5.78 – 5.68 (m), 4.90 (dd, J = 44.4, 13.7 Hz,), 4.21 (ddd, J = 22.6, 12.2, 6.4 Hz, C(O)-OCH₂), 3.51 (s, CH₂-OH), 2.23 (ddt, J = 29.1, 14.8, 6.8 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.26 (s, CH₂-CH₂-CH₂).

NMR Data for _{CALB-UV}PE-M6: ¹H NMR (700 MHz, C6D4Cl2) δ 5.73 (ddt, J = 16.9, 10.0, 6.5 Hz), 5.01 – 4.78 (m), 3.54 – 3.49 (m, CH₂-OH), 2.32 – 2.15 (m, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.26 (s, CH₂-CH₂-CH₂).

NMR Data for _{CPBA}PE: ¹H NMR (700 MHz, C6D4Cl2) δ 5.34 (t, J = 4.9 Hz), 4.04 (t, J = 6.8 Hz, C(O)-OCH₂), 3.82 (s, CH₂-Cl), 3.52 (s, CH₂-OH), 2.25 (dt, J = 21.8, 7.2 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.24 (d, J = 19.9 Hz, CH₂-CH₂-CH₂).

NMR Data for _{CPBA}PE-M6: ¹H NMR (700 MHz, C6D4Cl2) δ 5.33 (t, J = 4.9 Hz), 4.04 (t, J = 6.5 Hz, C(O)-OCH₂), 3.81 (s, CH₂-Cl), 3.52 (d, J = 8.8 Hz, CH₂-OH), 2.24 (dq, J = 24.6, 9.0, 8.0 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.24 (d, J = 19.9 Hz, CH₂-CH₂-CH₂).

NMR Data for _{CALB-CPBA}PE: ¹H NMR (700 MHz, C6D4Cl2) δ 4.03 (q, J = 6.5 Hz, C(O)-OCH₂), 3.82 (s, CH₂-Cl), 3.54 – 3.50 (m, CH₂-OH), 2.23 (ddd, J = 25.5, 12.8, 6.7 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.78 – 0.70 (m, CH₂-CH₂-CH₂).

NMR Data for _{CALB-CPBA}PE-M6: ¹H NMR (700 MHz, C6D4Cl2) δ 4.04 (t, J = 6.7 Hz, C(O)-OCH₂), 3.82 (t, J = 6.4 Hz, CH₂-Cl), 3.52 (d, J = 8.4 Hz, CH₂-OH), 2.24 (ddt, J = 24.0, 16.4, 7.0 Hz, CH₂-C(O)-CH₂/CH₂-C(O)-O), 1.24 (d, J = 19.9 Hz, CH₂-CH₂-CH₂).

¹H NMR Figure

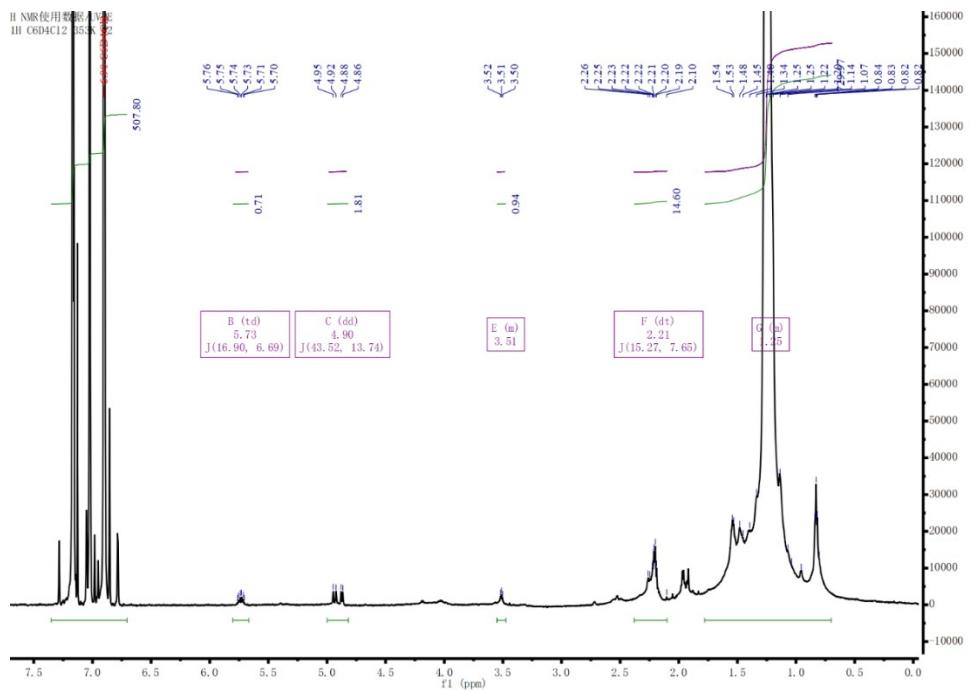


Fig. S4. ¹H NMR data for _{UVPE}.

