

Supplementary Information

Selective, Catalytic Oxidation of Polyethylene Surfaces

Cristian P. Woroch,^{1,2} Liana Klivansky,² Declan P. McCarthy,² Heidi Miao,¹ Zachary Fink,^{2,3} Xiaobing Zuo,⁴ Christopher Guthrie,¹ Cheng Wang,³ Brett A. Helms,² and John F. Hartwig*¹
¹*Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States*
²*The Molecular Foundry and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States*
³*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States*
⁴*X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*

*Corresponding author: **John F. Hartwig** - *Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States; Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*
Email: jhartwig@berkeley.edu

Contents

1. Supplemental Methods.....	2
1.1. Synthesis of diiron μ -nitrido tetra- <i>tert</i> -butyl phthalocyanine dimer ([Fe(^t Bu ₄ Pc)] ₂ N, 1). ..	2
1.2. Extraction of organic peroxides into tBuPh.....	3
1.3. Atomic force microscopy for surface roughness determination.	3
1.4. Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements and analysis.	3
2. Supplemental Discussion	4
2.1. Oxidation of octadecane catalyzed by 1.	4
2.2. Investigation of the mechanism of C–H oxidation catalyzed by 1.	7
2.3. Comparison of 1 to other PE oxidation catalysts for functionalization of PE films.....	10
2.4. Understanding ketone selectivity in the oxidation of PE with 1.....	11
2.5. Analyzing the impacts of functionalization on microstructure with self-nucleation.	12
2.6. Impact of extent of oxidation and oxidation method on adhesion properties.....	17
2.7. Reprocessing PE oxidized at the solid–liquid interface.....	18
2.8. Analyzing crystalline microstructure of PE samples by WAXS and SAXS.	32
3. Supplemental Figures.....	39
4. Supplemental Tables.....	104
5. Supplementary References.....	107

1. Supplemental Methods

1.1. Synthesis of diiron μ -nitrido tetra-*tert*-butyl phthalocyanine dimer ([Fe(^tBu₄Pc)]₂N, 1).

The synthesis of diiron μ -nitrido tetra-*tert*-butyl phthalocyanine dimer ([Fe(^tBu₄Pc)]₂N, 1) was adapted from previous literature reports.^{49,50} In a multi-neck flask equipped with a reflux condenser and under an inert atmosphere, 4-*tert*-butylphthalodinitrile (3.2 g, 17 mmol, 4.0 equiv) was dissolved in ethylene glycol (60 mL) at 65 °C. Iron pentacarbonyl (850 mg, 4.3 mmol, 1.0 equiv) was added dropwise with a syringe. The reaction flask was heated to 200 °C under flowing nitrogen for 4 h. The reaction mixture was next diluted with water (~100 mL) and filtered. The blue solid was washed thrice with water (~3×50 mL) and once with a small quantity of methanol (~10 mL) before drying in a vacuum oven at 120 °C overnight to yield the monomeric iron *tert*-butyl phthalocyanine (Fe(^tBu₄Pc)) as a blue solid (1.6 g, 46% yield).

Dimerization of the monomeric species was conducted in smaller batches in a round-bottom flask charged with Fe(^tBu₄Pc) (0.30 g, 0.38 mmol, 1.0 equiv), sodium azide (1.5 g, 23 mmol, 58 equiv), and xylenes (50 mL) under a flowing nitrogen atmosphere (**Caution:** NaN₃ is potentially explosive and should be handled with care). The reaction mixture was brought to reflux behind a blast shield

and allowed to reflux overnight. The reaction mixture was subsequently cooled and chromatographed on neutral alumina. The alumina was washed thrice with dichloromethane (~3×20 mL) before the product was eluted with 10 v/v% ethanol in dichloromethane. The product solution was evaporated before drying in a vacuum oven at 120 °C overnight to yield the nitrido-bridged iron tert-butyl phthalocyanine dimer ([Fe(^tBu₄Pc)]₂N, **1**) as a blue solid (215 mg, 71% yield).

1.2. Extraction of organic peroxides into ^tBuPh.

Tert-butyl hydroperoxide (^tBuOOH, 70 wt% in H₂O) and *tert*-butylbenzene (^tBuPh) were added to a 40-mL scintillation vial in a 2:1 volume ratio and mixed thoroughly. The resulting emulsion was allowed to settle overnight in a refrigerator (4 °C). The organic layer was decanted and used without further purification. Quantification of ^tBuOOH was performed by ¹H NMR spectroscopy using CH₂Br₂ as an internal standard and iodometric titration to determine an average ^tBuOOH concentration of 5.7 M.

2-Methyl-1-phenylprop-2-yl hydroperoxide (MPHP) was synthesized by modification of previously reported methods.^{51,52} 2-Methyl-1-phenylpropan-2-ol (1.2 mL, 7.8 mmol) and hydrogen peroxide (16.2 mL, 159 mmol, 20.4 equiv) were added to a scintillation vial and stirred overnight at 65 °C. At the end of the reaction, MPHP was extracted in an analogous method to ^tBuOOH and used without further purification.

1.3. Atomic force microscopy for surface roughness determination.

Atomic force microscopy (AFM) was performed using a NanoSurf FLEXAFM at the UC Berkeley Biomolecular Nanotechnology Center. Samples were dried *in vacuo* prior to measurement. For each sample, three independent 10 × 10 μm² regions were analyzed. Root-mean-square roughness (*R_q*) was calculated from the AFM height maps using the following expression (Eq. 1):

$$R_q = \sqrt{\frac{\sum (Z_i - Z_{avg})^2}{N}} \quad (\text{Eq. 1})$$

where *Z_i* is the height at a given pixel, *Z_{avg}* is the average height across the height map, and *N* is the number of total pixels.

1.4. Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements and analysis.

SAXS and WAXS measurements were performed at the 12-ID-B beamline of the Advanced Photon Source at Argonne National Laboratory (Lemont, IL). The beamline is equipped with a Dectris Eiger 9M detector for SAXS and a Pilatus 300K detector for WAXS. The wavelength, λ, of X-ray radiation was set to 0.9322 Å. The sample-to-detector distance ranges were set such that the SAXS detector covers a *q* range of 0.003–0.85 Å⁻¹ and the WAXS detector covers 0.8–2.7 Å⁻¹, respectively, where *q*=4π**sin*(θ)/λ (2θ is the scattering angle, λ is the X-ray wavelength). The exposure time was set to 0.3 seconds. The 2-D scattering images were azimuthally averaged to generate 1-D SAXS/WAXS [*I*(*q*) vs *q*] curves using the beamline software.

SAXS profiles were fitted using a Beaucage-type unified model consisting of a low- q Porod contribution, crossover term, constant background, and Gaussian scattering peaks. Domain spacing was calculated from the peak position ($d = \frac{2\pi}{q^*}$), while the domain correlation length was estimated from the peak width using a Scherrer-type relationship: $\xi = \frac{0.9(2\pi)}{FWHM_q}$ where $FWHM_q = 2\sqrt{2\ln(2)}\sigma$.

WAXS profiles were deconvoluted using Gaussian peak fitting to separate the amorphous halo and crystalline polyethylene reflections ((110) and (200)) with a linear background contribution: $I(q) = I_{am} + I_{110} + I_{200} + I_{bg}$. Crystallinity was calculated from integrated peak areas: $X_c = \frac{A_c}{A_c + A_a} \times 100$ where A_c and A_a correspond to the integrated crystalline and amorphous scattering contributions, respectively. All fits were performed using nonlinear least-squares optimization with constrained peak positions and widths.

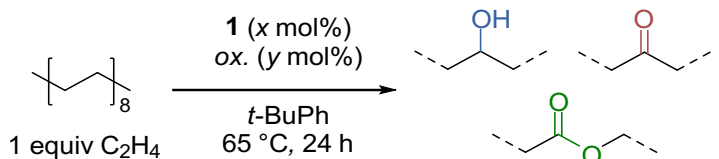
2. Supplemental Discussion

2.1. Oxidation of octadecane catalyzed by **1**.

Although the oxidation of liquid alkanes catalyzed by **1** has been reported,^{40–43} the substrate was also the solvent in the previously reported conditions. We aimed to identify a new set of conditions specifically for functionalization of PE films without dissolving the polymer. A series of solvents were screened for their ability to swell but not dissolve high-density PE (HDPE) at moderate temperature (65 °C) (**Table S10**). We calculated the swelling ratio by measuring the weight of a 100- μ m-thick HDPE film before and after incubating in the specified solvent. While several solvents readily swelled HDPE, *tert*-butylbenzene (*t*BuPh) was identified as the most promising, due to its lack of halogens and benzylic sites that could undergo oxidation. An evaluation of the effect of temperature on solubility showed that PE dissolves in *t*BuPh above 80 °C (**Table S11**); thus, the maximum operating temperature was restricted to 65 °C. To identify suitable conditions of PE that met the above constraints, octadecane (C₁₈H₃₈) was used as a model substrate.

Under the above constraints, an investigation of the efficacy of various oxidants revealed that organic hydroperoxides were the only oxidants that led to selective oxidation in the presence of catalytic amounts of **1** (**Table S1**). Of these, *tert*-butyl hydroperoxide (*t*BuOOH) was selected for its miscibility with *t*BuPh, predictable oxidation behavior, and low cost. An investigation of the effect of catalyst loading on the extent of oxidation was performed with 0.1 equivalents of oxidant, with respect to ethylene repeat units. This study showed that low loadings of catalyst (0.001 mol%) were sufficient for maximum oxidation (**Extended Data Table 2**). The maximum yield with respect to oxidant loading of 36% was obtained with a low loading of oxidant (0.05 equivalents), but higher loadings of oxidant were needed to obtain the highest total extent of oxidation. With 0.001 mol% of **1** and 0.3 equivalents of *t*BuOOH, the extent of oxidation reached a maximum value of 1.8 mol%. A time course of the reaction suggested the extent of oxidation reaches a maximum value after approximately 20 hours (**Fig. S1**). Control reactions in the absence of catalyst or oxidant confirm that both are required for oxidation (**Table S2**, **Table S4**). Other catalysts led to oxidation of octadecane under similar conditions, but only **1** yielded greater than 0.5 mol% ketone while maintaining miscibility in the organic mixture (**Extended Data Table 1**).

Table S1. Oxidation of octadecane with other oxidants.

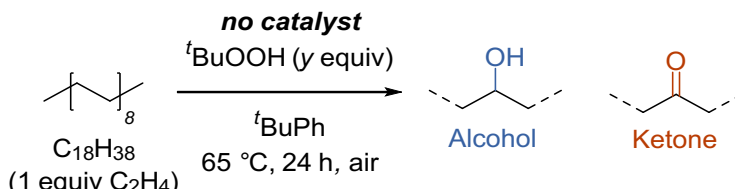


1 (x mol%)
ox. (y mol%)
t-BuPh
65 °C, 24 h
1 equiv C₂H₄

Entry	x (×10 ⁻⁴ mol%)	Oxidant	y (mol%)	Alcohol (mol%) ^a	Ketone (mol%) ^a	Ester (mol%) ^a
1	—	DTBP ^c	10%	0.0%	0.0%	0.0%
2	20	DTBP	10%	0.0%	0.0%	0.0%
3	—	DCP	10%	0.0%	0.0%	0.0%
4	20	DCP	10%	0.0%	0.0%	0.0%
5	—	H ₂ O ₂	20%	0.0%	0.0%	0.0%
6	20	H ₂ O ₂	20%	0.0%	0.0%	0.0%
7	—	TBPB	10%	0.0%	0.0%	0.0%
8	20	TBPB	10%	0.0%	0.1%	0.0%
10	—	CHP	20%	0.0%	0.0%	0.0%
11	20	CHP	20%	0.4%	1.8%	0.0%
12	—	PAA	20%	0.0%	0.0%	0.0%
13	20	PAA	20%	0.0%	0.0%	0.0%
14	—	mCPBA	20%	0.3%	0.2%	0.2%
15	20	mCPBA	20%	0.3%	0.3%	0.4%
16	—	H ₂ O ₂ -urea	20%	0.0%	0.0%	0.0%
17	20	H ₂ O ₂ -urea	20%	0.0%	0.0%	0.0%
18	—	Oxone	20%	0.0%	0.0%	0.0%
19	20	Oxone	20%	0.0%	0.0%	0.0%

Conditions: C₁₈H₃₈ (1.5 mmol C₂H₄ repeat units), *oxidant*, **1**, ^tBuPh (1 M wrt. C₁₈H₃₈), 24 h. Crude products analyzed by ¹H NMR spectroscopy with a CH₂Br₂ internal standard. Oxidants: DTBP = di-*tert*-butyl peroxide, DCP = dicumyl peroxide, H₂O₂ = hydrogen peroxide (30 wt% in water), TBPB = *tert*-butyl peroxybenzoate, MPHP = 2-methyl-1-phenylprop-2-yl hydroperoxide, CHP = cumene hydroperoxide, PAA = peracetic acid, mCPBA = meta-chloroperoxybenzoic acid, H₂O₂-urea = hydrogen peroxide–urea adduct. ^a mol% with respect to ethylene repeat units (C₂H₄).

Table S2. Oxidation of octadecane in the absence of catalyst.



no catalyst
^tBuOOH (y equiv)
^tBuPh
65 °C, 24 h, air
C₁₈H₃₈
(1 equiv C₂H₄)

Entry	y (equiv)	Alcohol (mol%) ^a	Ketone (mol%) ^a
1	2%	0.0%	0.0%
2	20%	0.0%	0.0%
3	40%	0.0%	0.0%
4	60%	0.0%	0.0%

5	100%	0.0%	0.0%
---	------	------	------

Conditions: C₁₈H₃₈ (1.5 mmol C₂H₄ repeat units), ^tBuOOH, ^tBuPh (1 M wrt. C₁₈H₃₈), air, 24 h. Crude products analyzed by ¹H NMR spectroscopy with a CH₂Br₂ internal standard. ^a mol% with respect to ethylene repeat units (C₂H₄).

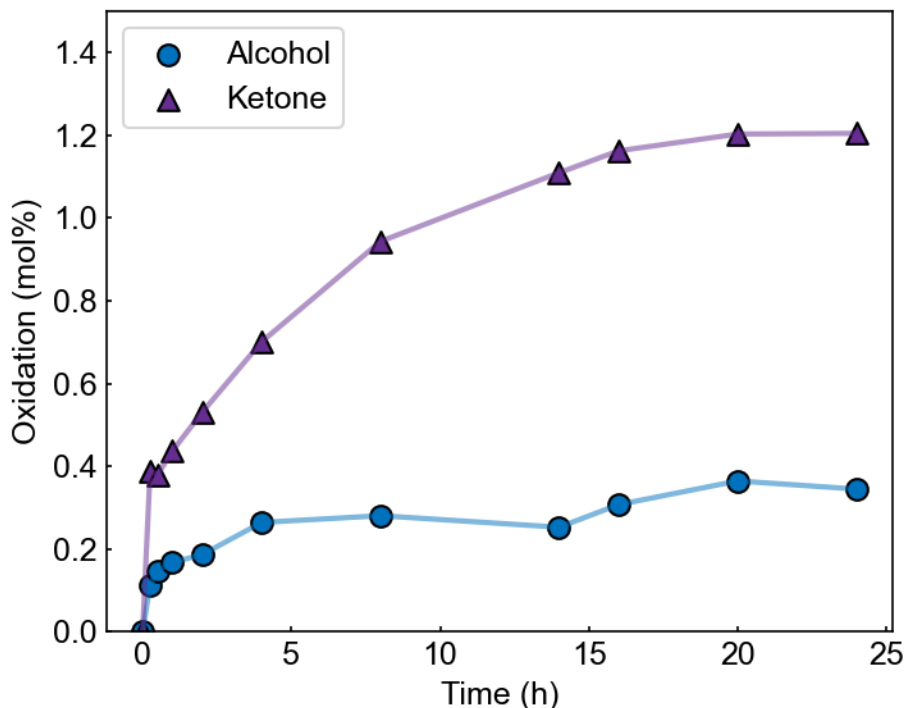


Fig. S1 | Time course of oxidation of octadecane (0.001 mol% **1**, 0.3 equiv ^tBuOOH).

2.2. Investigation of the mechanism of C–H oxidation catalyzed by **1**.

Mechanistic studies of the oxidation of octadecane were conducted to clarify how complex **1** catalyzes oxidation of C–H bonds at modest temperatures (e.g. 65 °C). Iodometric titration was initially used to monitor the rate of oxidant consumption with and without catalyst (**Fig. S2**). The consumption of ^tBuOOH in the presence of 0.001 mol% **1** occurs with a ~10× greater first-order rate constant than without **1** (0.025 min^{−1} versus 0.002 min^{−1}). Previous work has proposed that **1** promotes homolytic cleavage of ^tBuOOH, yielding an active iron-oxo (Fe^(IV)=O) species and *tert*-butoxy radical (**Fig. S3**),⁴² both of which can abstract a C–H bond from the substrate to yield a carbon-centered radical. The carbon-centered radical can subsequently be intercepted by ^tBuOOH

to promote a radical chain pathway, intercepted by O_2 , or undergo radical rebound with the $Fe^{(III)}-OH$ (Fig. S3).

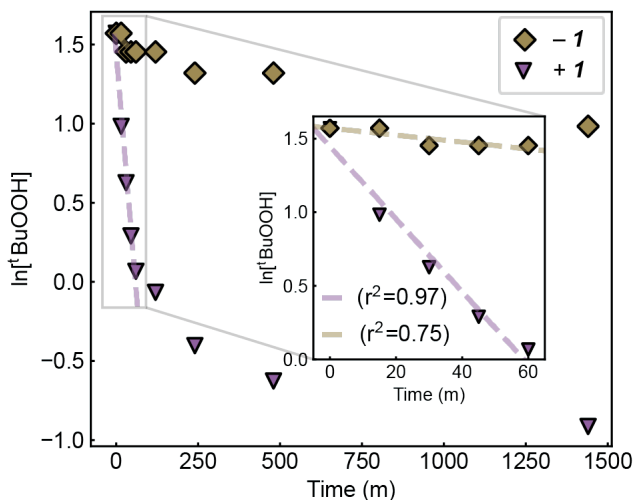


Fig. S2 | Iodometric titration monitoring the concentration of $tBuOOH$ over the course of the oxidation reaction both with and without catalyst (+1 and -1, respectively), plotted $\ln[tBuOOH]$ versus time with initial time points ($t \leq 1$ h) fit with a first-order kinetic equation.

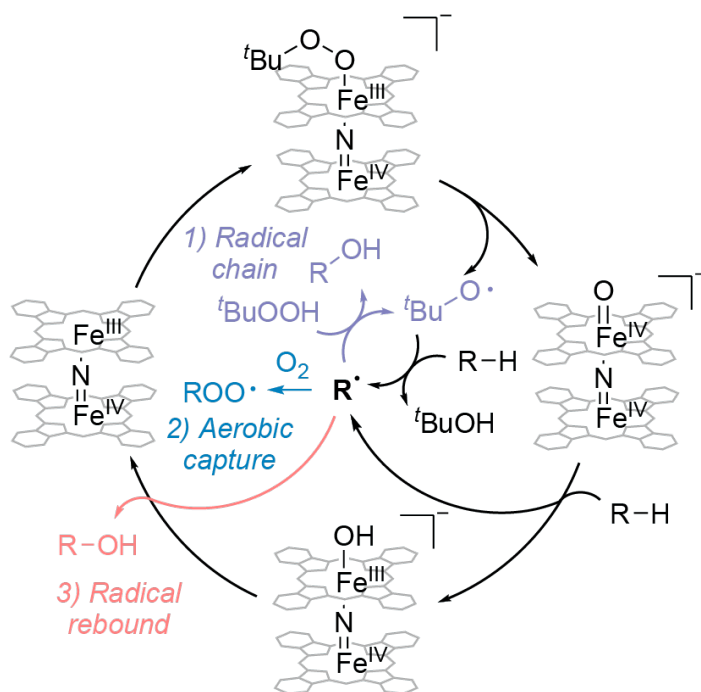


Fig. S3 | Proposed oxidation mechanism with radical chain, aerobic capture, and radical rebound pathways highlighted.

The oxidation of octadecane catalyzed by **1** yielded 1.5% oxidation with respect to ethylene repeat units with 80% selectivity for the ketone. To investigate the relative contributions of each C-H oxidation pathway, the procedure for the oxidation of octadecane was varied. The impact of

aerobic radical capture was studied by performing the reaction under N₂. When conducted under N₂ in the absence of O₂, the overall oxidation yield was reduced by approximately 45%, suggesting that aerobic radical capture is a large contributor to overall oxidation and yields a mixture of oxidized products by autoxidation pathways (**Table S4**, entry 5).^{54,55}

The contribution of the radical chain pathway was investigated by replacing *t*BuOOH with 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH). Upon reaction with **1**, MPPH undergoes rapid β -scission releasing acetone and the less active benzyl radical species.^{51,52} When MPPH was used instead of *t*BuOOH, no oxidation was observed, supporting the hypothesis that radical rebound is not responsible for C–H oxidation (**Table S4**, entry 6). This hypothesis is corroborated by the addition of BHT, which traps free radicals and suppresses radical chain pathways. The oxidation of octadecane in the presence of 0.5 equivalents of BHT yielded no oxidized products (**Table S4**, entry 9). The oxidation of a series of model alkanes containing different ratios of primary (1°), secondary (2°), and tertiary (3°) C–H bonds further supports a free-radical mechanism. The regioselectivities from the oxidation of 2,4-dimethylpentane, 2,2,4,4-tetramethylpentane, and adamantane are all consistent with previous measurements of radical C–H abstraction (3°/2° $\approx$ 4; 2°/1° $\approx$ 7),⁵⁶ reinforcing the hypothesis that oxidation results from free-radical pathways (**Fig. s4**).