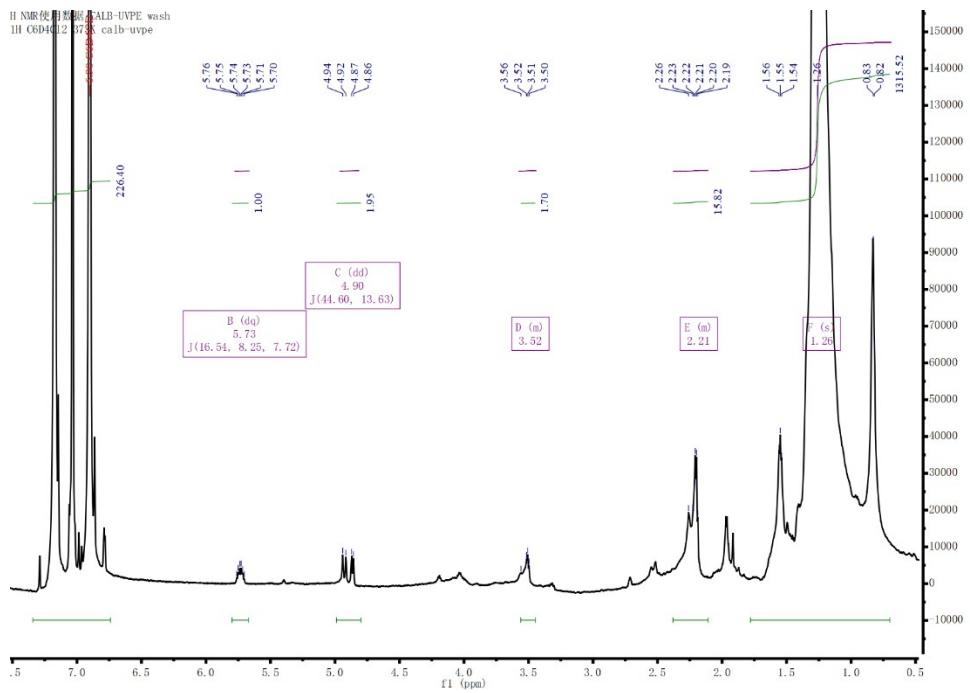


Fig. S5. ¹H NMR data for _{CALB-UVPE}.

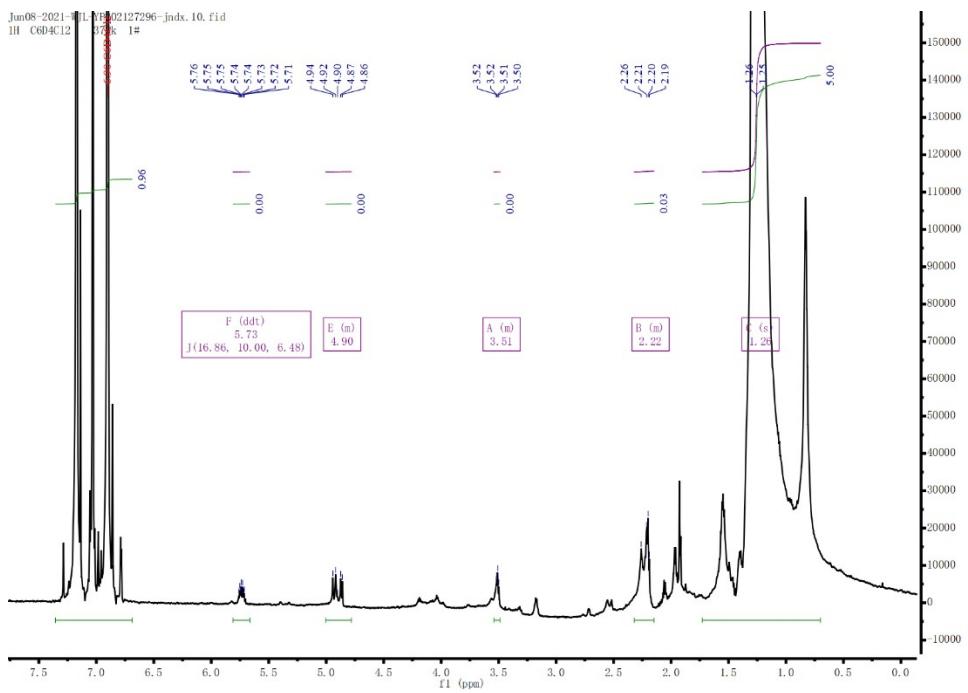


Fig. S6. ¹H NMR data for _{CALB-UVPE-M6}.