Table S4. Effect of varying the reaction conditions for the oxidation of octadecane.

Reaction scheme: Octadecane (C₁₈H₃₈, 1 equiv C₂H₄) reacts with **1** (0.01 mol%), *t*BuOOH (0.3 equiv), and *t*BuPh at 65 °C for 24 h to yield an Alcohol and a Ketone.

Entry	Deviation	Alcohol (mol%) ^a	Ketone (mol%) ^a	Total (mol%)
1	None	0.3%	1.2%	1.5%
2	No 1 , no <i>t</i> BuOOH	0.0%	0.0%	0.0%
3	No <i>t</i> BuOOH	0.0%	0.0%	0.0%
4	No 1	0.0%	0.1%	0.1%
5	N ₂ instead of air	0.2%	0.9%	1.1%
6	MPPH instead of <i>t</i> BuOOH	0.0%	0.0%	0.0%
7	Dark	0.3%	1.1%	1.4%
8	0.25 equiv BHT	0.0%	0.1%	0.2%
9	0.5 equiv BHT	0.0%	0.0%	0.0%

Conditions: C₁₈H₃₈ (1.5 mmol C₂H₄ repeat units), **1**, *t*BuOOH, *t*BuPh (1 M wrt. C₁₈H₃₈), air, 24 h. Crude products analyzed by ¹H NMR spectroscopy with a CH₂Br₂ internal standard. ^a mol% with respect to ethylene repeat units (C₂H₄).

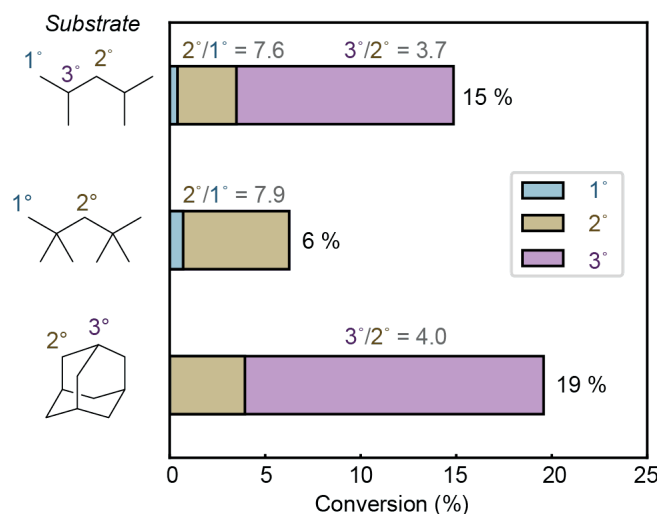


Fig. S4 | Oxidation of various alkane substrates under standard conditions (0.001 mol% **1**, 0.3 equiv ^tBuOOH, 65 °C, 24 h) highlighting regiochemistry of oxidation.

2.3. Comparison of **1** to other PE oxidation catalysts for functionalization of PE films.

To assess whether other known systems for the catalytic oxidation of PE solutions also lead to efficient oxidation of PE films, we tested two previously reported methods for PE oxidation catalyzed by Ni and Ru complexes. However, we conducted these reactions at the 65 °C temperature that avoids dissolution of the substrate (**Table S5**), rather than the reported 80 °C and 120 °C on polymer solutions.^{24,25} At this low temperature, neither reported method functionalized the PE films with the same efficiency as was reported for functionalization of PE in solution. The iron-catalyzed method reported here occurs with greater than five times the level of oxidation of PE films and with less than 1% of the catalyst loading used for the reported oxidation of polymer solutions.

Table S5. Oxidation of PE films with previously reported methods compared to this work.

$ \begin{array}{ccc} \text{PE film} & \xrightarrow[\text{65 } ^\circ\text{C, 24 h}]{\text{catalyst (x mol\%)}, \text{oxidant (y equiv), solv.}} & \text{oxo-PE} \\ (1 \text{ equiv C}_2\text{H}_4) & & \end{array} $						
Entry	Cat.	<i>x</i> (mol%)	Ox.	<i>y</i> (equiv)	Solv	Ketone (mol%) ^a
1	—	—	<i>m</i> CPBA	0.1	DCE	0.1
2	[Ni(Me ₄ Phen) ₃] [BPh ₄] (Ref ²⁵)	0.10	<i>m</i> CPBA	0.1	DCE	0.1
3	—	—	DCPNO	0.1	DCE	0.0
4	Ru(TPFPP) (CO) (Ref ²⁴)	0.10	DCPNO	0.1	DCE	0.0

5	—	—	^t BuOOH	0.3	^t BuPh	0.0
6	[Fe(^t Bu ₄ Pc)] ₂ N (this work)	0.001	^t BuOOH	0.3	^t BuPh	0.6

Conditions: LDPE film (20 mg, 50 μ m, 1 equiv), 65 °C, air, 24 h. DCE = dichloroethane. ^a mol% with respect to ethylene repeat units (C₂H₄).

2.4. Understanding ketone selectivity in the oxidation of PE with 1.

Model studies on the oxidation of octadecane with **1** suggest that a substantial quantity of alcohols form, even though ketones are the major product (**Extended Data Table 2**). Free-radical oxidation of alkanes typically produces both alcohols and ketones. However, the oxidation of PE with **1** under the conditions reported here does not produce observable quantities of hydroxyl groups. To investigate the difference between the oxidation of light alkanes and the PE studied here, we oxidized alkanes and polyethylene of varying molar mass by our method. We determined the quantities of hydroxyl and oxo groups by ¹H NMR spectroscopy (**Table S6**). Small quantities of alcohol were observed for all substrates except the LDPE film. The selectivity for the ketone product correlated with the molar mass of the substrate.

We hypothesize that selectivity under the reaction conditions is dictated by diffusion. In a free-radical oxidation mechanism, ketones are formed by oxidation of the alcohol. Because the bond dissociation energy of a C–H bond α to an alcohol is lower than that of an alkane C–H bond, the oxidation of an alcohol to a ketone is typically faster than the oxidation of an alkane to an alcohol. Under the reaction conditions, light alkanes diffuse more rapidly than polymer chains. When alcohols form from light alkanes, they diffuse from the catalyst and the large concentration of alkane can compete with the small amount of alcohol. Because the polymer chains diffuse more slowly, the alcohol diffuses from the catalyst slowly, and the catalyst reacts with the alcohol to form ketone prior to diffusion. Ongoing work seeks to test this hypothesis further and to determine how differences in diffusion between small molecules and macromolecules affect this selectivity.

Table S6. Oxidation of alkanes and polyethylene of different molar masses catalyzed by **1**.

Entry	Substrate	Ketone (mol%)	Alcohol (mol%)	Selectivity (%)
1	Cyclohexane	0.84%	0.32%	72%
2	Octadecane	1.07%	0.35%	75%
3	Paraffin Wax	1.34%	0.30%	82%
4	Low MW PE ($M_{n,SEC}$ = 2.4 kDa, $M_{w,SEC}$ = 7.9 kDa, Powder)	1.06%	0.15%	88%
5	LDPE film (50 μ m) ($M_{n,SEC}$ = 7.2 kDa, $M_{w,SEC}$ = 57.4 kDa)	0.37%	0.00%	>99%

2.5. Analyzing the impacts of functionalization on microstructure with self-nucleation.

Modification of a polymer with new functional groups can influence the size, distribution, and prevalence of crystallites within a bulk material. Successive self-nucleation and annealing (SSA) experiments using DSC are a powerful strategy for quantifying the impact of new functional groups on the crystallite distribution and crystalline microstructure.^{57,58} In SSA, a semi-crystalline polymer is sequentially heated and cooled to thermally fractionate crystals by size. The analysis of the fraction crystal melting temperatures and melting enthalpies offers insight into the distribution of crystallites in the bulk material.

To develop a method for SSA on our polymers, we initially performed self-nucleation measurements at different self-seeding temperatures (T_s) using pristine LDPE and HDPE to identify the ideal self-seeding temperature ($T_{s,ideal}$) (**Fig. S5a,d**).⁵⁸ The $T_{s,ideal}$ as indicated by the measurement with the maximum observed crystallization temperature (T_c) without evidence of annealing in the melting endotherm was 115 °C for LDPE and 135 °C for HDPE (**Fig. S5b,c,e,f**).

We then performed SSA measurements on pristine and oxidized PE samples using seven or eight T_s steps starting from $T_{s,ideal}$ and decreasing by 5 °C per cycle before a final ramp to melt all crystallites. Pristine LDPE, LDPE oxidized in solution, and LDPE oxidized as a film all displayed clear thermal fractionation, as indicated by the successive melting endotherms in the final temperature ramp (**Fig. S6a**). By contrast, thermal fractionation was not pronounced for samples of HDPE and oxidized HDPE, which agrees well with previous reports (**Fig. S6b**).^{59,60} Therefore, we selected only the LDPE samples for further analysis. We repeated the thermal fractionation by SSA of the pristine and oxidized LDPE materials with two additional sections from each sample so that each measurement was reproduced in triplicate (**Fig. S7–Fig. S9**).

The melting temperature and melting enthalpy of each endotherm in the final SSA temperature ramp of the LDPE and oxidized LDPE measurements were calculated by integrating each of the individual peaks (**Table S7**). The average total enthalpy was calculated by summing the enthalpies of the individual endotherms. The average total enthalpy of LDPE oxidized as a film (57.7 ± 0.9 J/g) was greater than the average total enthalpy of LDPE oxidized in solution (52.1 ± 2.8 J/g) and not statistically distinguishable from the average total enthalpy of pristine LDPE (59.1 ± 0.5 J/g). For crystals seeded at 115 °C, pristine LDPE and LDPE oxidized as a film had nearly identical melting enthalpies, whereas LDPE oxidized in solution had a lower enthalpy. These results indicate that LDPE oxidized in solution is less crystalline and has fewer large crystallites than pristine LDPE and LDPE oxidized as a film.

New functional groups which cannot co-crystallize with the PE repeat unit will disrupt crystallite formation and therefore limit crystallite size. To more precisely quantify how functionalization impacts the distribution of the crystallites, we calculated how functionalization impacts crystallite size and the average ethylene sequence length between disruptions from branch points or functional groups. The thickness of a crystal that has an observed melting temperature (T_m) can be determined using the Thomson–Gibbs equation (Eq. 2):

$$L_c = \frac{2\sigma_e T_m^0}{\Delta H_u (T_m^0 - T_m)} \quad (\text{Eq. 2})$$

where L_c is the lamellar thickness, σ_e is the surface energy of PE (0.007 J/m²), T_m^0 is the equilibrium melting temperature of PE (141.5 °C), and ΔH_u is the enthalpy of fusion (288×10^6 J/mol).^{61,62} In addition, the average ethylene sequence length (n_{avg}) can be estimated from the following previously reported relationships (Eq. 3) (Eq. 4):^{61,63,64}

$$n_{avg} = \frac{X}{1-X} \quad (\text{Eq. 3})$$

$$-\ln(X) = -0.331 + \frac{135.5}{T_m} \quad (\text{Eq. 4})$$

Using these relationships, we computed the average L_c and n_{avg} for pristine LDPE, LDPE oxidized in solution, and LDPE oxidized as a film (**Fig. S10**). The average L_c for LDPE functionalized as a film (6.2 nm) was the same as that of pristine LDPE and greater than that of LDPE functionalized in solution (6.1 nm). Similarly, the n_{avg} for LDPE functionalized as a film (41.9 repeat units) was comparable to that of pristine LDPE (42.3 repeat units) and greater than that of LDPE functionalized in solution (41.0 repeat units). These results further demonstrate that the functionalization of PE at the solid–liquid interface minimally impacts the bulk crystalline microstructure, whereas functionalization of PE in solution leads to a decrease in crystallinity and average crystallite size even at low degrees of functionalization.

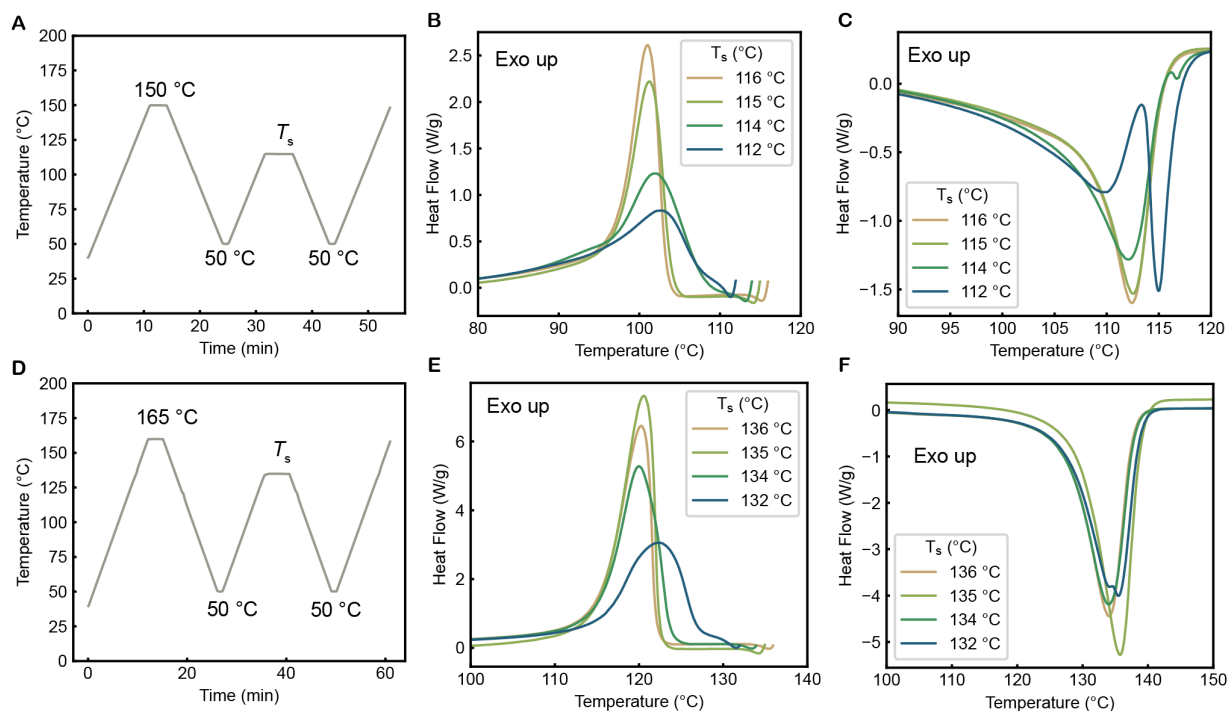


Fig. S5 | Self-nucleation DSC experiments on pristine PE. **a)** Example of the temperature program for self-nucleation of LDPE (ramp rate = 10 °C/min). **b)** The second cooling ramp for self-nucleation experiments of pristine LDPE at different T_s , showing the crystallization exotherm. **c)** The third heating ramp of pristine LDPE self-nucleation experiments at different T_s showing the melting endotherm. **d)** Example of the self-nucleation temperature program for HDPE (ramp rate = 10 °C/min). **e)** The second cooling ramp of pristine HDPE self-nucleation experiments at different T_s showing the crystallization exotherm. **f)** The third heating ramp for self-nucleation experiments of pristine HDPE at different T_s , showing the melting endotherm.

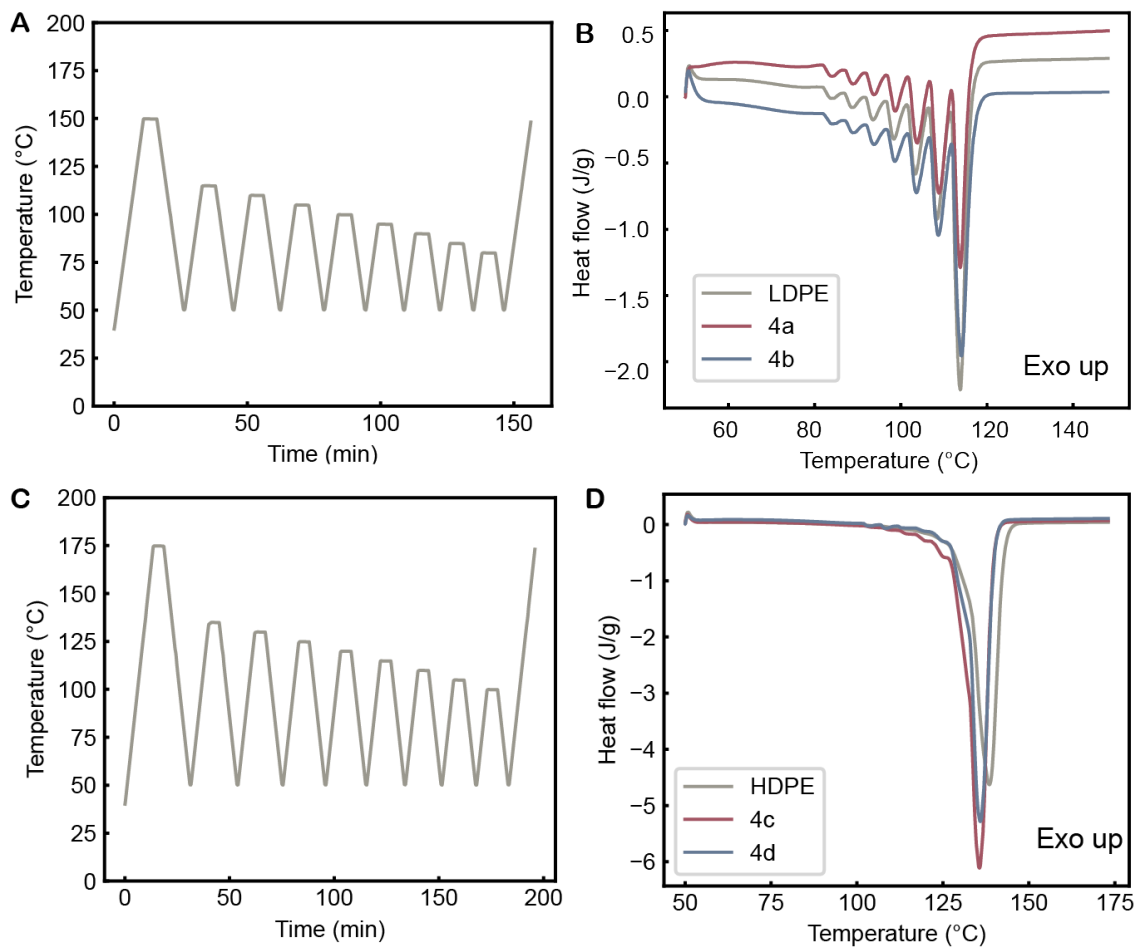


Fig. S6 | Successive self-nucleation and annealing. **a)** The SSA temperature program for LDPE (ramp rate = 10 °C/min). **b)** The final heating ramp in an SSA measurement with pristine LDPE, LDPE oxidized in solution (**4a**), and LDPE oxidized as a film (**4b**). **c)** The SSA temperature program for HDPE (ramp rate = 10 °C/min). **d)** The final heating ramp in an SSA measurement for pristine HDPE, HDPE oxidized in solution (**4c**), and HDPE oxidized as a film (**4d**).

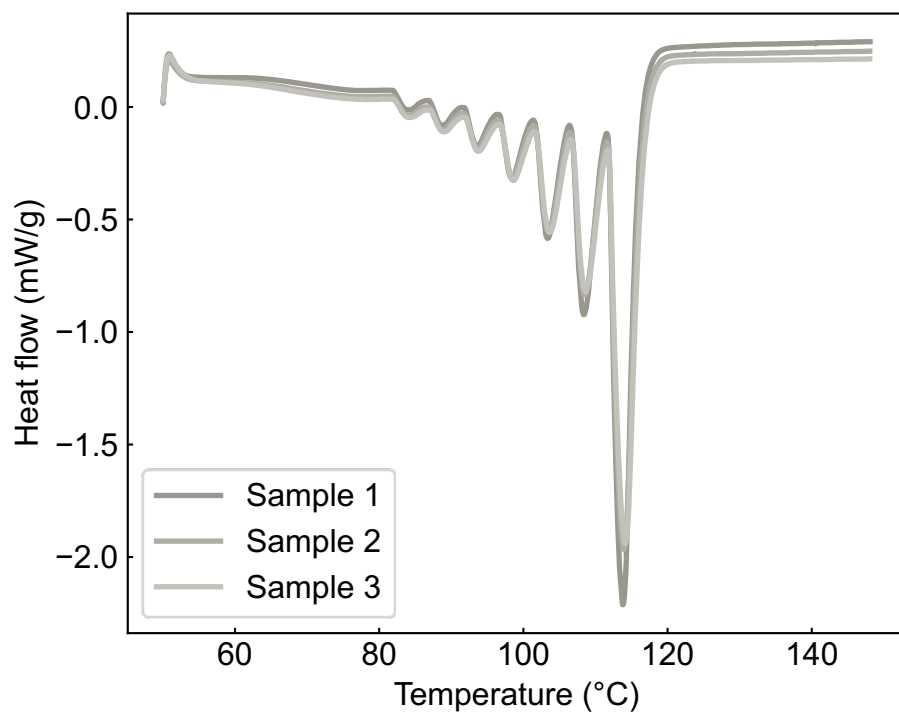


Fig. S7 | Thermal fractionation by SSA of three samples from pristine LDPE.