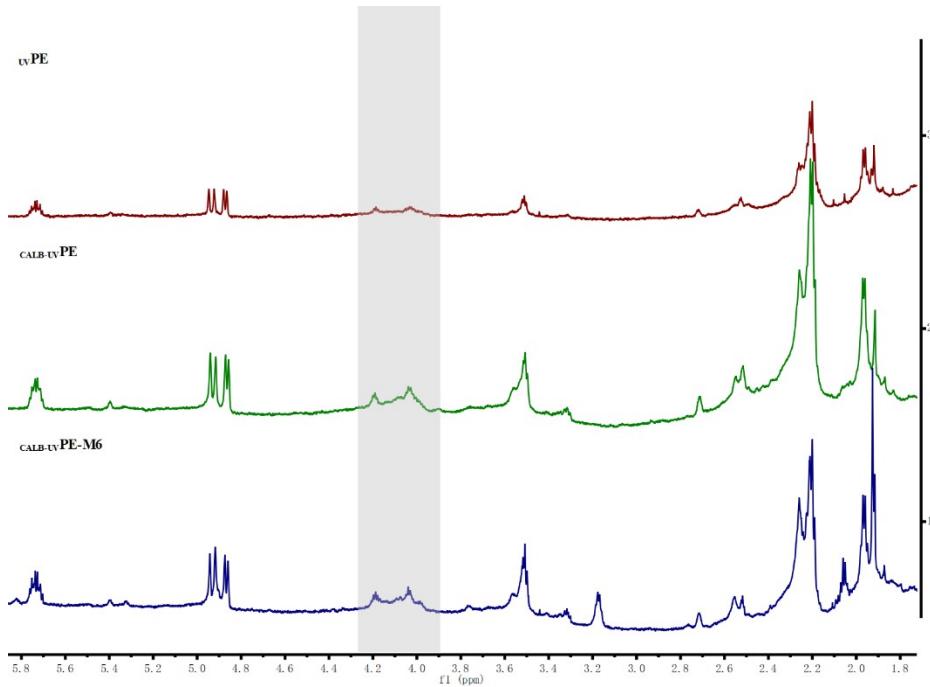


Fig. S7. A comparison of ¹H NMR data on _{UVPE}, _{CALB-UVPE}, and _{CALB-UVPE-M6}. In the figure, the red, green, and blue lines are _{UVPE}, _{CALB-UVPE}, and _{CALB-UVPE-M6}, respectively, and gray area is C(O)-OCH₂.

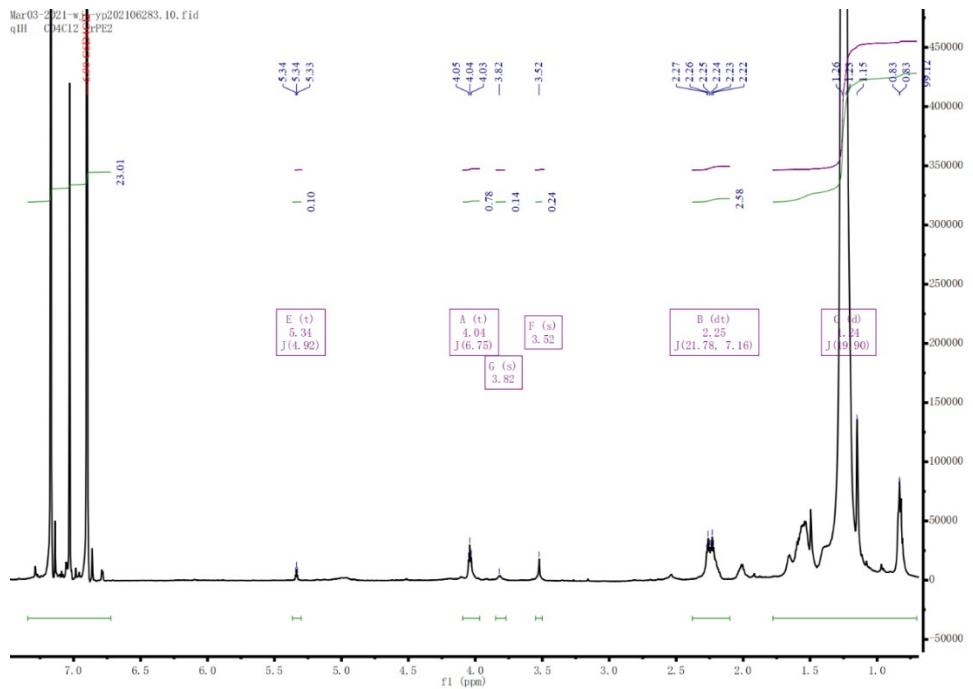


Fig. S8. ^1H NMR data for CPBAPE.

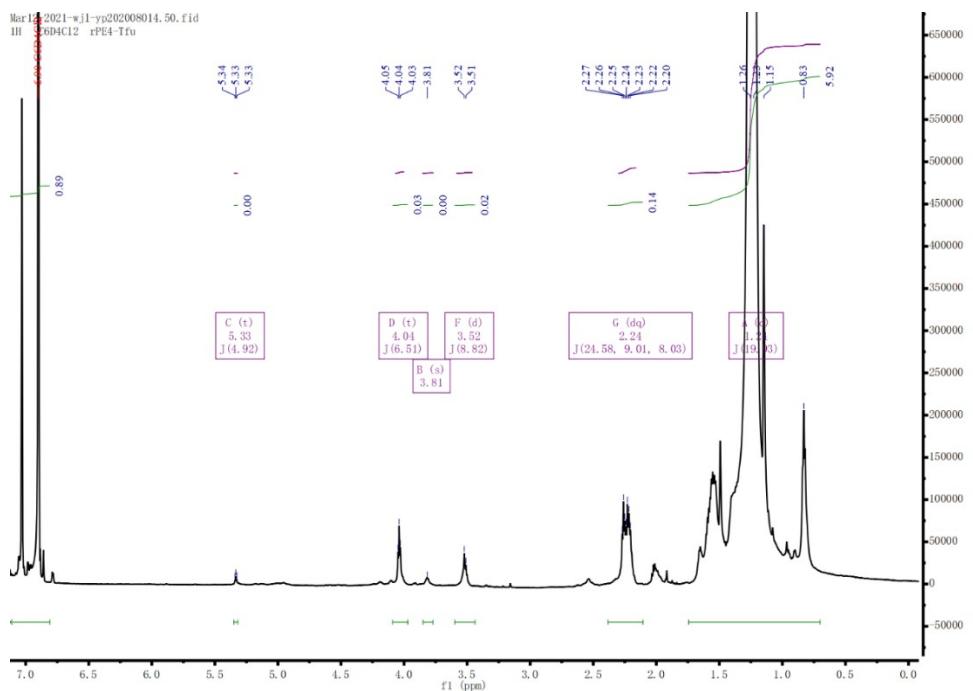


Fig. S9. ^1H NMR data for $_{\text{CPBA}}\text{PE-M6}$.

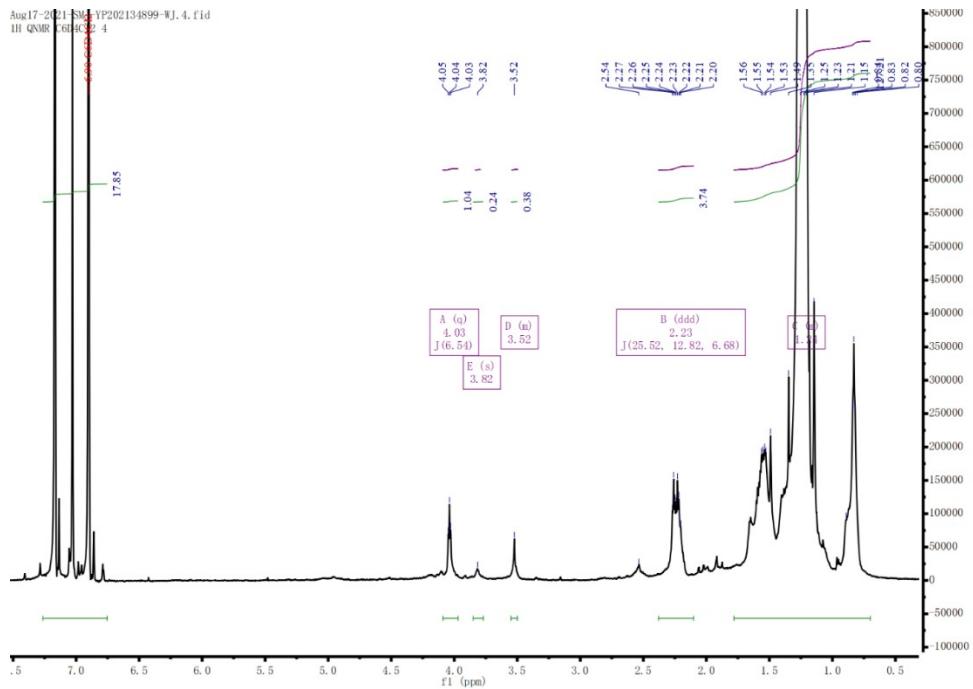


Fig. S10. ^1H NMR data for CALB-CPBAPE .