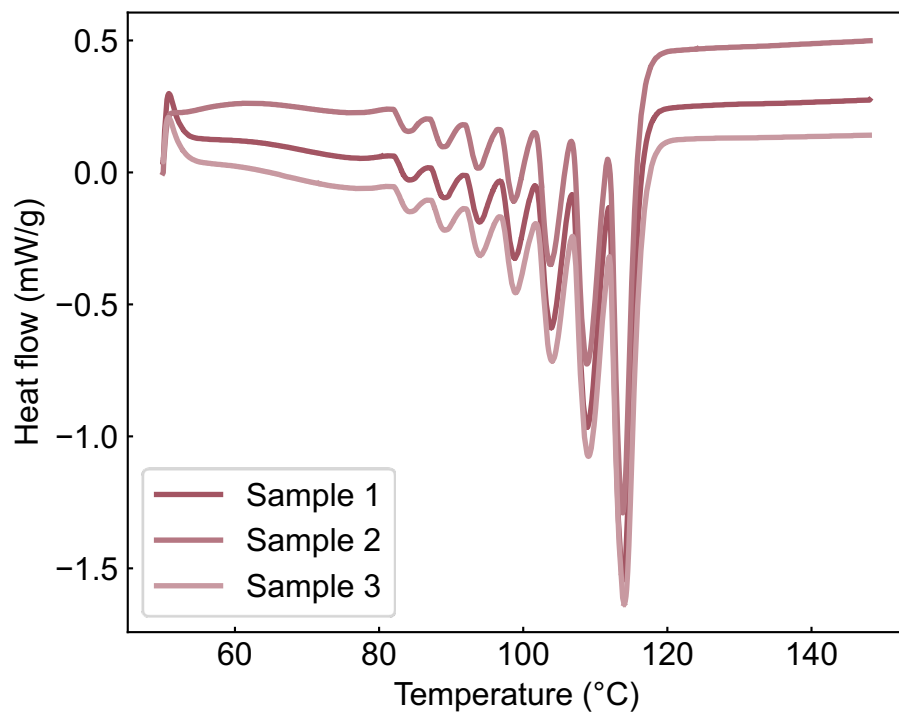


Fig. S8 | Thermal fractionation by SSA of three samples from LDPE oxidized in solution (**4a**).

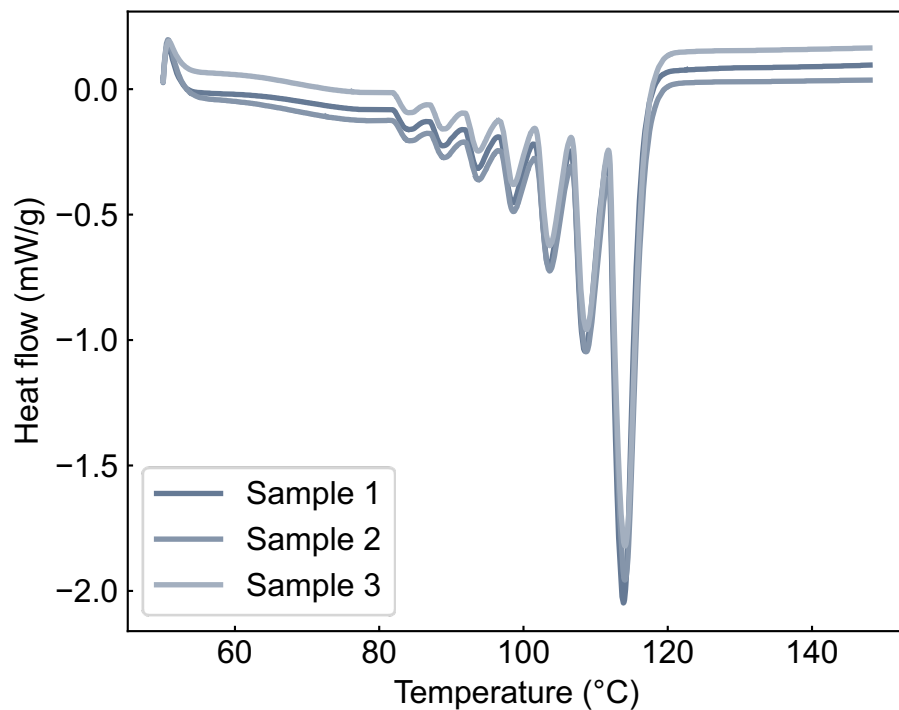


Fig. S9 | Thermal fractionation by SSA of three samples from LDPE oxidized as a film (**4b**).

Table S7. Enthalpy of melting from final heating ramp of SSA experiments of LDPE and oxidized LDPE.

T_s (°C)	T_m (°C)	Enthalpy (J/g)		
		LDPE	4a	4b
115	114	26.3 ± 0.3	18.3 ± 2.0	25.4 ± 0.4
110	108	12.9 ± 0.3	14.1 ± 1.3	13.1 ± 0.6
105	104	8.9 ± 0.1	8.9 ± 1.1	8.9 ± 0.1
100	98	5.4 ± 0.1	5.3 ± 0.8	5.3 ± 0.1
95	93	3.3 ± 0.0	3.3 ± 0.5	3.1 ± 0.2
90	89	1.8 ± 0.0	1.8 ± 0.3	1.5 ± 0.3
85	84	0.5 ± 0.0	0.5 ± 0.0	0.4 ± 0.0
Total		59.1 ± 0.5	52.1 ± 2.8	57.7 ± 0.9

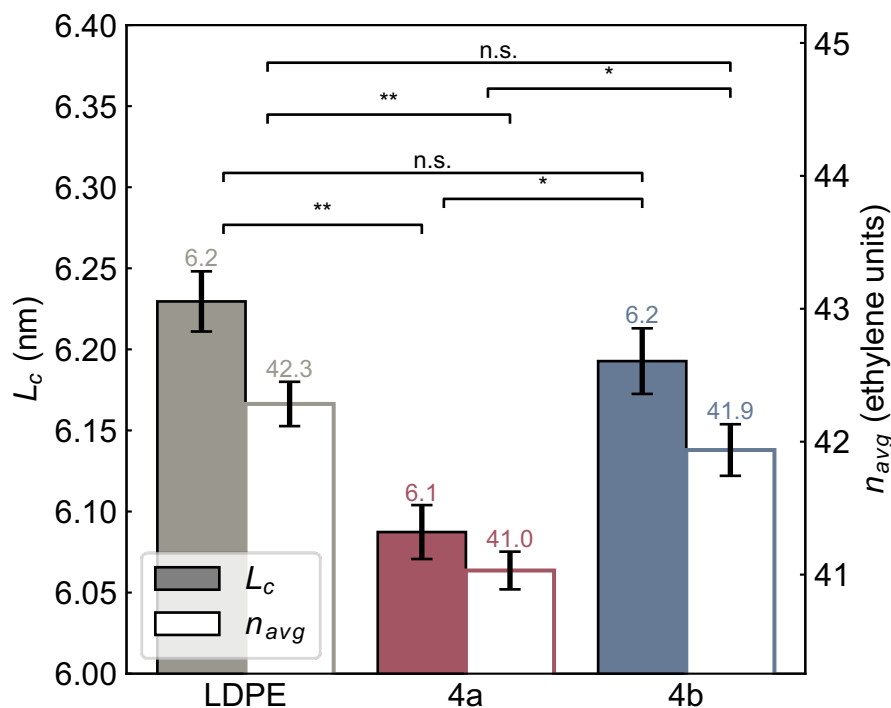


Fig. S10 | Average lamellar thickness and ethylene sequence length of pristine LDPE, LDPE oxidized in solution (**4a**), and LDPE oxidized as a film (**4b**) from measurements performed in triplicate.

2.6. Impact of extent of oxidation and oxidation method on adhesion properties.

To determine how extent of oxidation impacts adhesion for the different treatment methods, we oxidized samples of PE in solution and as films with different extents of oxidation. We modulated the functionalization of PE functionalized in solution by varying the oxidant amount between 0.1 and 0.5 equivalents relative to ethylene repeat units. Under these conditions, the functionalization levels ranged from 0.1 to 0.8 mol% (**Extended Data Table 3**). We next modulated the extent of oxidation of PE films by varying the film thickness. By varying the film thickness between 30 and 300 μm , we produced PE films with 0.1 to 0.6 mol% ketone groups as measured by NMR spectroscopy (**Extended Data Table 4**). We subjected each sample to lap-shear melt adhesive testing using glass as the substrate.

To evaluate whether the method of oxidation (e.g. film vs. solution) fundamentally alters the relationship between chemical functionalization and adhesion strength, a two-way analysis of covariance (ANCOVA) was performed (**Table S8**). In this model, lap-shear strength was defined as the dependent variable, process type (film vs. solution) and resin type (HDPE vs. LDPE) as categorical independent factors, and ketone concentration (mol%) as a continuous covariate. The analysis indicated that process type was a statistically significant predictor of lap-shear strength after controlling for the covariate ($p = 1.0 \times 10^{-6}$). Other factors such as resin type did not exert a statistically significant effect on the outcome.

Table S8. ANCOVA of oxidation process, resin type, and extent of oxidation.

Factor	Sum of Squares	df	F-statistic	p-value
--------	----------------	----	-------------	---------

Process	175.7	1	27.712	1.0×10^{-6}
Resin	16.8	1	2.655	0.11
Process / Resin	0.0	1	0.001	0.97
Ketone	144.2	1	22.751	9.0×10^{-6}
Ketone / Process	40.5	1	6.390	0.01
Ketone / Resin	0.2	1	0.026	0.87
Ketone / Process / Resin	3.9	1	0.615	0.44
Residual	456.4	72		

2.7. Reprocessing PE oxidized at the solid–liquid interface

We examined how the thermomechanical properties of PE oxidized as a film changed after multiple cycles of reprocessing. Samples of LDPE and HDPE oxidized with 0.3 mol% of ketone were subjected to tensile and glass lap-shear adhesion tests. Following the tests, the films were melted in a hot press at 15 °C above the melting temperature (125 °C for LDPE, 150 °C for HDPE) and pressed into a film between sheets of PTFE. Tensile and glass lap-shear adhesion tests were repeated on the reprocessed films. The material was subsequently reprocessed a second time and analyzed again. Additionally, a small aliquot was extracted at each stage and analyzed by DSC to determine the melting temperature and crystallinity of the reprocessed material.

We conducted tensile tests of five replicate samples for both LDPE and HDPE oxidized at the solid–liquid interface and reprocessed twice (**Fig. S11a**, **Fig. S12–Fig. S15**). The average elongation at break (ϵ_b) values for LDPE oxidized as a film before reprocessing, after a first round of reprocessing, and after a second round of reprocessing were 132%, 172%, and 261%, respectively, though the difference was not statistically significant. Similarly, the ϵ_b values for HDPE oxidized as a film before reprocessing, after a first round of reprocessing, and after a second round of reprocessing were 312%, 460%, and 321%, respectively, but these samples also did not differ from each other with statistical significance. While the average elongation at break values varied between tests, the Young's modulus values were more consistent. The average Young's modulus (E) values for LDPE oxidized as a film before and after each reprocessing round were 0.3 GPa. Likewise, the E values for HDPE oxidized as a film before and after two rounds of reprocessing were 1.2 GPa and 1.1 GPa, though a statistically significant drop was observed after a single round of reprocessing to a value of 1.0 GPa.

We next assessed adhesion strength with lap-shear adhesion tests on glass substrates (**Fig. S11b**, **Fig. S16–Fig. S19**). The average glass lap-shear strength value of LDPE oxidized as a film with 0.3 mol% ketones was 5.9 MPa. Upon reprocessing, the average glass lap-shear strength significantly decreased to 1.5 MPa. A second round of reprocessing saw a slightly increased average glass lap-shear strength of 3.2 MPa. The difference in average lap-shear strength between the two reprocessing rounds was not statistically significant. These results indicate that the lap-shear strength of LDPE oxidized at the solid–liquid interface degrades upon reprocessing. By contrast, the glass lap-shear strength of HDPE oxidized as a film with 0.3 mol% ketones did not differ significantly after two rounds of reprocessing. After oxidizing HDPE at the solid–liquid interface, the average glass lap-shear strength of the material was 6.9 MPa, which was not

statistically differentiated from the average glass lap-shear strength from the first or second reprocessing rounds of 6.7 MPa and 9.4 MPa, respectively.

We studied the impacts of reprocessing on crystallinity and melting temperature by DSC (**Fig. S11c, Fig. S20–Fig. S23**). The melting temperature of pristine LDPE on the first DSC heating cycle was 112.4 °C. The melting temperatures of LDPE oxidized as a film before reprocessing, after a single reprocessing cycle, and then after a second reprocessing cycle were 112.4 °C, 112.5 °C, and 112.7 °C, respectively. Likewise, the melting temperature of pristine HDPE on the first DSC heating cycle was 132.0 °C, which was similar to the melting temperatures of HDPE oxidized as a film before reprocessing, after a single reprocessing cycle, and then after a second reprocessing cycle of 134.7 °C, 132.2 °C, and 132.1 °C. We conclude that neither oxidation at the solid–liquid interface nor reprocessing after oxidation significantly impacts the melting temperature of PE.

The crystallinity (X_c) of each sample was computed by integrating the area under the melting endotherm of the first heating ramp and dividing the area by the melt enthalpy of a perfect polyethylene crystal (293 J/g).⁶⁵ We observed that the crystallinity of pristine LDPE was 24.6%. The crystallinities of LDPE oxidized as a film before reprocessing, after a single reprocessing cycle, and then after a second reprocessing cycle were 26.1%, 25.1%, and 26.1%, respectively. While these values differed from that of pristine LDPE, we did not observe a consistent relationship between reprocessing and crystallinity. Likewise, we observed that the crystallinity of pristine HDPE was 58.3%, but the crystallinities of HDPE oxidized as a film before reprocessing, after a single reprocessing cycle, and then after a second reprocessing cycle were 65.1%, 59.6%, and 56.0%, respectively. We believe the minor differences in crystallinity do not represent a systematic trend and can be attributed to a small degree of randomness inherent in crystallization.

In sum, we observe that reprocessing PE film which has been oxidized at the solid–liquid interface does not significantly impact bulk thermal or mechanical properties of the material over two reprocessing cycles; however, we did observe a decrease in the surface adhesive properties of LDPE upon reprocessing. We hypothesize that the decrease in surface adhesive properties of LDPE is attributed to its comparatively high melt flow index, which more readily allows its polar groups to migrate away from the surface during reprocessing.

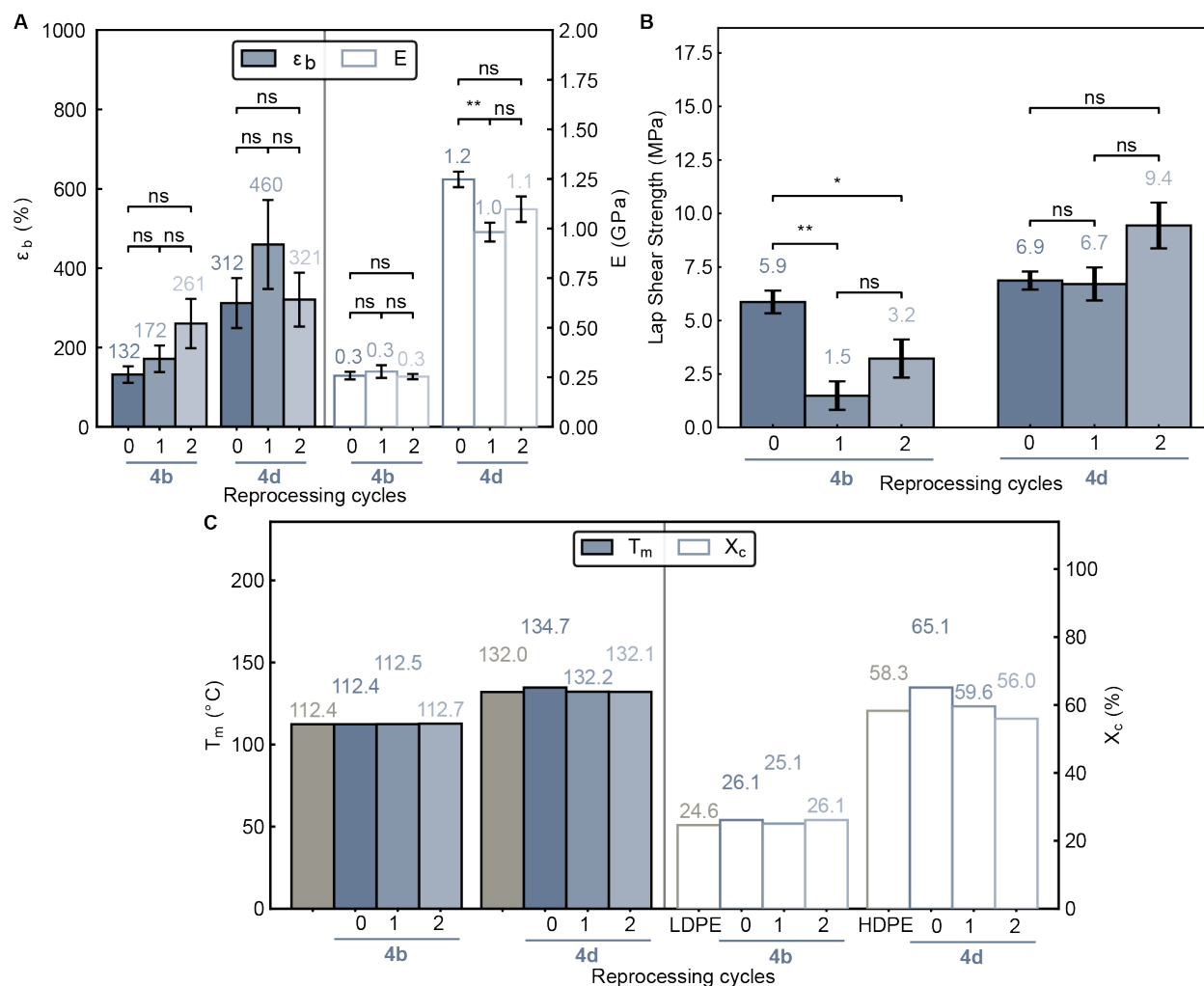
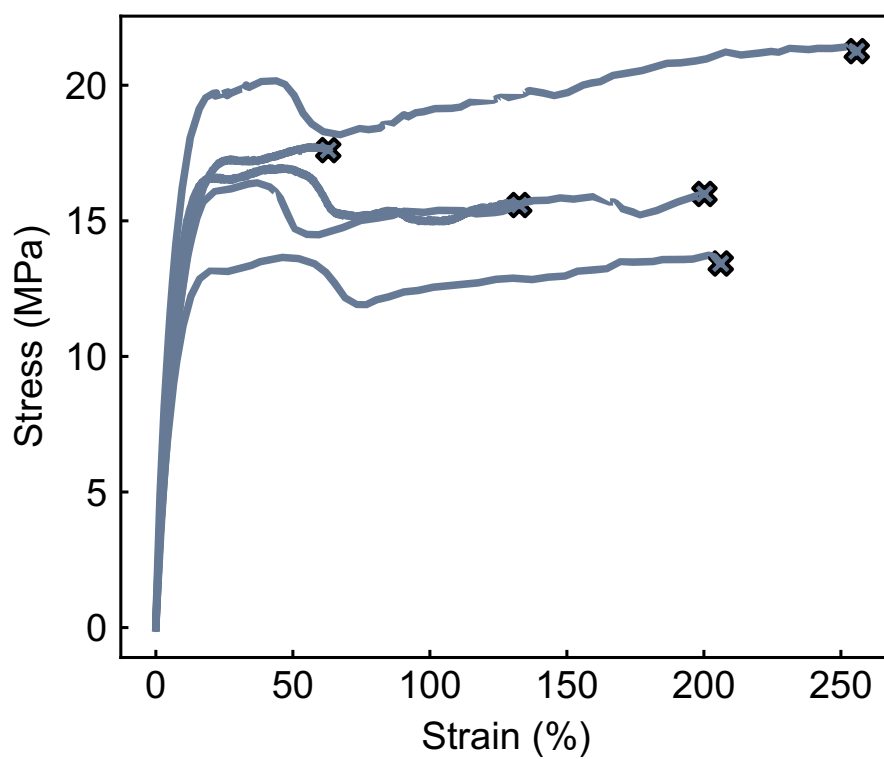
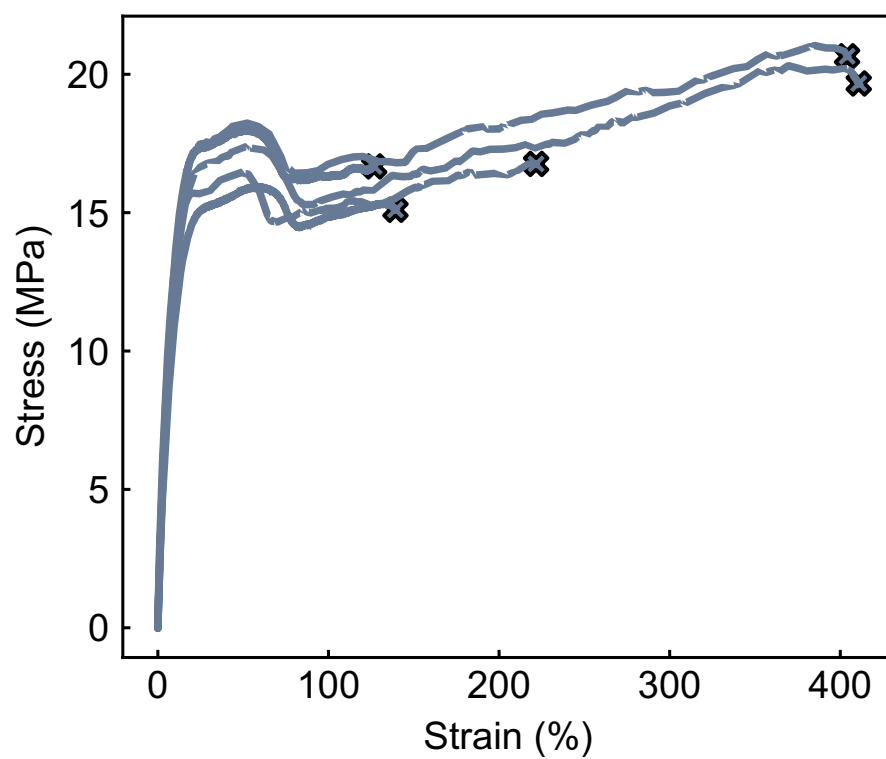


Fig. S11 | Thermomechanical properties of PE oxidized at the solid-liquid interface after reprocessing. a) Average elongation at break and Young's modulus obtained from tensile tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2). **b)** Average glass lap-shear adhesion strengths obtained from glass lap-shear tests of film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2). **c)** Melting temperature and crystallinity obtained from a first cycle of DSC (5 °C/min) of pristine PE and film-oxidized PE before reprocessing (0), after a single reprocessing cycle (1), and after two reprocessing cycles (2).



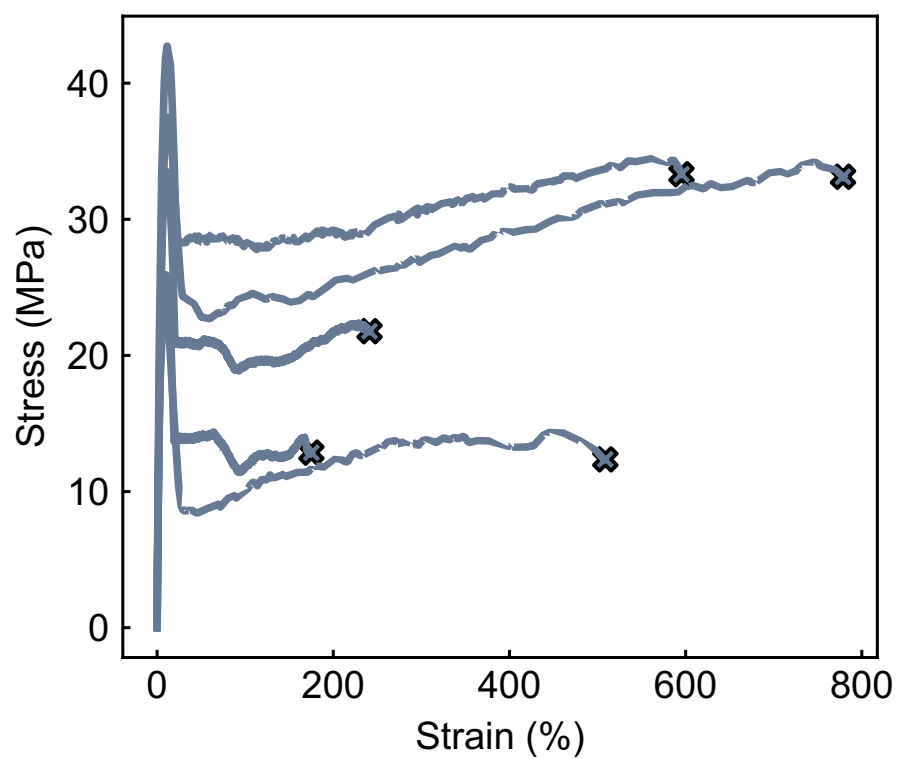
Entry	ϵ_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	200	246.3	16.4	16.0
2	63	198.8	17.6	17.6
3	206	247.1	13.7	13.4
4	256	377.9	20.2	21.3
5	133	326.1	17.0	15.6

Fig. S12 | Tensile data for reprocessed film-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



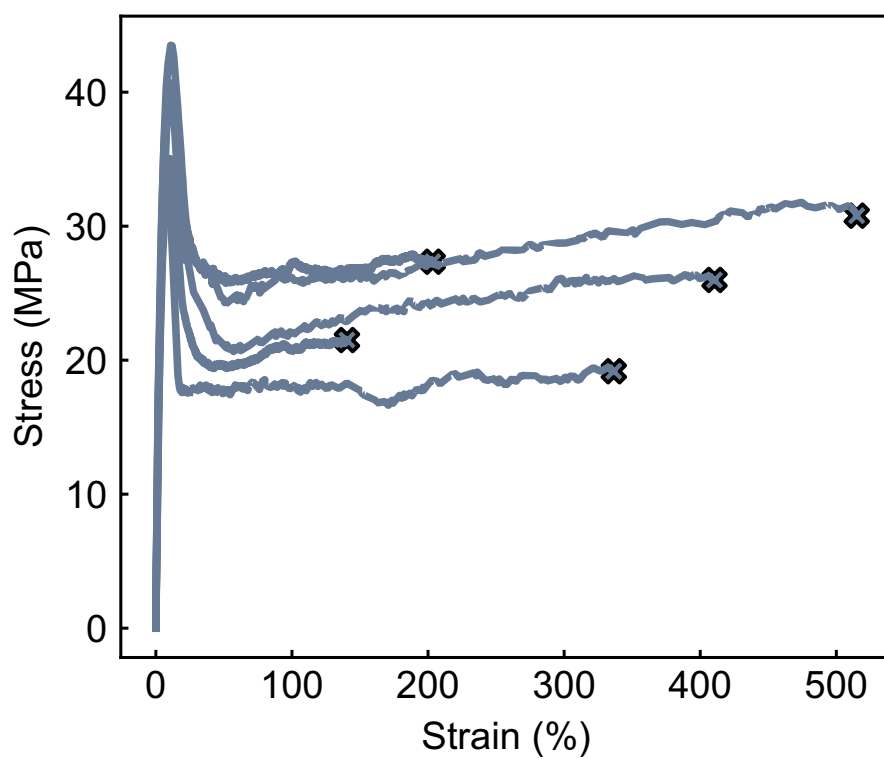
Entry	ϵ_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	411	251.1	17.3	19.7
2	404	229.1	18.2	20.7
3	127	258.7	18.0	16.7
4	222	301.2	16.5	16.8
5	139	228.9	15.8	15.1

Fig. S13 | Tensile data for twice-reprocessed film-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



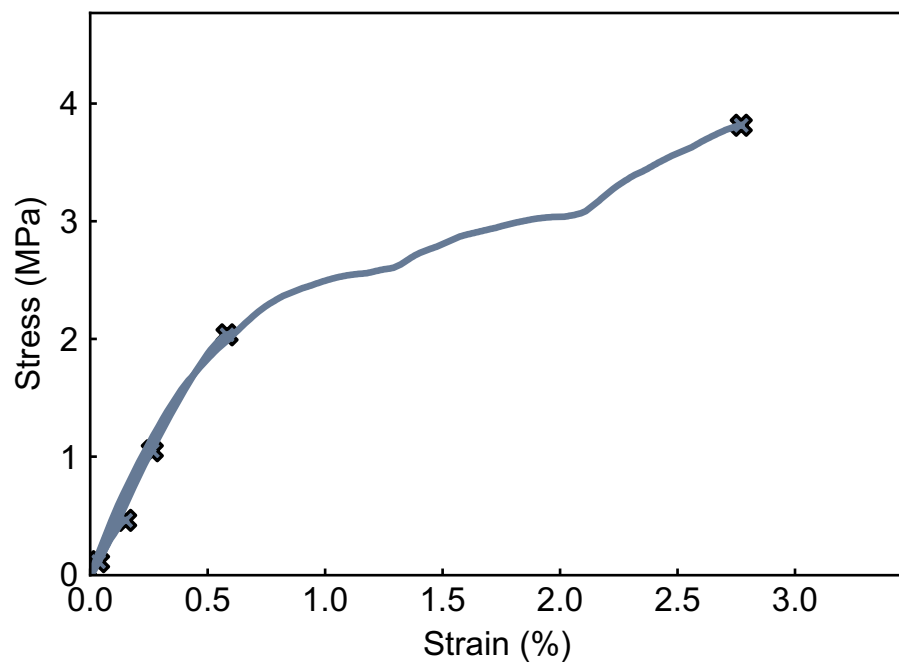
Entry	ϵ_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	595	1154	42.8	33.3
2	175	928.8	25.9	12.9
3	779	884.5	37.5	33.1
4	509	933.1	24	12.4
5	241	1009.8	33.5	21.8

Fig. S14 | Tensile data for reprocessed film-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



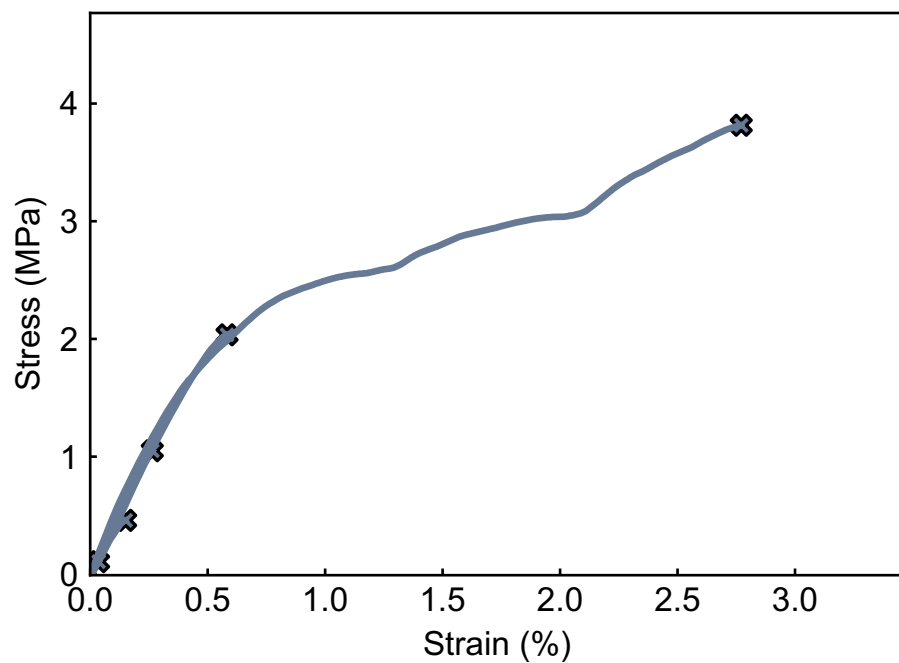
Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	140	994.4	35.0	21.5
2	515	925.8	39.7	30.8
3	203	1097.0	43.5	27.3
4	410	1189.5	40.7	26.0
5	336	1280.8	32.9	19.2

Fig. S15 | Tensile data for twice-reprocessed film-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



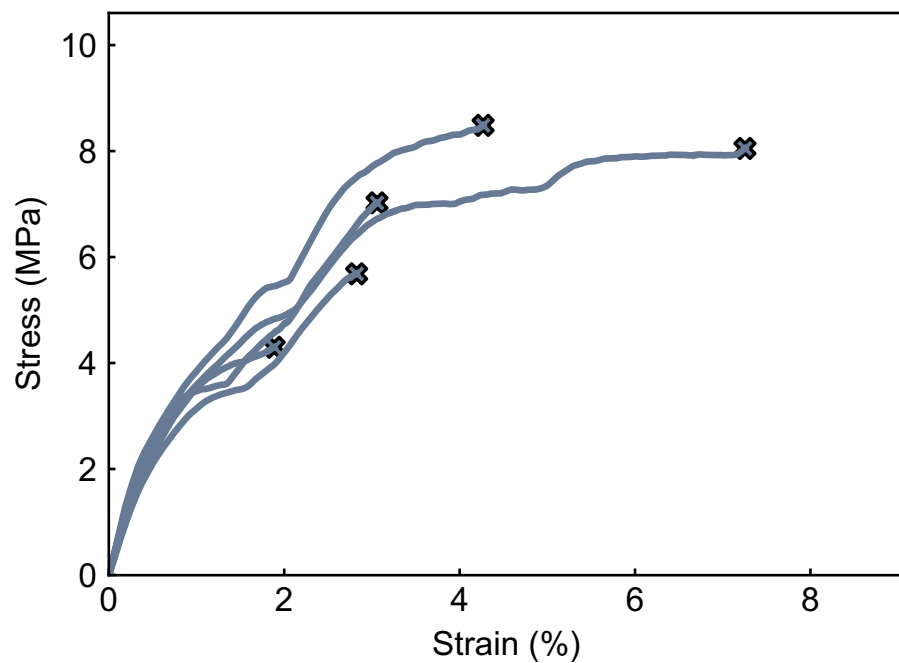
Entry	U_T (MPa)	Failure
1	3.82	Adhesive
2	0.11	Adhesive
3	0.46	Adhesive
4	1.05	Adhesive
5	2.03	Adhesive

Fig. S16 | Glass lap-shear adhesion data for reprocessed film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



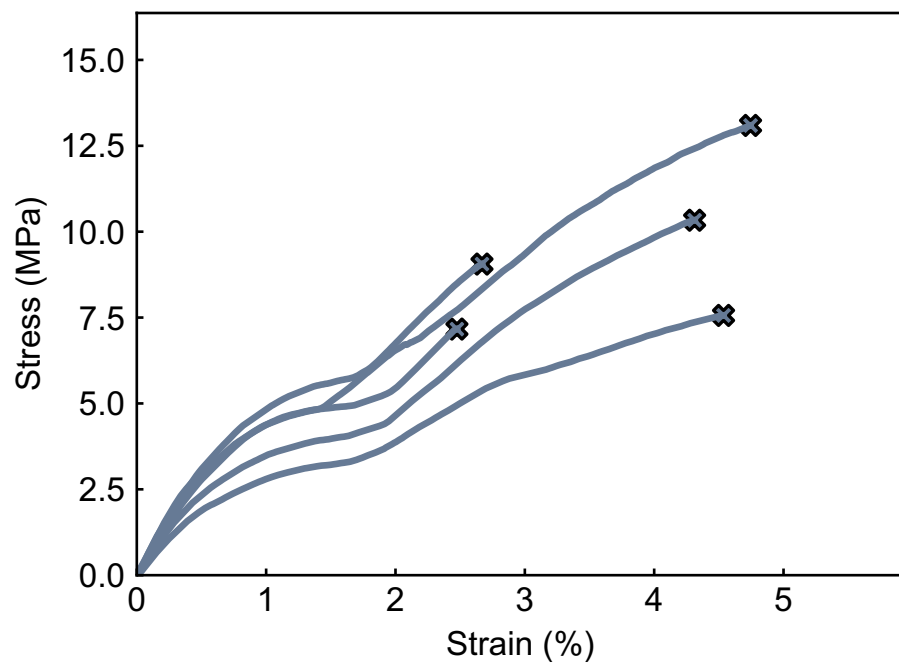
Entry	U_T (MPa)	Failure
1	4.31	Adhesive
2	5.31	Adhesive
3	3.33	Adhesive
4	3.18	Adhesive
5	0.00	Adhesive

Fig. S17 | Glass lap-shear adhesion data for twice-reprocessed film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



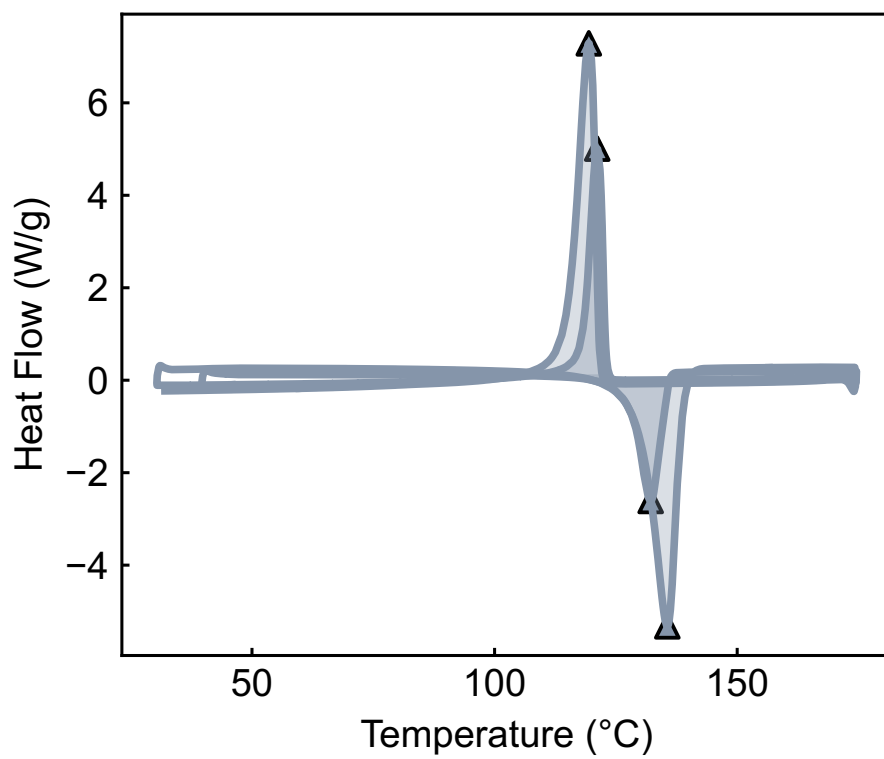
Entry	U_T (MPa)	Failure
1	7.02	Adhesive
2	4.30	Adhesive
3	8.05	Adhesive
4	5.68	Adhesive
5	8.48	Adhesive

Fig. S18 | Glass lap-shear adhesion data for reprocessed film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



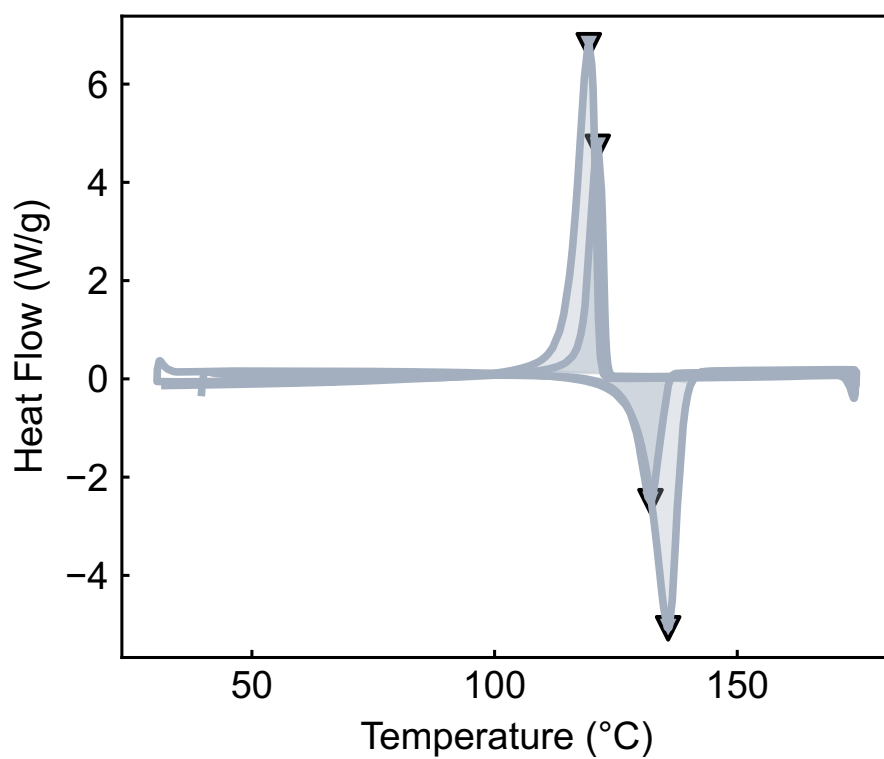
Entry	U_T (MPa)	Failure
1	13.09	Cohesive
2	7.56	Adhesive
3	9.06	Cohesive
4	10.33	Adhesive
5	7.16	Adhesive

Fig. S19 | Glass lap-shear adhesion data for twice-reprocessed film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



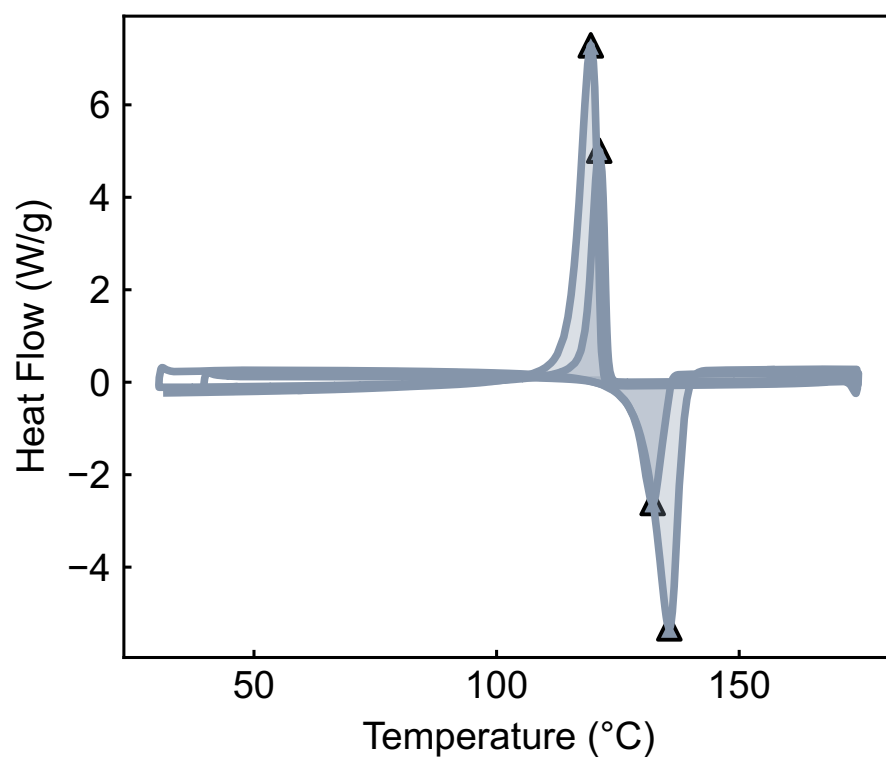
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	112.5	73.5	101.3	-82.8
2	10	112.3	80.6	99.4	-81.3

Fig. S20 | Differential scanning calorimetry of reprocessed film-oxidized LDPE (0.3 mol%).