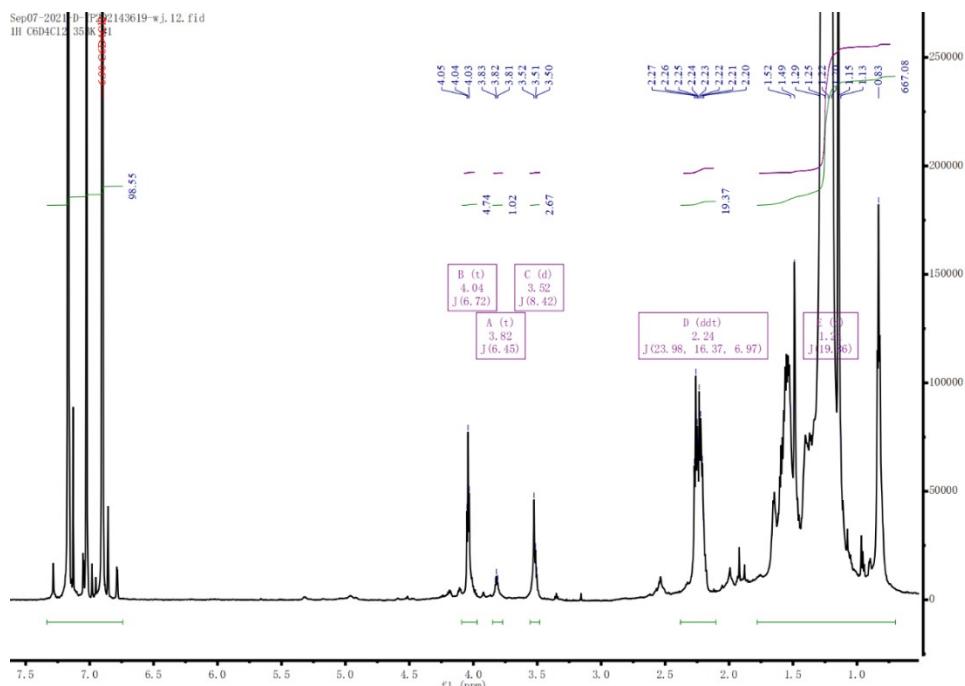


Fig. S11. ^1H NMR data for $_{\text{CALB-CPBA}}\text{PE-M6}$.

¹³C NMR Figure

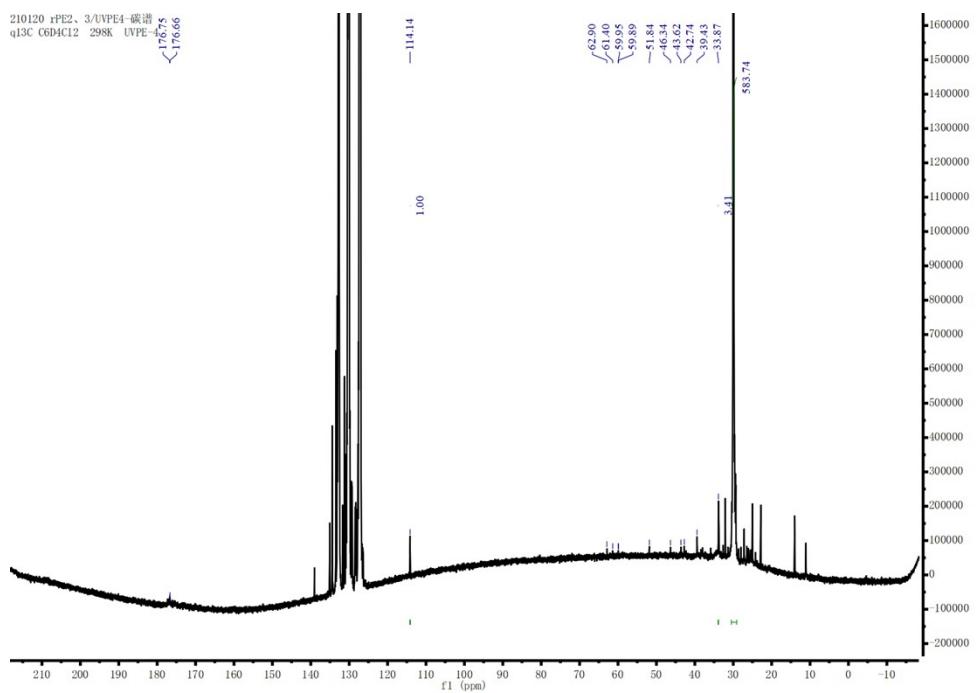


Fig. S12. ¹³C NMR data for UVPE.