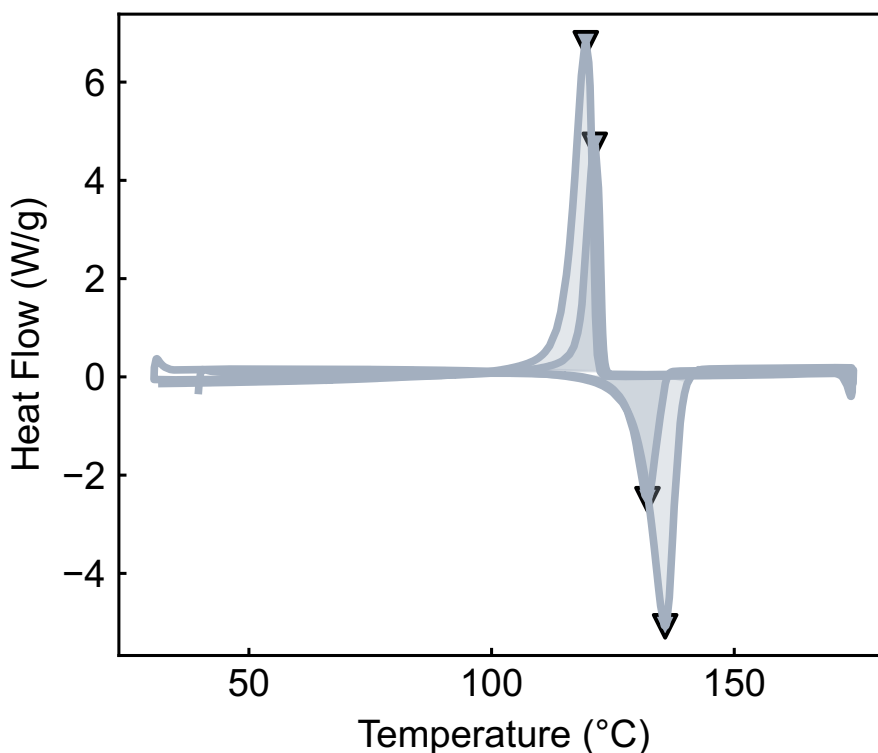
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	112.7	76.5	101.6	-81.7
2	10	113.4	82.3	99.6	-84.4

Fig. S21 | Differential scanning calorimetry of twice-reprocessed film-oxidized LDPE (0.3 mol%).



Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	132.2	174.6	121.2	-203.2
2	10	135.6	200.9	119.4	-201.3

Fig. S22 | Differential scanning calorimetry of reprocessed film-oxidized HDPE (0.3 mol%).



Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	132.1	164	121.2	-196.4
2	10	135.8	193.7	119.4	-194.7

Fig. S23 | Differential scanning calorimetry of twice-reprocessed film-oxidized HDPE (0.3 mol%).

2.8. Analyzing crystalline microstructure of PE samples by WAXS and SAXS.

We compared the crystalline microstructure of PE oxidized in solution and PE oxidized at the solid–liquid interface by wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) measurements (**Table S9**). WAXS measurements were first used to analyze the crystallinity and unit cell parameters before and after functionalization (**Fig. S24–Fig. S27**). Pristine PE has major reflections at $1.49\text{--}1.53\text{ \AA}^{-1}$ from the (110) plane and $1.66\text{--}1.69\text{ \AA}^{-1}$ from the (200) plane.^{66,67} LDPE oxidized in solution and LDPE oxidized as a film had reflections at $1.53\text{ \AA}^{-1}$ and $1.69\text{ \AA}^{-1}$. Similarly, HDPE oxidized in solution and HDPE oxidized as a film had reflections at $1.54\text{ \AA}^{-1}$ and $1.71\text{ \AA}^{-1}$. No additional major reflections were identified in either sample. Since we do not observe either new crystalline reflections or major differences in the scattering vector, we conclude that functionalization does not introduce a new major crystalline phase.

The crystallinity of each sample was obtained by deconvolution of the WAXS profile (see Supplemental Methods). Crystallinity (X_c) of pristine LDPE is between 30% and 55% and X_c of pristine HDPE is between 60% and 80%.^{66,68} The X_c of LDPE oxidized in solution was 41.8%, which was less than that of LDPE oxidized at the solid–liquid interface which was 42.1%.

Similarly, the X_c of HDPE oxidized in solution was 56.1%, which was less than that of HDPE oxidized at the solid–liquid interface which was 60.6%. For both LDPE and HDPE, we observe that PE oxidized at the solid–liquid interface is more crystalline than PE oxidized in solution.

SAXS measurements were used to probe the mesoscale morphology of pristine and functionalized PE by analyzing the lamellar periodicity (L) (see Supplemental Methods) (**Fig. S28–Fig. S31**). The lamellar periodicity is defined as the sum of the average amorphous domain size (L_a) and the average crystalline lamellar size (L_c), which can be calculated from the following equation (Eq. 5):⁶⁹

$$L_c = L \times X_c \quad (\text{Eq. 5})$$

where X_c is the crystallinity measured by WAXS. We observed that the L of LDPE oxidized in solution was 22.5 nm and the L of HDPE oxidized in solution was 22.0 nm. These values were smaller than the respective values of L for LDPE oxidized as a film which was 23.8 nm and for HDPE oxidized as a film which was 25.0 nm. Using the X_c values for the respective samples, we determined that the L_c of LDPE oxidized in solution was 9.4 nm and the L_c of HDPE oxidized in solution was 12.4 nm, which were smaller values than the L_c of LDPE oxidized as a film which was 10.0 nm and the L_c of HDPE oxidized as a film which was 15.2 nm. Correspondingly, we determined that the L_a of LDPE oxidized in solution was 13.1 nm and the L_a of HDPE oxidized in solution was 9.7 nm, which were smaller values than the L_a of LDPE oxidized as a film which was 13.8 nm and the L_a of HDPE oxidized as a film which was 9.9 nm. These results indicate that relative to the oxidation of a PE film, the oxidation of PE in solution decreases L by decreasing both L_a and L_c , but for a highly crystalline material like HDPE, the decrease in L_c is a larger contributor to the observed change.

Table S9. Summary of parameters obtained by WAXS and SAXS analysis of pristine and oxidized PE samples.

Sample	q_{110} ($\text{\AA}^{-1}$)	q_{200} ($\text{\AA}^{-1}$)	X_c (%)	L (nm)	L_c (nm)	L_a (nm)
4a	1.53	1.69	41.8	22.5	9.4	13.1
4b	1.53	1.69	42.1	23.8	10.0	13.8
4c	1.54	1.71	56.1	22.0	12.4	9.7
4d	1.54	1.71	60.6	25.0	15.2	9.9

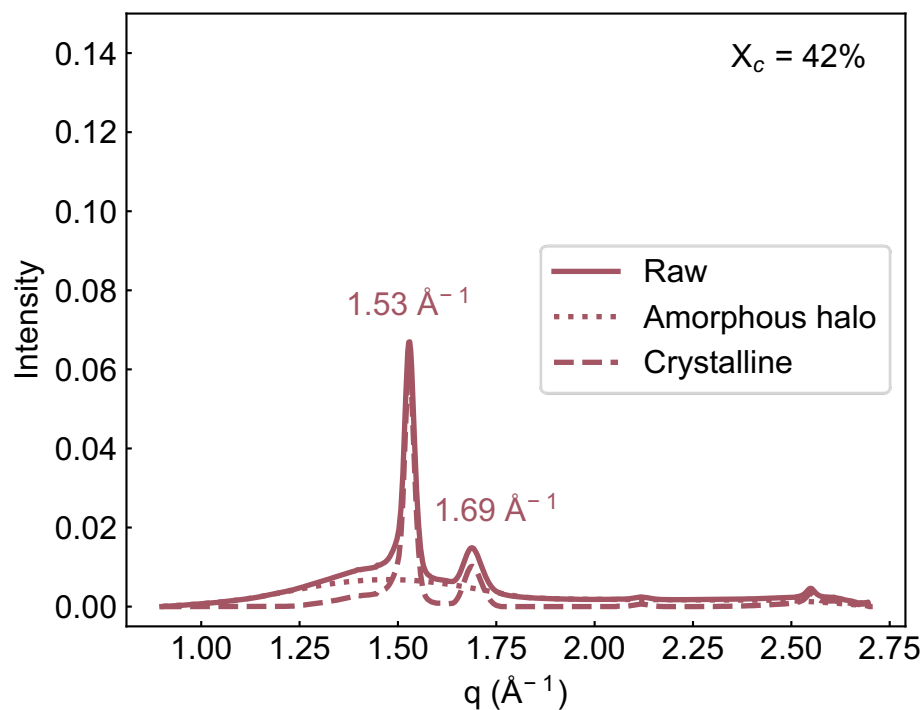


Fig. S24 | WAXS profile of LDPE oxidized in solution (**4a**) (0.3 mol% ketone).

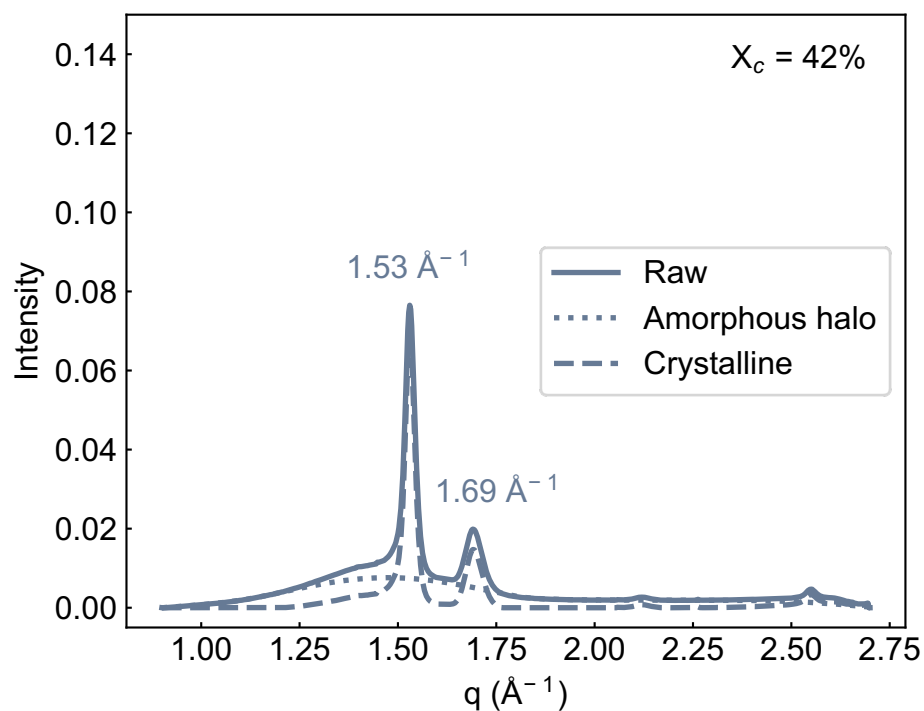


Fig. S25 | WAXS profile of LDPE oxidized at the solid-liquid interface (**4b**) (0.3 mol% ketone).

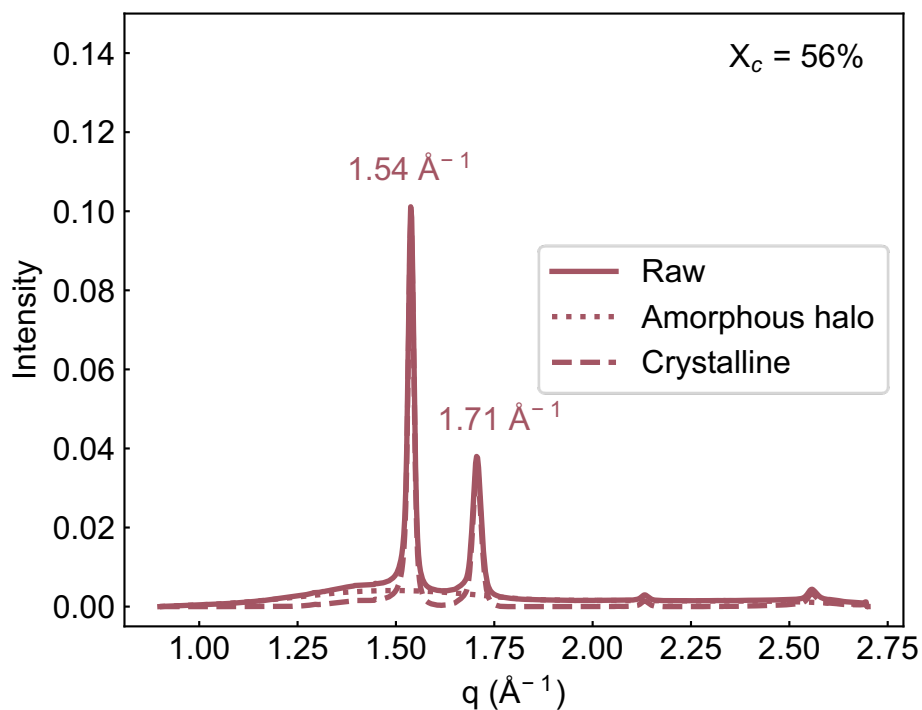


Fig. S26 | WAXS profile of HDPE oxidized in solution (**4c**) (0.3 mol% ketone).

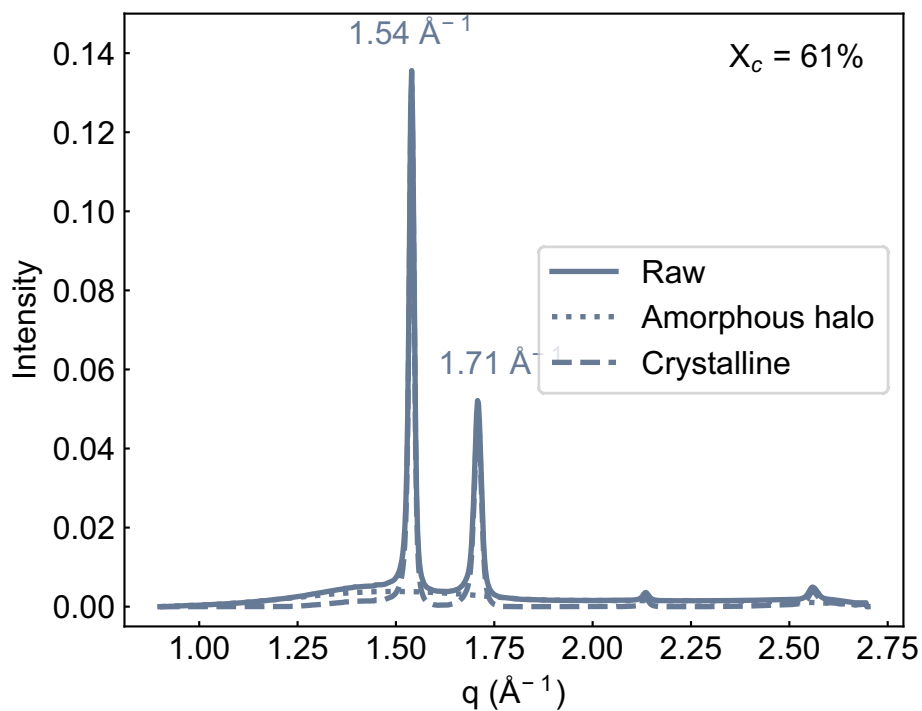


Fig. S27 | WAXS profile of HDPE oxidized at the solid-liquid interface (**4d**) (0.3 mol% ketone).

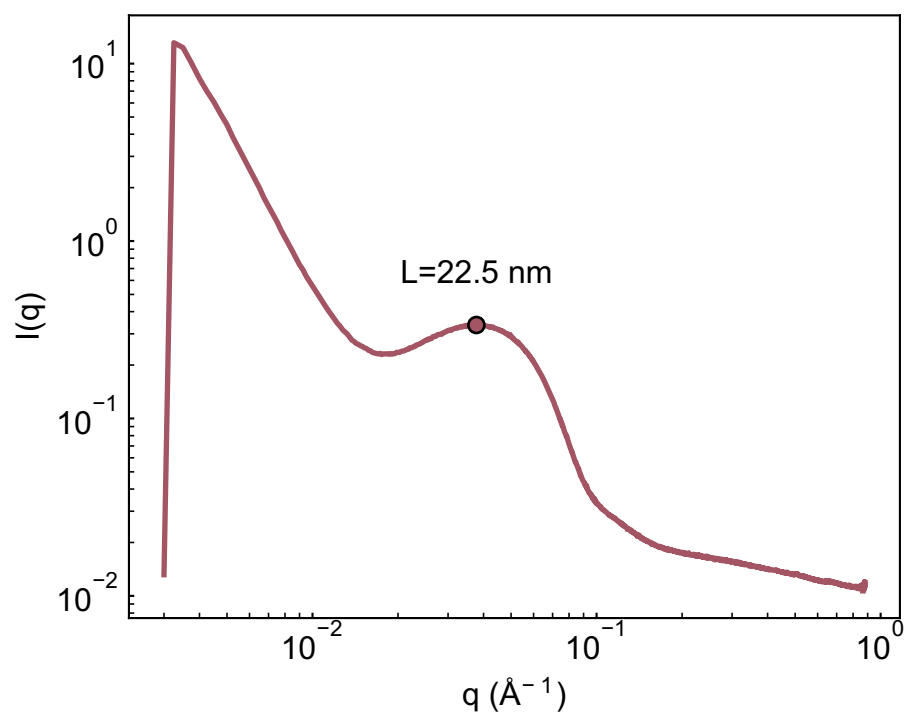


Fig. S28 | SAXS profile of LDPE oxidized in solution (**4a**) (0.3 mol% ketone).

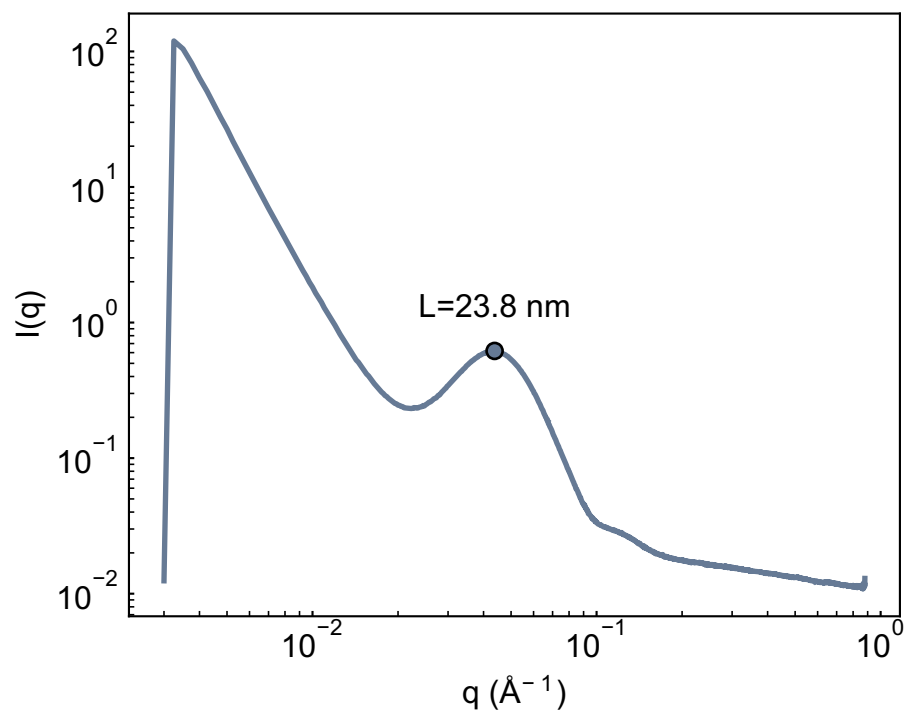


Fig. S29 | SAXS profile of LDPE oxidized at the solid-liquid interface (**4b**) (0.3 mol% ketone).

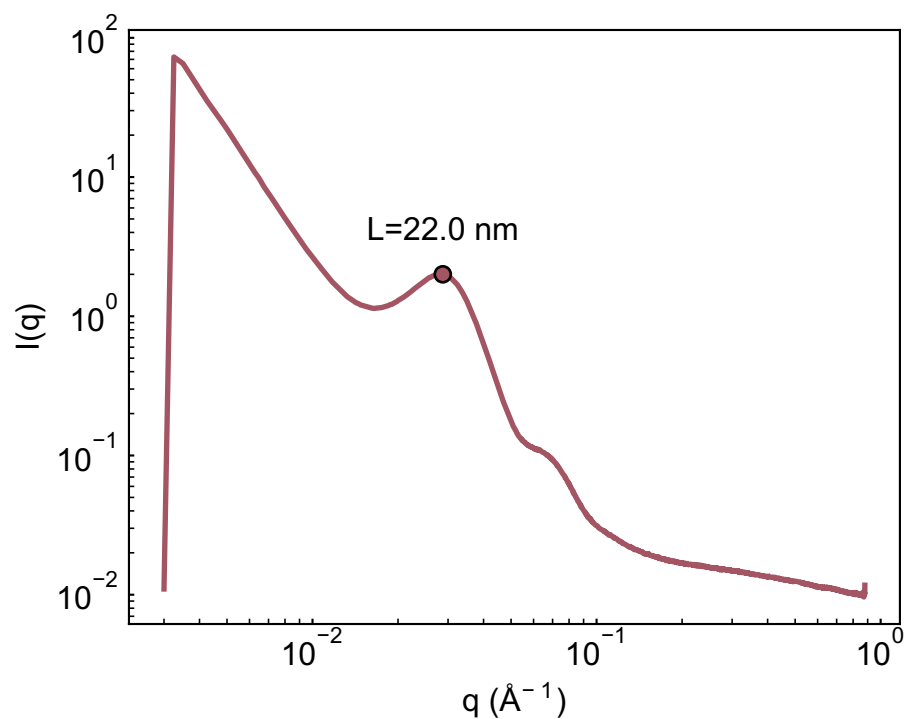


Fig. S30 | SAXS profile of HDPE oxidized in solution (**4c**) (0.3 mol% ketone).

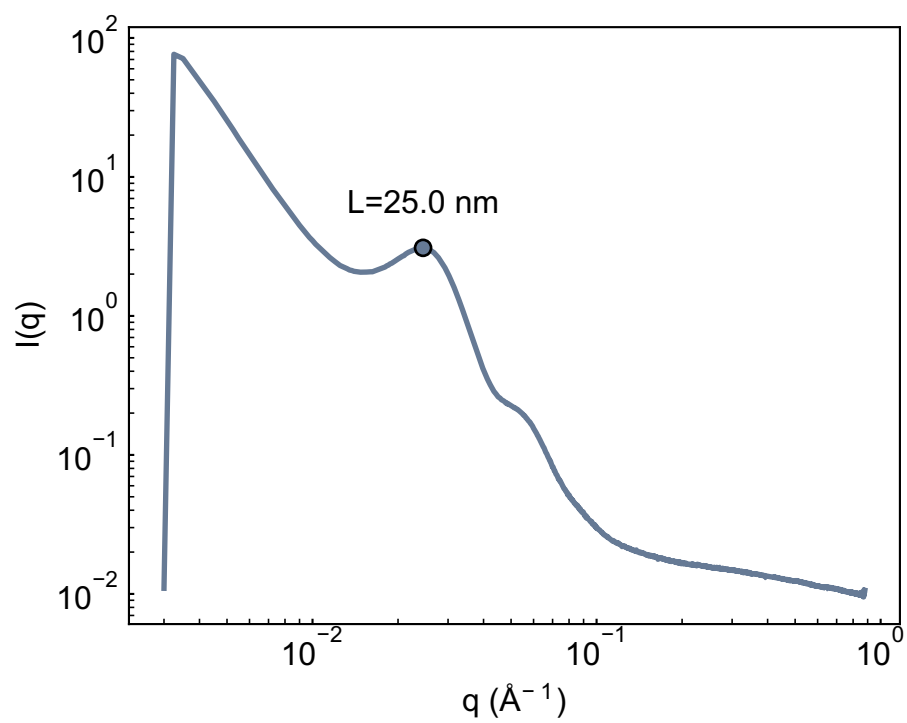
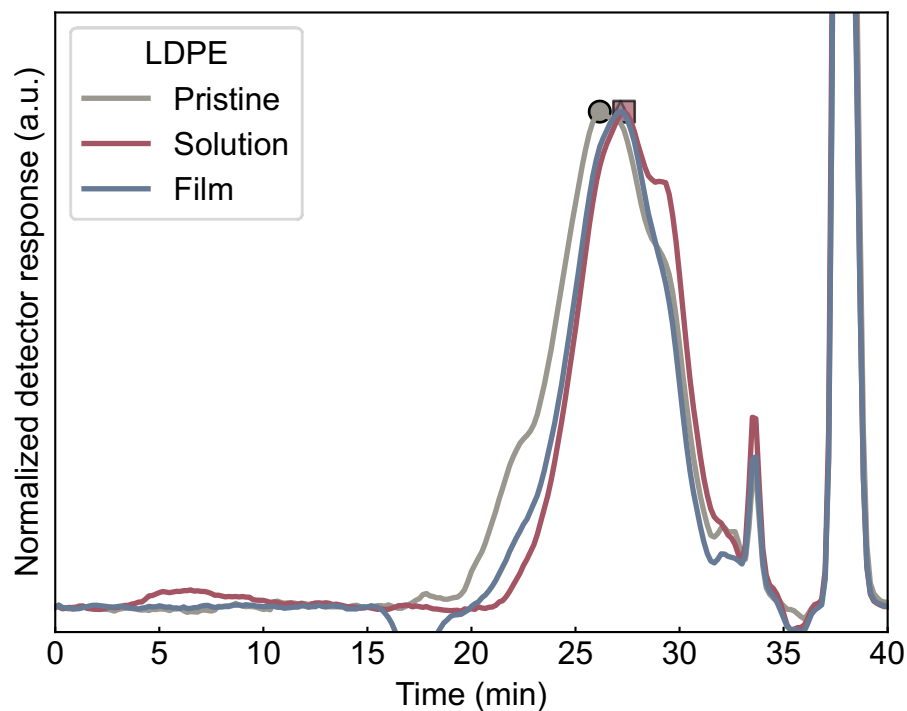


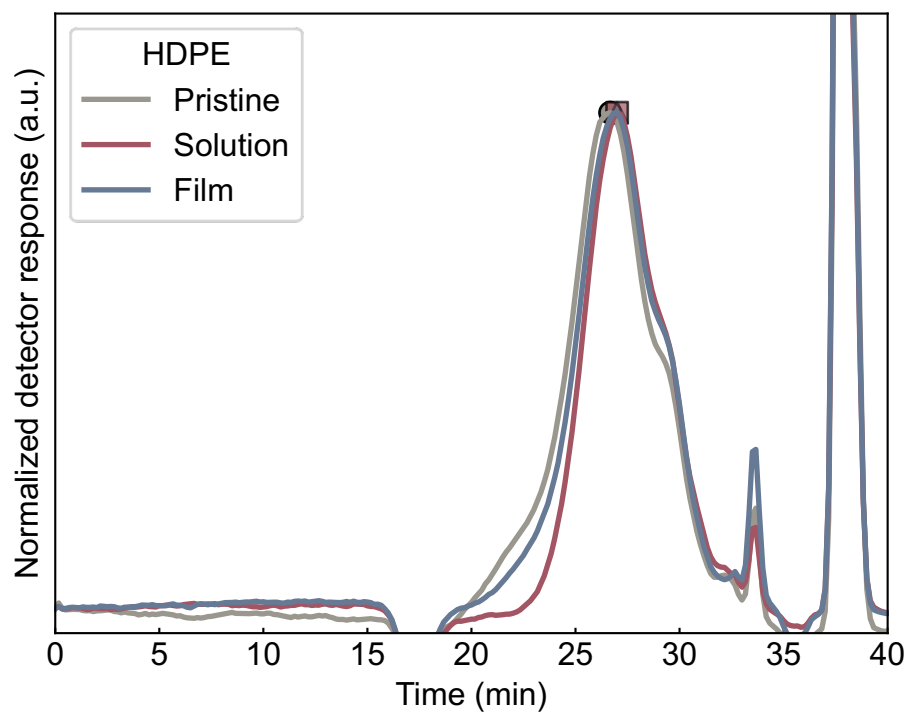
Fig. S31 | SAXS profile of HDPE oxidized at the solid–liquid interface (**4d**) (0.3 mol% ketone).

3. Supplemental Figures



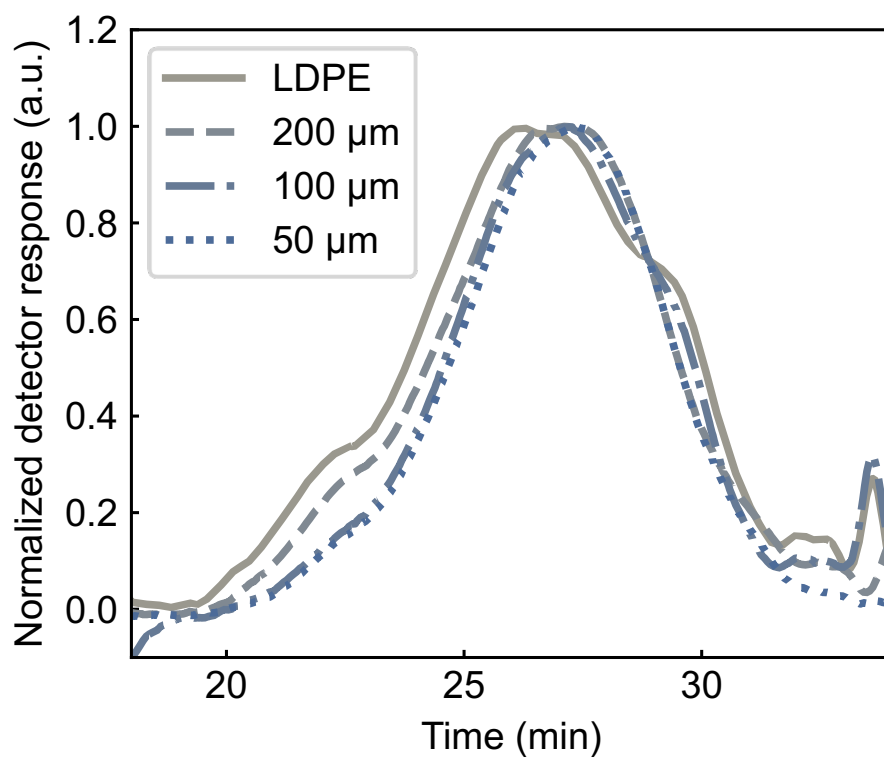
Name	M_n (kDa)	M_w (kDa)	$\bar{D}$
Pristine LDPE	7.2	57.4	8.0
Solution-oxidized LDPE	4.1	19.0	4.7
Film-oxidized LDPE	6.7	37.0	5.6

Fig. S32 | HT SEC data for pristine LDPE (gray), solution-oxidized LDPE (0.3 mol% ketone) (red), and film-oxidized LDPE (0.3 mol% ketone) (blue) (1 mg/mL in 1,2,4-trichlorobenzene, 1 mL/min, PE standards).



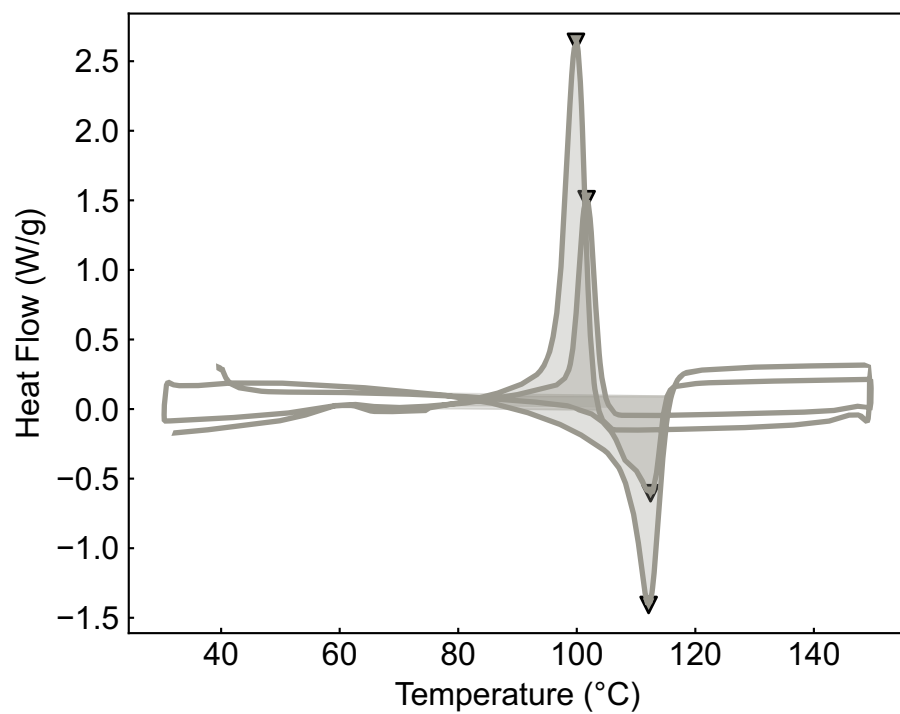
Name	M_n (kDa)	M_w (kDa)	$\bar{D}$
Pristine HDPE	7.0	28.1	4.0
Solution-oxidized HDPE	4.6	15.3	3.3
Film-oxidized HDPE	6.2	26.5	4.3

Fig. S33 | HT SEC data for pristine HDPE (gray), solution-oxidized HDPE (0.3 mol% ketone) (red), and film-oxidized HDPE (0.3 mol% ketone) (blue) (1 mg/mL in 1,2,4-trichlorobenzene, 1 mL/min, PE standards).



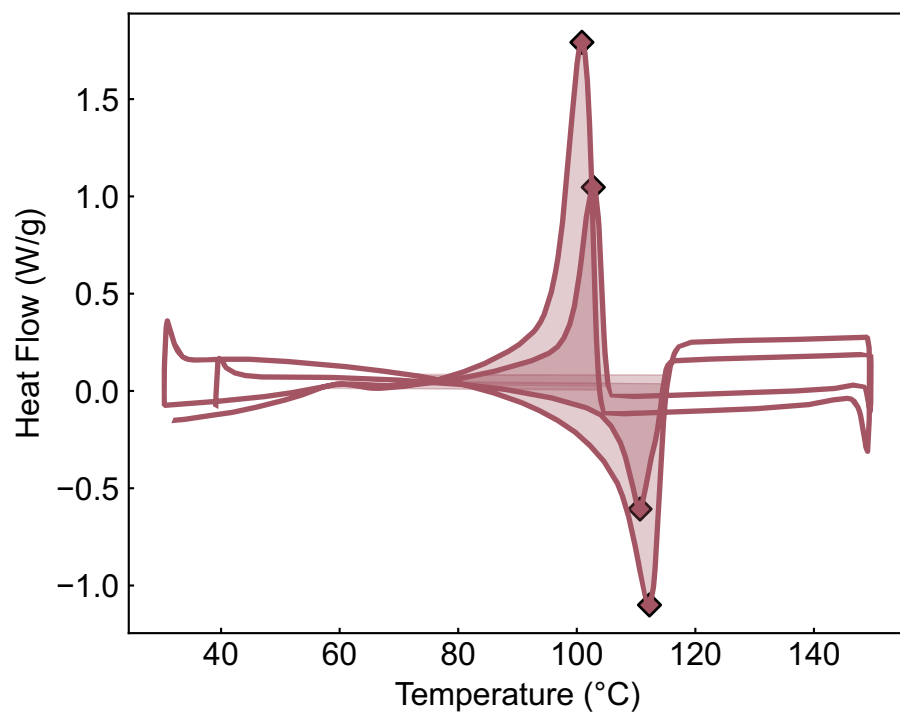
Name	M_n (kDa)	M_w (kDa)	$\bar{D}$
Pristine LDPE	7.2	57.1	8.0
Film-oxidized LDPE (200 μm)	6.9	46.6	6.7
Film-oxidized LDPE (100 μm)	6.7	37.0	5.6
Film-oxidized LDPE (50 μm)	5.9	28.3	4.8

Fig. S34 | HT SEC data for pristine LDPE (gray) and LDPE oxidized as films (blue) with thicknesses of 200 μm , 100 μm , and 50 μm (1 mg/mL in 1,2,4-trichlorobenzene, 1 mL/min, PE standards).



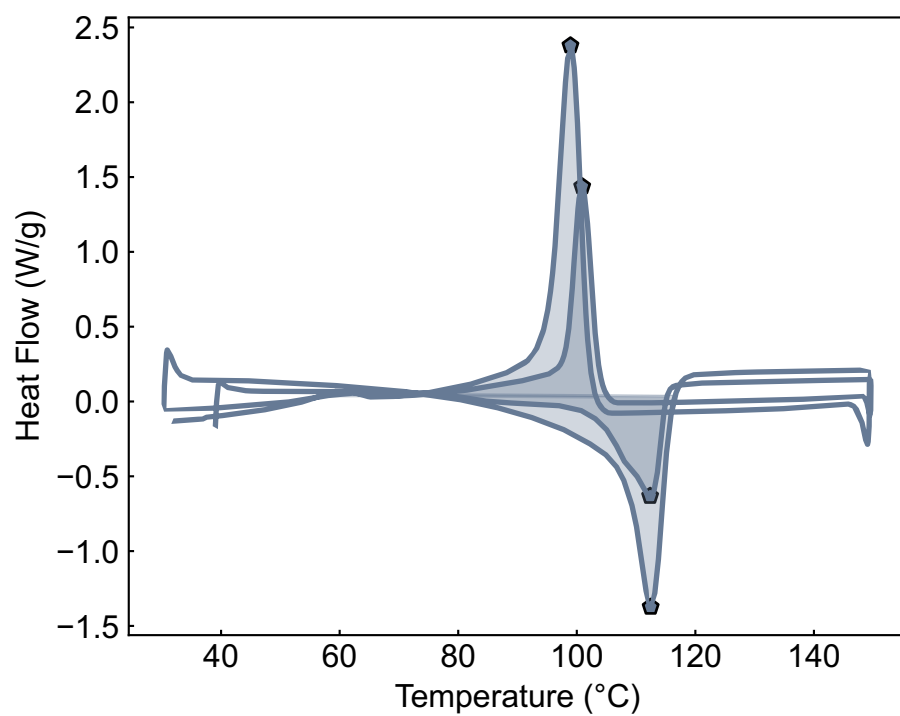
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	112.4	72.1	101.7	-80.2
2	10	112.1	78.2	99.9	-79.5

Fig. S35 | Differential scanning calorimetry of pristine LDPE.



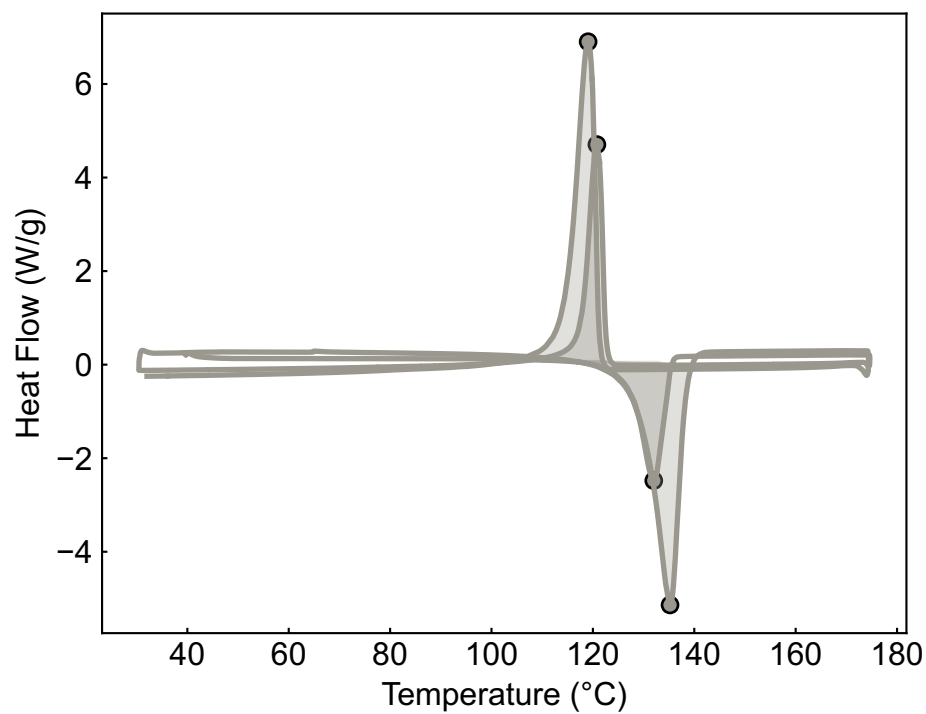
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	110.7	66.7	102.8	-77.1
2	10	112.3	75.9	100.9	-77.0

Fig. S36 | Differential scanning calorimetry of solution-oxidized LDPE (0.3 mol%).



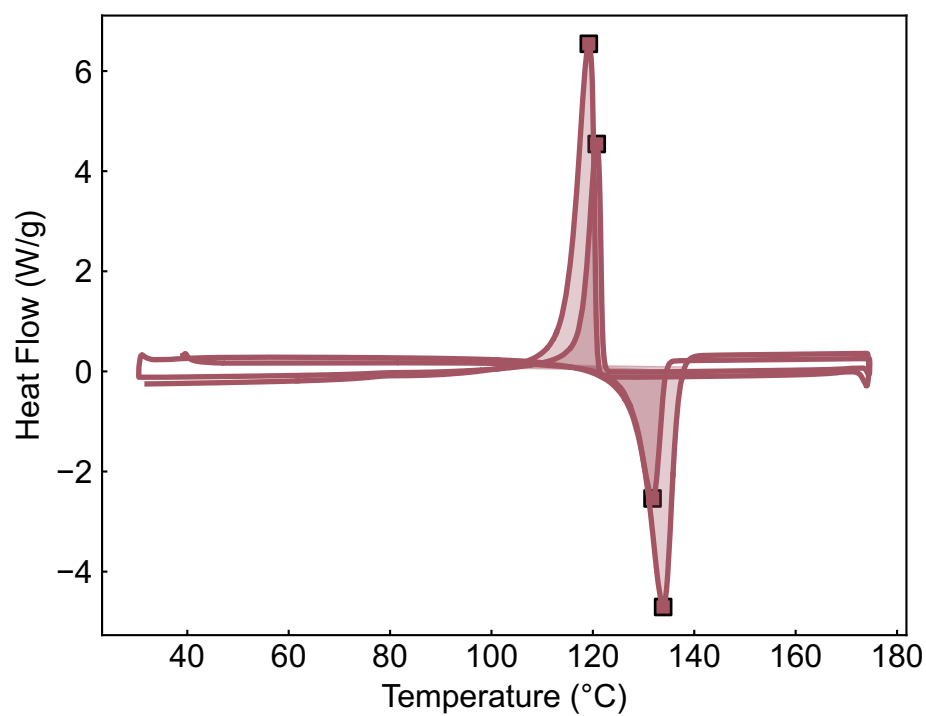
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	112.4	76.5	100.9	-82.2
2	10	112.5	80.5	98.9	-81.9

Fig. S37 | Differential scanning calorimetry of film-oxidized LDPE (0.3 mol%).