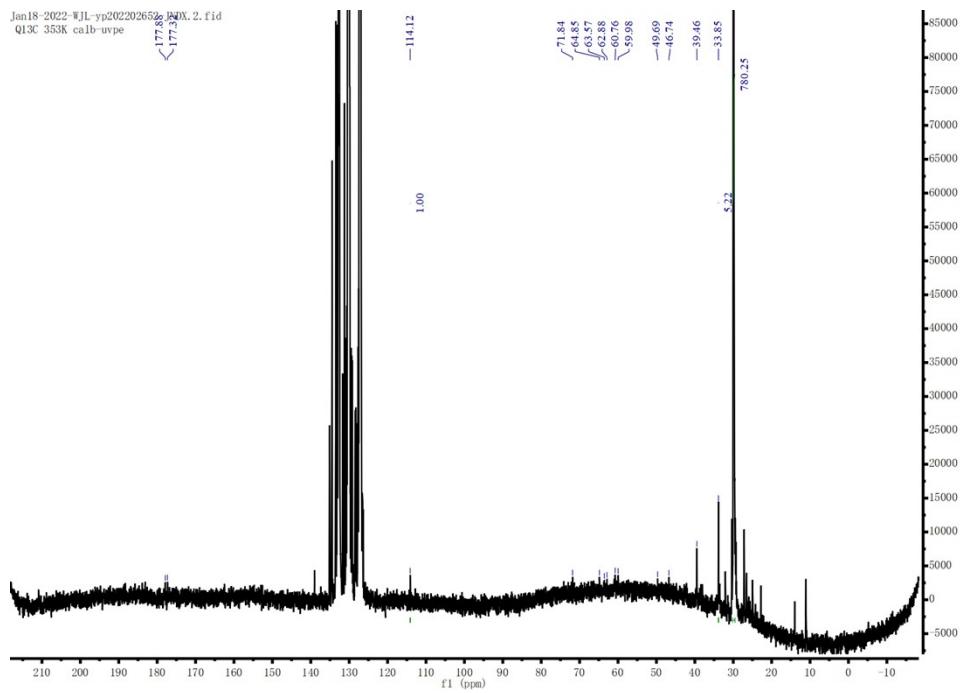


Fig. S13. ¹³C NMR data for CALB-UVPE.

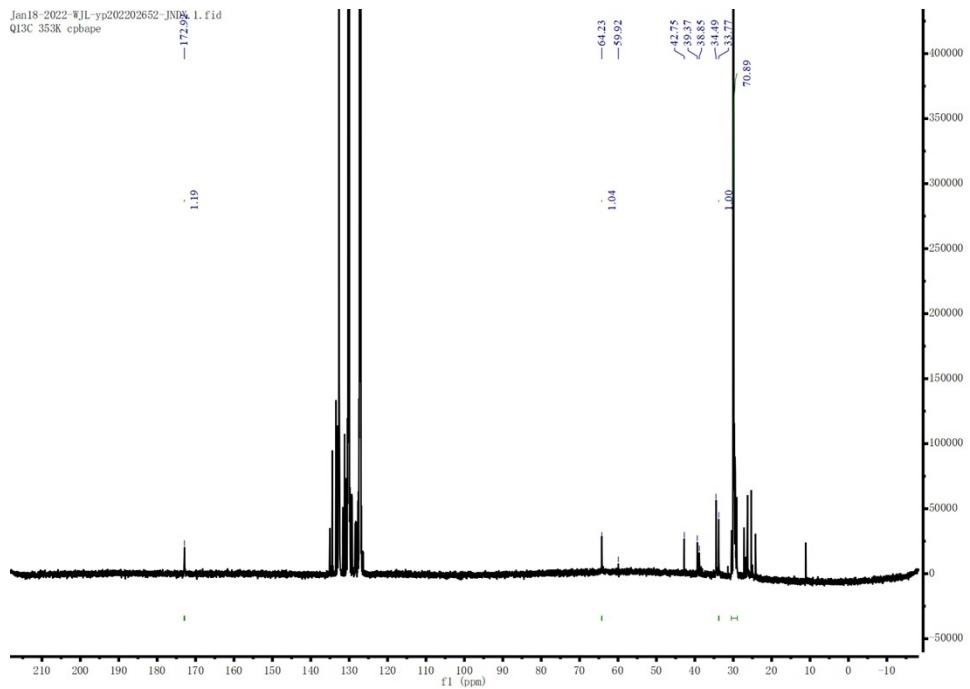


Fig. S14. ¹³C NMR data for _{CPBA}PE.

GC-MS Data

Table S1 Results of GC-MS for the experimental group CALBPE and the control group EA-CALBPE .

Type	Name	Formula	CAS#	$\xi_{(\text{CALBPE})}$	$\xi_{(\text{EA-CALBPE})}$
Alkanes	Tridecane	C13H28	629-50-5	6.33%	-
Alkanes	Heptadecane	C17H36	629-78-7	1.16%	-
Alkanes	Octadecane	C18H38	593-45-3	2.09%	-
Alkanes	Docosane	C22H46	629-97-0	3.41%	-
Alkanes	Hentriaccontane	C31H64	630-04-6	4.13%	-
Acid	Decanoic acid	C10H20O2	334-48-5	1.85%	-
Acid	Dodecanoic acid	C12H24O2	143-07-7	1.42%	-
Acid	Tridecanoic acid	C13H26O2	638-53-9	0.84%	-
Acid	Tetradecanoic acid	C14H28O2	544-63-8	3.02%	-
Acid	Pentadecanoic acid	C15H30O2	1002-84-2	0.80%	-
Acid	Palmitic Acid	C16H32O2	57-10-3	22.20%	64.51%
Acid	Heptadecanoic acid	C17H34O2	506-12-7	0.94%	-
Acid	Octadecanoic acid	C18H36O2	57-11-4	24.09%	35.49%
Acid	Eicosanoic acid	C20H40O2	506-30-9	0.80%	-
Acid	Behenic acid	C22H44O2	112-85-6	4.93%	-
Ester	Undecanoic acid, ethyl ester	C13H26O2	627-90-7	1.93%	-
Ester	Dodecanoic acid, ethyl ester	C14H28O2	106-33-2	1.95%	-
Ester	Tetradecanoic acid, ethyl ester	C16H32O2	124-06-1	2.51%	-
Ester	Pentadecanoic acid, ethyl ester	C17H34O2	41114-00-5	2.80%	-
Ester	Hexadecanoic acid, ethyl ester	C18H36O2	628-97-7	5.73%	-
Ester	Heptadecanoic acid, ethyl ester	C19H38O2	14010-23-2	1.88%	-
Ester	Octadecanoic acid, ethyl ester	C20H40O2	111-61-5	2.56%	-
Ester	Nonadecanoic acid, ethyl ester	C21H42O2	18281-04-4	1.70%	-
Ester	Eicosanoic acid, ethyl ester	C22H44O2	18281-05-5	0.92%	-

Note: “_” represents that the substance is not detected.

Table S2 Results of GC-MS for the enzymatic hydrolysate of oxidized polyethylene treated with *T. fusca* cutinase M6.

Type	Name	Formula	CAS#	$\xi_{(\text{CALB-CPBA PE-M6})}$	$\xi_{(\text{CALB-CPBA PE-B})}$	$\xi_{(\text{CALB-UV PE-M6})}$	$\xi_{(\text{CALB-UV PE-B})}$	$\xi_{(\text{CPBAPE-M6})}$	$\xi_{(\text{CPBAPE-B})}$
Alkanes	Octane	C8H18	111-65-9	-	0.71%	0.62%	0.42%	0.41%	1.00%
Alkanes	Nonane	C9H20	111-84-2	0.04%	-	-	-	-	-
Alkanes	Decane	C10H22	124-18-5	-	-	0.44%	0.54%	0.18%	-
Alkanes	Undecane	C11H24	1120-21-4	0.03%	-	-	-	0.65%	0.12%
Alkanes	Dodecane	C12H26	112-40-3	0.15%	0.24%	0.62%	-	-	0.68%
Alkanes	Tridecane	C13H28	629-50-5	0.11%	0.08%	-	-	-	-
Alkanes	Tetradecane	C14H30	629-59-4	0.29%	-	0.67%	0.81%	0.98%	0.87%
Alkanes	Pentadecane	C15H32	629-62-9	0.50%	3.54%	2.66%	2.39%	4.54%	4.47%
Alkanes	Hexadecane	C16H34	544-76-3	-	1.65%	2.45%	1.21%	3.63%	5.58%
Alkanes	Heptadecane	C17H36	629-78-7	0.06%	0.84%	0.44%	0.94%	2.10%	2.02%
Alkanes	Octadecane	C18H38	593-45-3	0.25%	2.94%	2.34%	1.54%	6.46%	16.57%
Alkanes	Nonadecane	C19H40	629-92-5	0.61%	6.70%	2.02%	2.90%	2.89%	6.10%
Alkanes	Eicosane	C20H42	112-95-8	0.61%	1.16%	1.14%	1.33%	1.00%	3.68%
Alkanes	Heneicosane	C21H44	629-94-7	0.10%	2.82%	2.26%	0.84%	2.37%	5.56%
Alkanes	Docosane	C22H46	629-97-0	0.13%	0.79%	0.54%	0.45%	-	1.94%
Alkanes	Tricosane	C23H48	638-67-5	-	0.98%	0.15%	0.52%	0.24%	0.74%
Alkanes	Tetracosane	C24H50	646-31-1	0.22%	0.66%	0.88%	0.93%	1.33%	1.56%
Alkanes	Hexacosane	C26H54	630-01-3	-	-	0.17%	-	-	-
Alkanes	Heptacosane	C27H56	593-49-7	0.40%	1.00%	1.24%	2.13%	2.36%	4.99%
Alkanes	Octacosane	C28H58	630-02-4	-	-	-	-	0.16%	-
Alkanes	Hentriacontanone	C31H64	630-04-6	0.43%	1.18%	2.06%	1.19%	1.72%	2.31%
Acid	Butyric acid	C4H8O2	107-92-6	-	-	0.71%	0.12%	0.24%	-
Acid	Pentanoic acid	C5H10O2	109-52-4	0.05%	-	-	0.56%	-	-
Acid	Hexanoic acid	C6H12O2	142-62-1	46.50%	7.08%	13.80%	15.12%	10.53%	1.31%
Acid	Heptanoic Acid	C7H14O2	111-14-8	0.02%	-	0.63%	0.02%	3.87%	-
Acid	Octanoic Acid	C8H16O2	124-07-2	38.19%	49.41%	36.76%	50.83%	38.02%	24.85%
Acid	Decanoic Acid	C10H20O2	334-48-5	3.84%	8.70%	6.02%	7.11%	4.06%	8.30%
Acid	Dodecanoic acid	C12H24O2	143-07-7	0.91%	2.58%	2.26%	2.19%	1.57%	1.66%

Acid	Myristoleic acid	C14H28O2	544-63-8	0.80%	1.75%	2.96%	1.86%	0.48%	0.25%
Acid	Palmitic Acid	C16H32O2	57-10-3	4.17%	4.05%	12.04%	3.06%	7.06%	4.39%
Acid	Octadecanoic acid	C18H36O2	57-11-4	1.59%	1.15%	3.98%	0.98%	2.84%	1.04%

Note: “-” shows that the substance was not detected. “B” shows the use of inactivated enzymes as the control group.