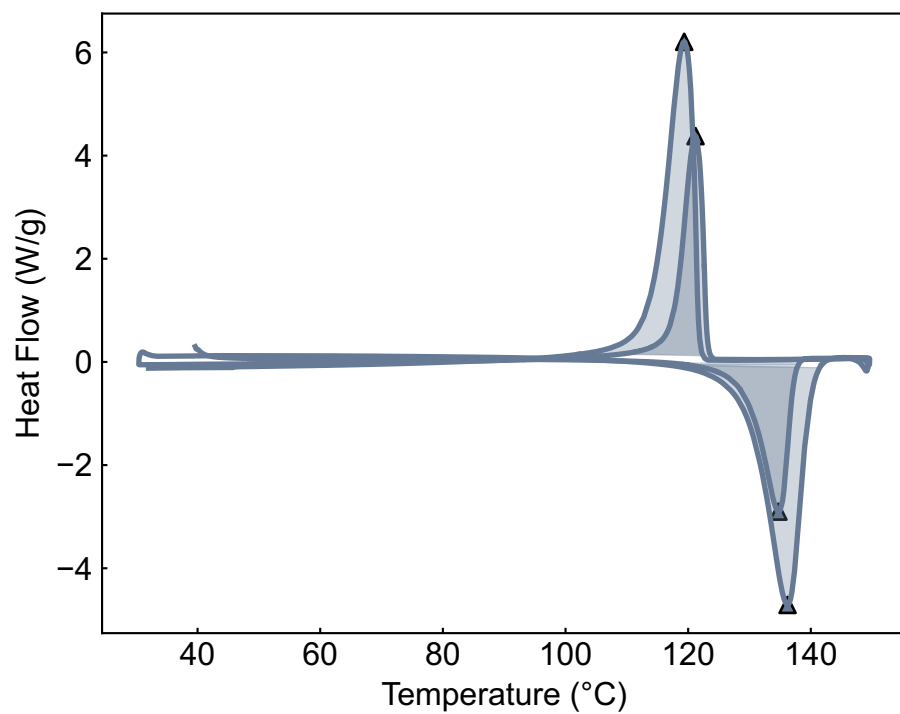
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	132.0	170.7	120.8	-197.2
2	10	135.2	197	119.1	-195.7

Fig. S38 | Differential scanning calorimetry of pristine HDPE.



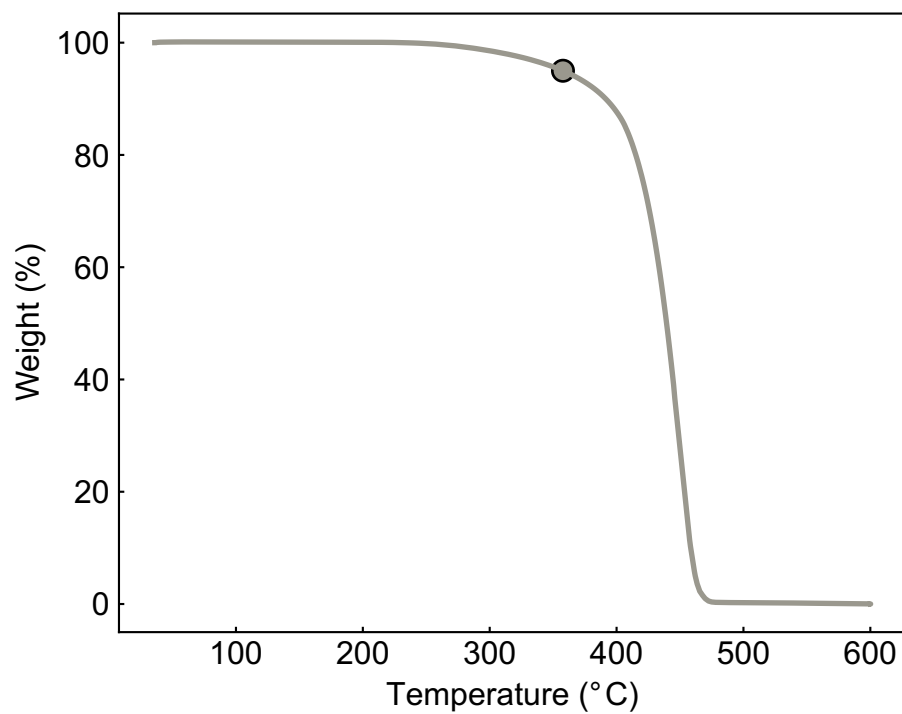
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	131.4	166.5	120.8	-178
2	10	133.9	177.9	119.2	-177.2

Fig. S39 | Differential scanning calorimetry of solution-oxidized HDPE (0.3 mol%).



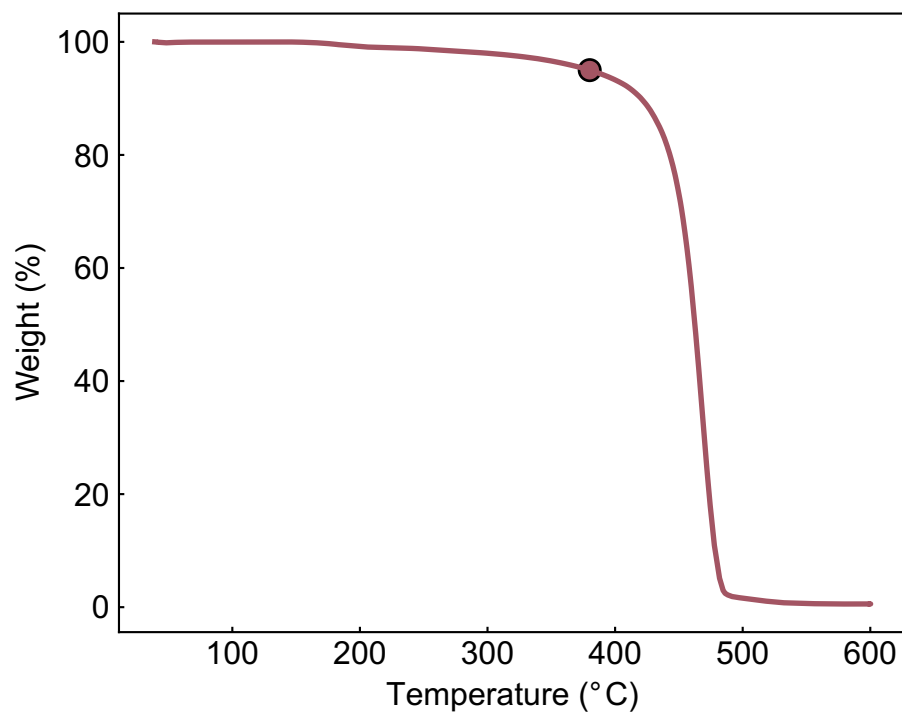
Cycle	Rate (°C/min)	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
1	5	134.7	190.8	121.2	-198.8
2	10	136.2	198.8	119.4	-197.7

Fig. S40 | Differential scanning calorimetry of film-oxidized HDPE (0.3 mol%).



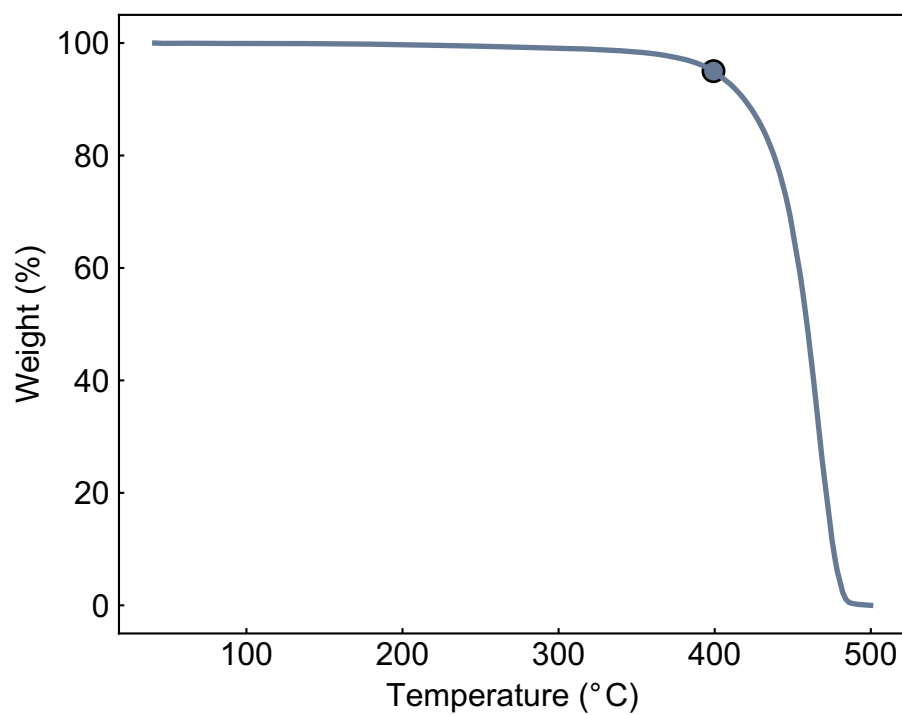
Name	$T_{d,5\%}$ (°C)
Pristine LDPE	357.7

Fig. S41 | Thermogravimetric analysis of pristine LDPE (10 °C/min, 50 mL/min N₂).



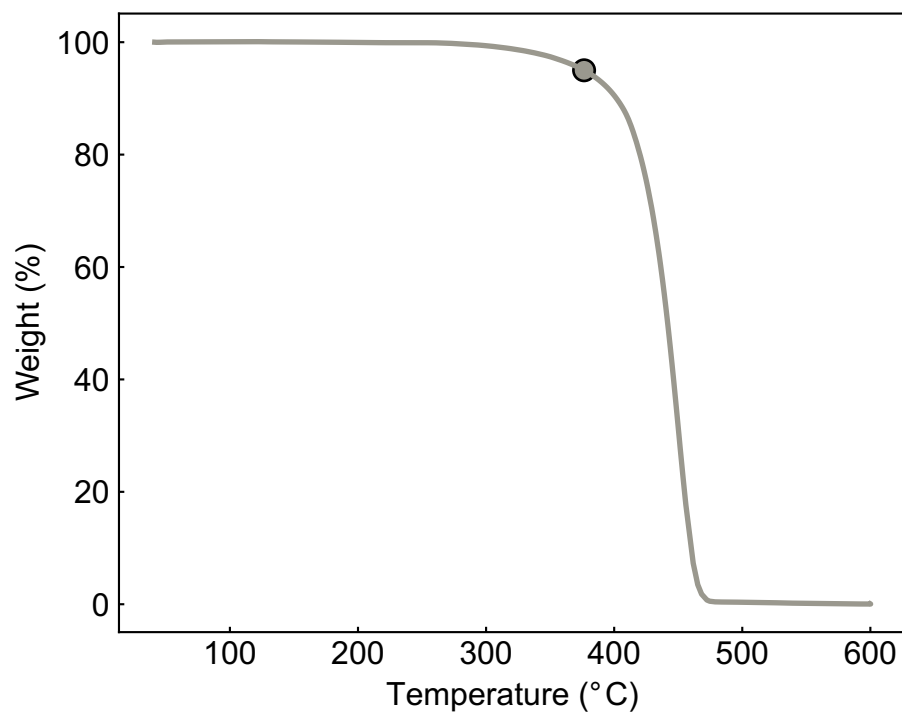
Name	$T_{d,5\%}$ (°C)
Solution-oxidized LDPE	380.1

Fig. S42 | Thermogravimetric analysis of solution-oxidized LDPE (0.3 mol%) (10 °C/min, 50 mL/min N₂).



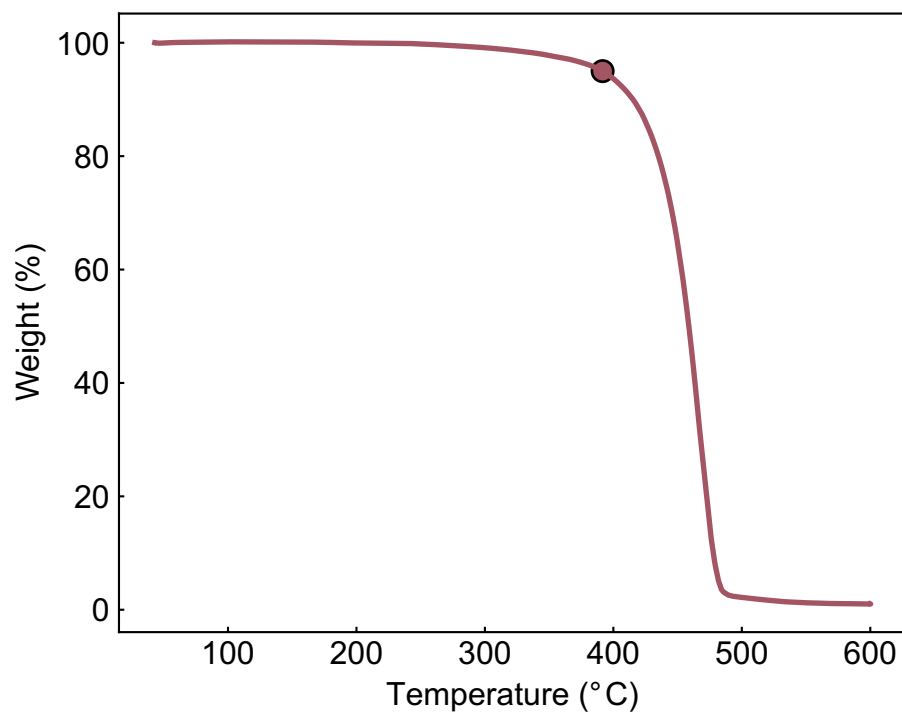
Name	$T_{d,5\%}$ (°C)
Film-oxidized LDPE	399.2

Fig. S43 | Thermogravimetric analysis of film-oxidized LDPE (0.3 mol%) (10 °C/min, 50 mL/min N₂).



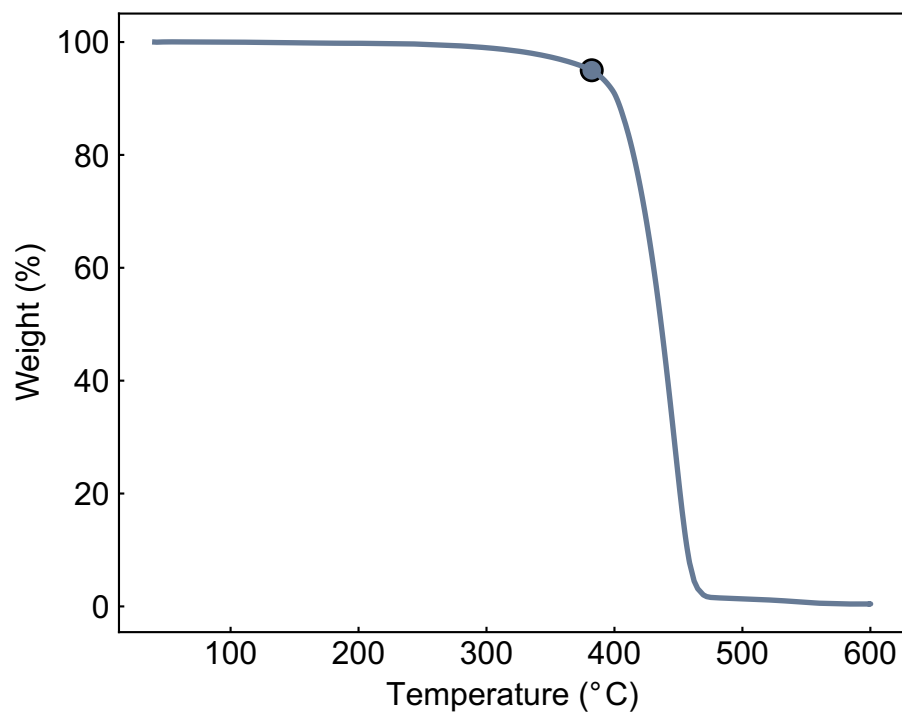
Name	$T_{d,5\%}$ (°C)
Pristine HDPE	376.5

Fig. S44 | Thermogravimetric analysis of pristine HDPE (10 °C/min, 50 mL/min N₂).



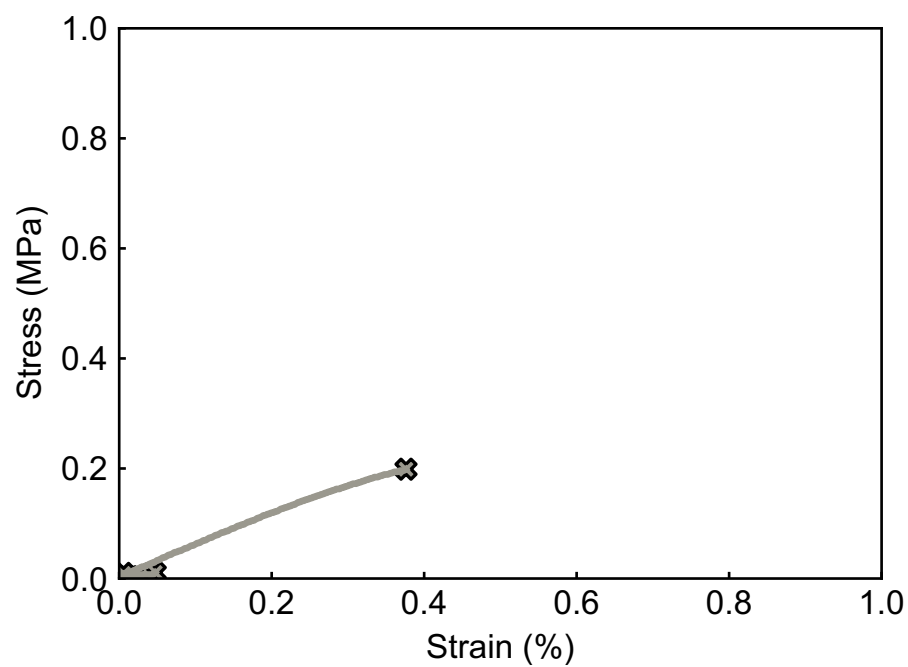
Name	$T_{d,5\%}$ (°C)
Solution-oxidized HDPE	391.6

Fig. S45 | Thermogravimetric analysis of solution-oxidized HDPE (0.3 mol%) (10 °C/min, 50 mL/min N₂).



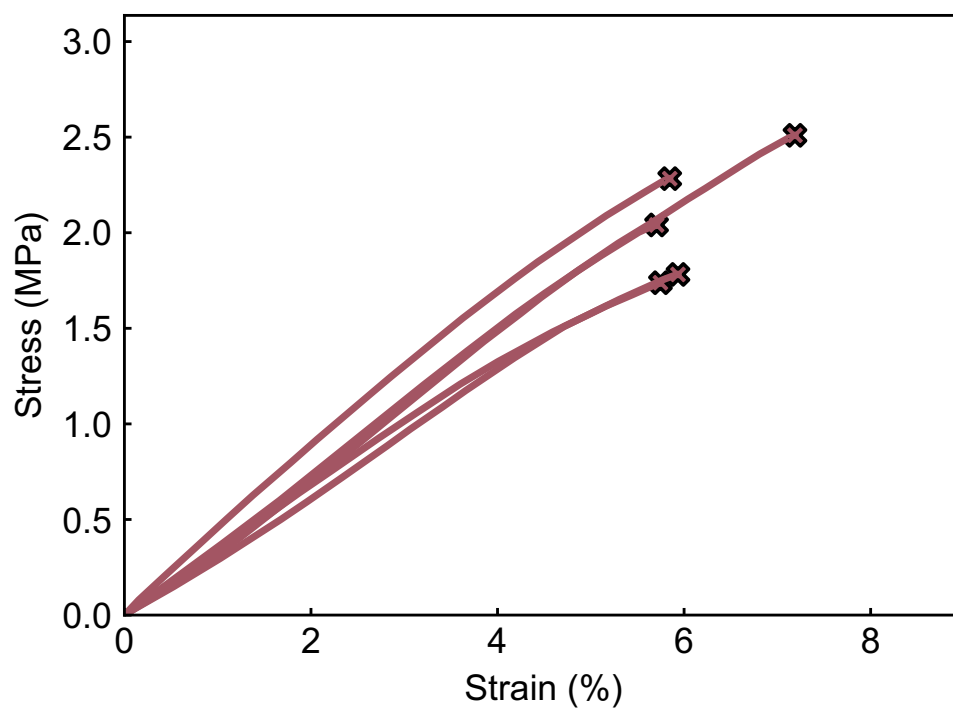
Name	$T_{d,5\%}$ (°C)
Film-oxidized HDPE	382.2

Fig. S46 | Thermogravimetric analysis of film-oxidized HDPE (0.3 mol%) (10 °C/min, 50 mL/min N₂).