Other data

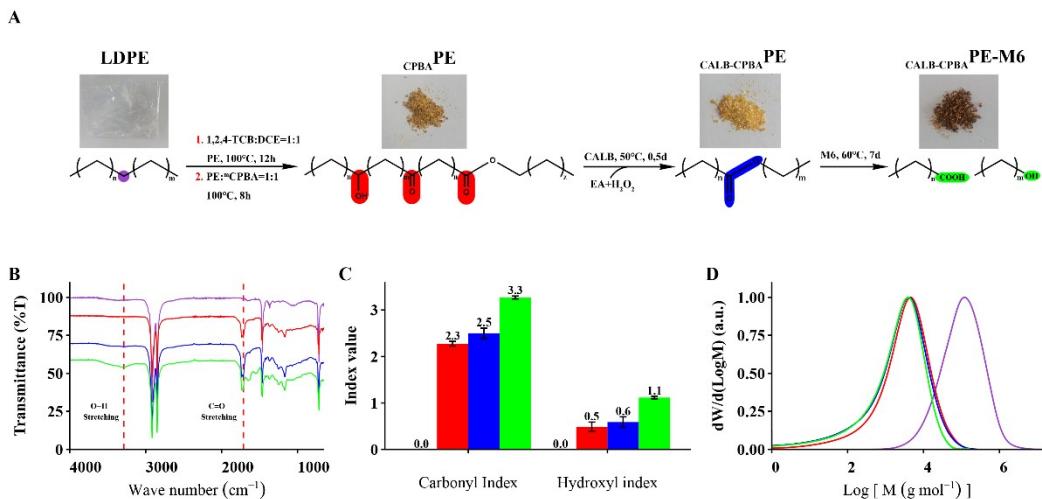


Fig. S15. LDPE degradation based on the ^mCPBA catalysis system, CALB-EA-H₂O₂ catalysis system, and *T. fusca* cutinase hydrolysis system (pathway III). (A) Schematic diagram of the preparation and degradation pathways of oxidized polyethylene in pathway III. (B) FT-IR spectrum (4000–400 cm⁻¹); the red dashed lines are the absorption peaks of O-H and C=O. (C) Comparison of TCI and HI in terms of LDPE, _{CPBA}PE, CALB-_{CPBA}PE, and CALB-_{CPBA}PE-M6. (E) HT-GPC results; distribution of the curves of dW/d (LogM)–LogM. The purple represents LDPE, red is _{CPBA}PE, blue is CALB-_{CPBA}PE, and green is CALB-_{CPBA}PE-M6.

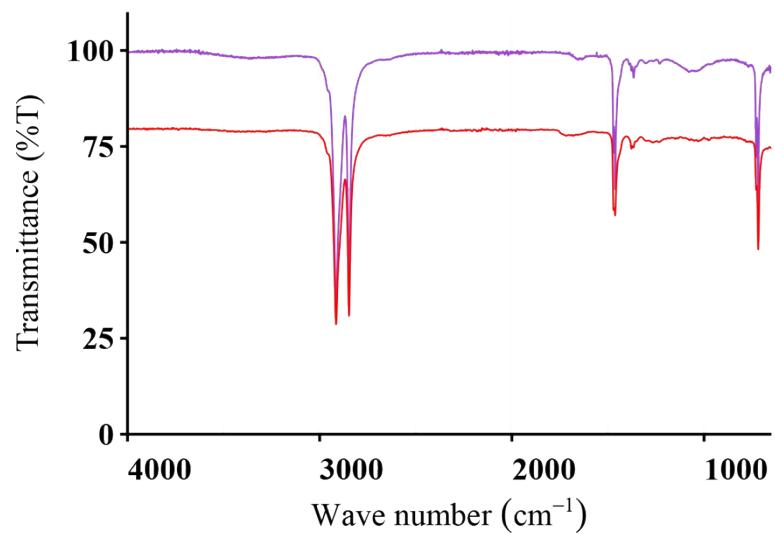


Fig S16. FT-IR data of *T.fusca* cutinase using LDPE as substrate. The red line is the result of *T.fusca* cutinase treatment and the purple line is LDPE.

Table S3 Results of HT-GPC and ^1H NMR detection of polyethylene samples in the pathway III.

Group	HT-GPC		\square	^1H NMR	
	Mw	Mn		A:E:K ^a	TF ^b
CALB-CPBAPE	6261	30	\square	24:33:43	4.95
CALB-CPBAPE-M6	4685	44	\square	32:27:41	5.31

a. A represents a hydroxyl group, E represents an ester bond, and K represents a carbonyl group

b. TF=A+E+K; the number of four functional groups per 100 degrees of polymerized polyethylene

c. Treatment of oxidized polyethylene with *T. fusca* cutinase M6