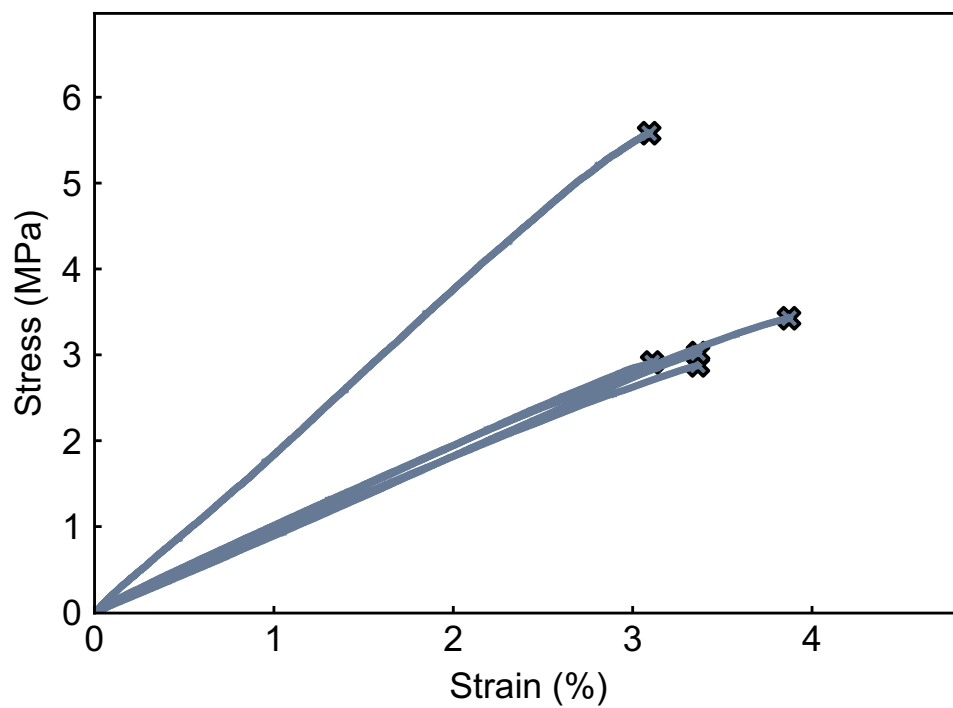
Entry	U_T (MPa)	Failure
1	0.00	Adhesive
2	0.01	Adhesive
3	0.01	Adhesive
4	0.20	Adhesive
5	0.00	Adhesive

Fig. S47 | Nylon lap-shear adhesion data for pristine LDPE (1.5 mm/min). (* = failed during pre-strain step).



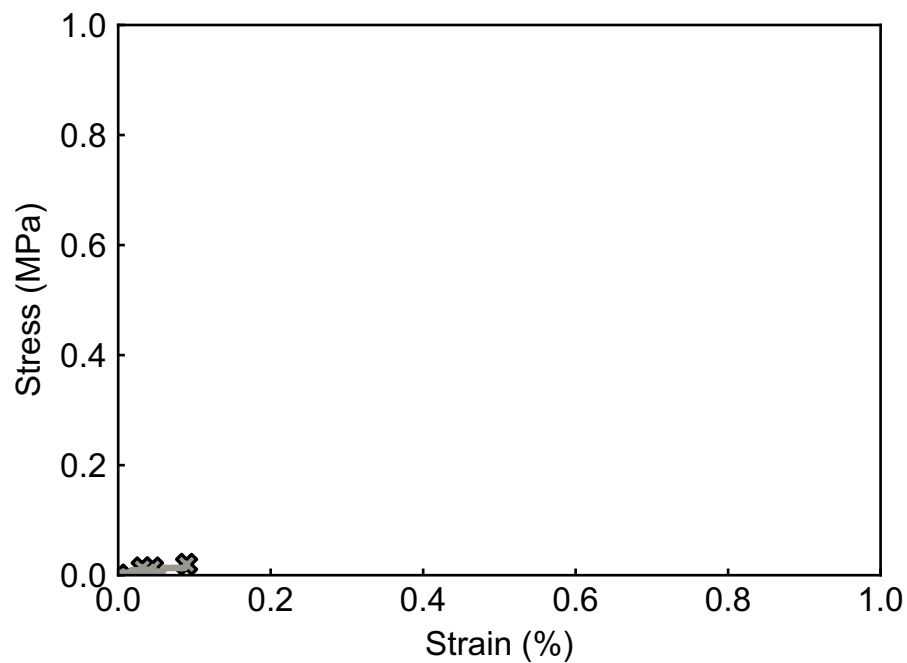
Entry	U_T (MPa)	Failure
1	2.04	Adhesive
2	2.51	Adhesive
3	1.74	Adhesive
4	1.78	Adhesive
5	2.28	Adhesive

Fig. S48 | Nylon lap-shear adhesion data for solution-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



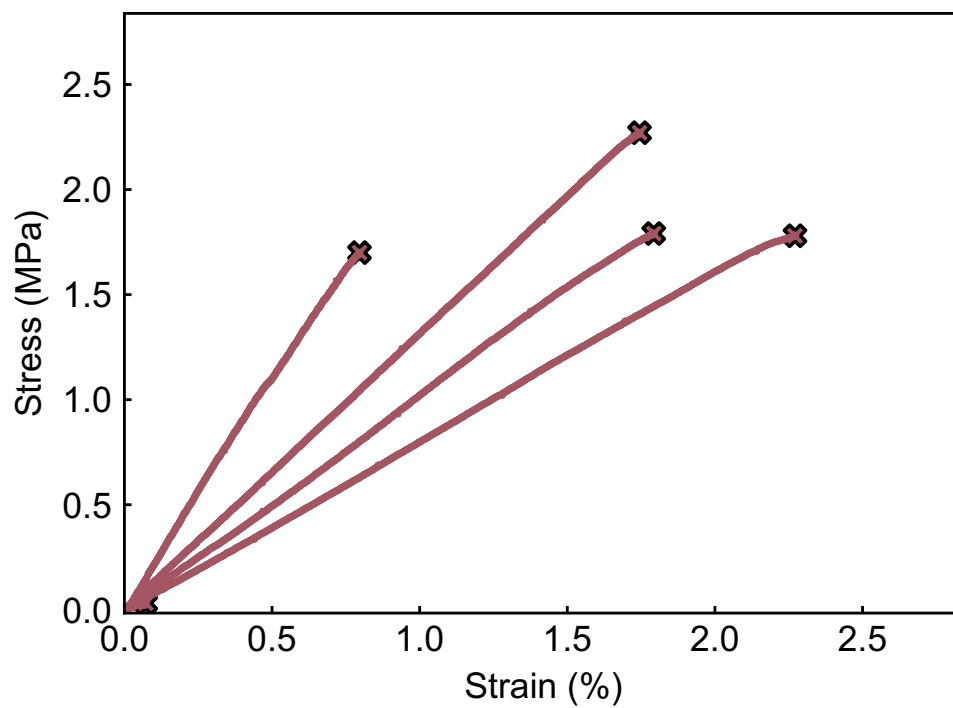
Entry	U_T (MPa)	Failure
1	2.91	Adhesive
2	3.43	Adhesive
3	2.88	Adhesive
4	5.58	Adhesive
5	3.02	Adhesive

Fig. S49 | Nylon lap-shear adhesion data for film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



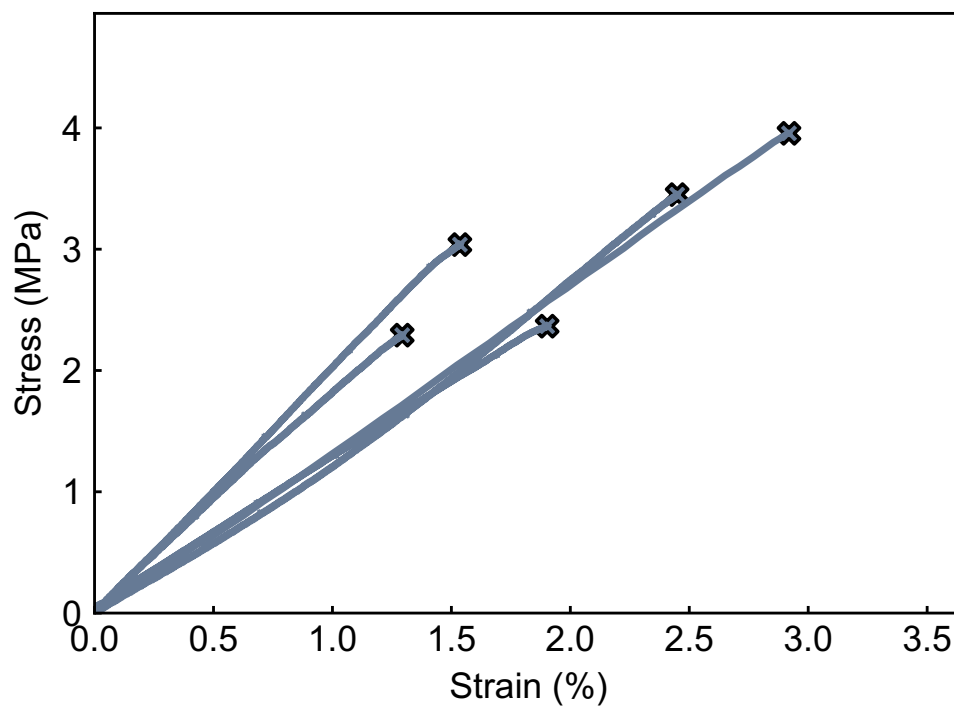
Entry	U_T (MPa)	Failure
1	0.01	Adhesive
2	0.02	Adhesive
3	0.01	Adhesive
4	0.00	Adhesive
5	0.00	Adhesive

Fig. S50 | Nylon lap-shear adhesion data for pristine HDPE (1.5 mm/min). (* = failed during pre-strain step).



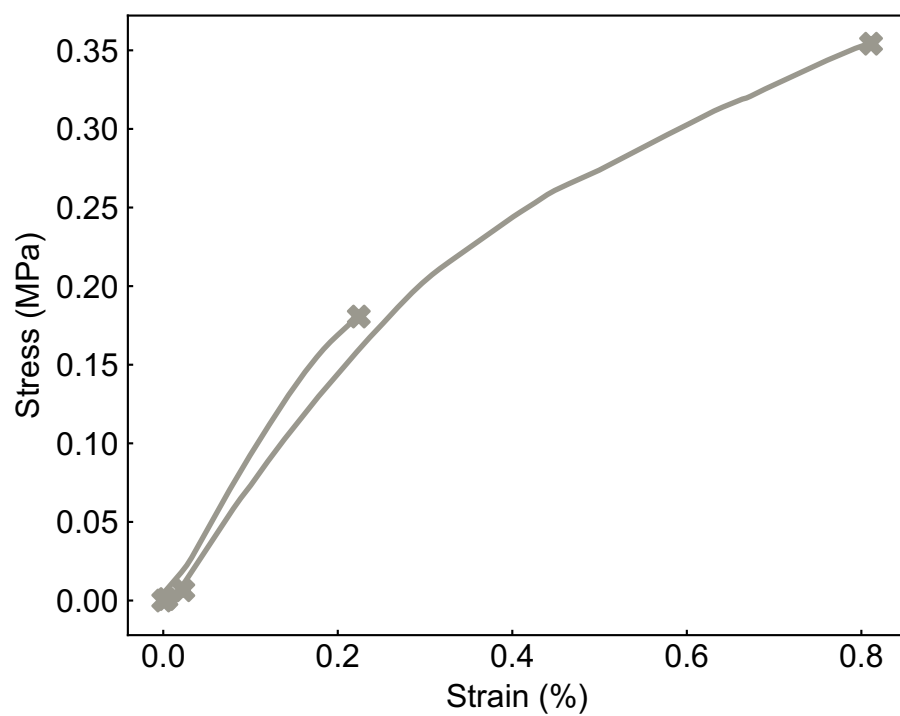
Entry	U_T (MPa)	Failure
1	1.78	Adhesive
2	1.79	Adhesive
3	2.27	Adhesive
4	0.03	Adhesive
5	1.70	Adhesive

Fig. S51 | Nylon lap-shear adhesion data for solution-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



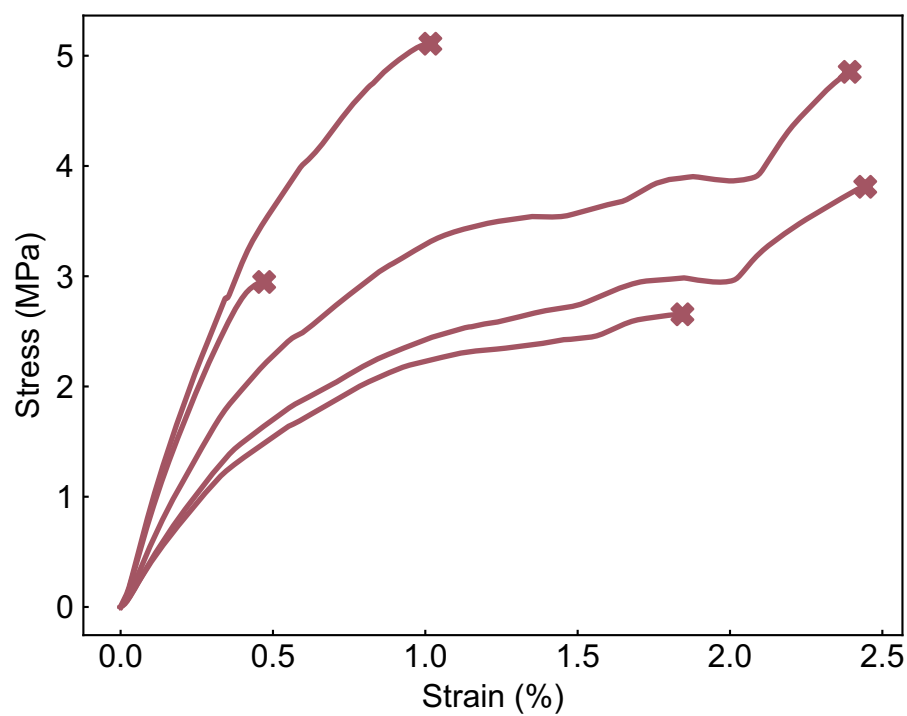
Entry	U_T (MPa)	Failure
1	3.45	Adhesive
2	2.37	Adhesive
3	2.29	Adhesive
4	3.04	Adhesive
5	3.96	Adhesive

Fig. S52 | Nylon lap-shear adhesion data for film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



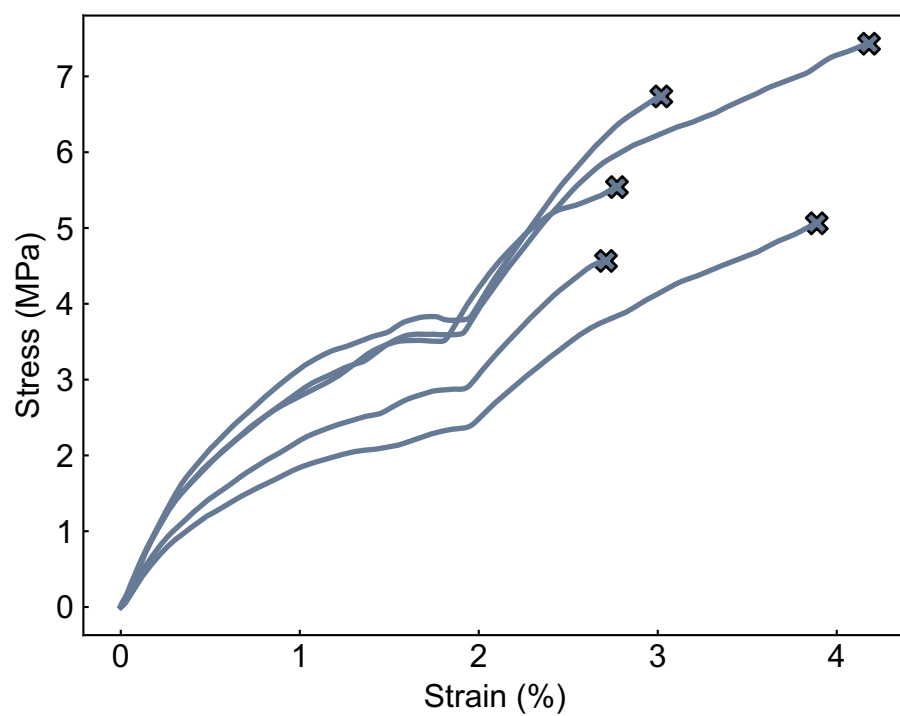
Entry	U_T (MPa)	Failure
1	0.18	Adhesive
2	0.35	Adhesive
3*	—	Adhesive
4*	—	Adhesive
5*	—	Adhesive

Fig. S53 | Glass lap-shear adhesion data for pristine LDPE (1.5 mm/min). (* = failed during pre-strain step).



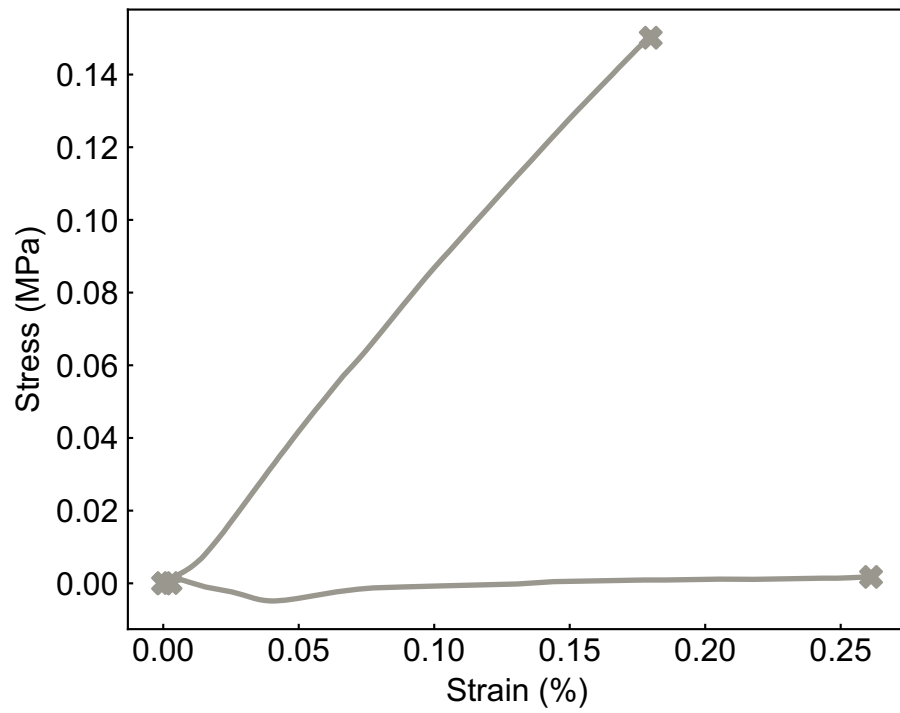
Entry	U_T (MPa)	Failure
1	2.95	Adhesive
2	2.65	Cohesive
3	5.11	Adhesive
4	3.81	Adhesive
5	4.85	Adhesive

Fig. S54 | Glass lap-shear adhesion data for solution-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min).



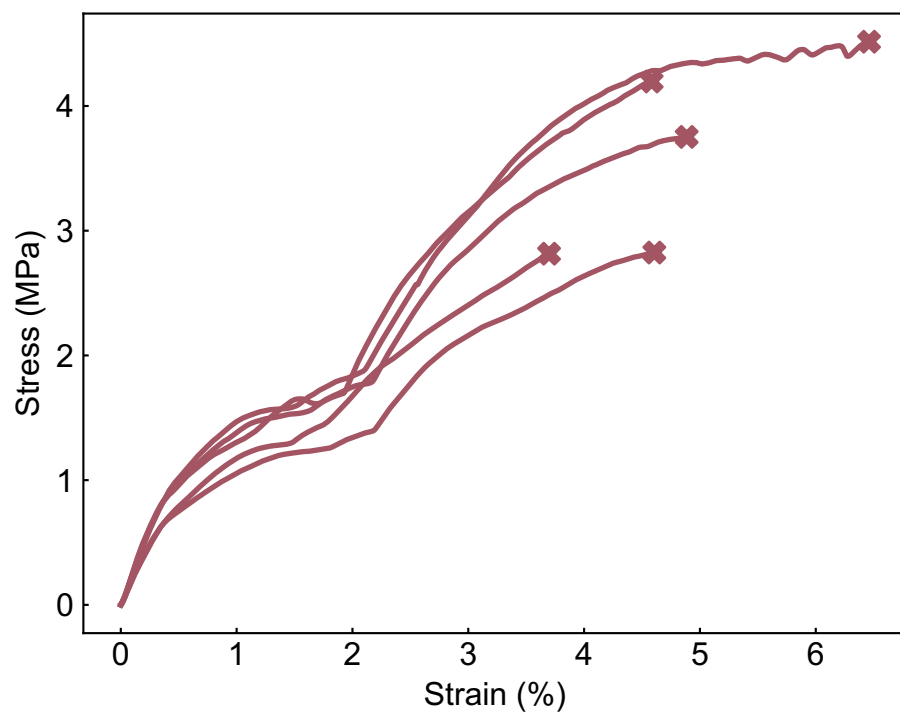
Entry	U_T (MPa)	Failure
1	7.43	Adhesive
2	6.74	Adhesive
3	4.57	Adhesive
4	5.06	Adhesive
5	5.54	Adhesive

Fig. S55 | Glass lap-shear adhesion data for film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min).



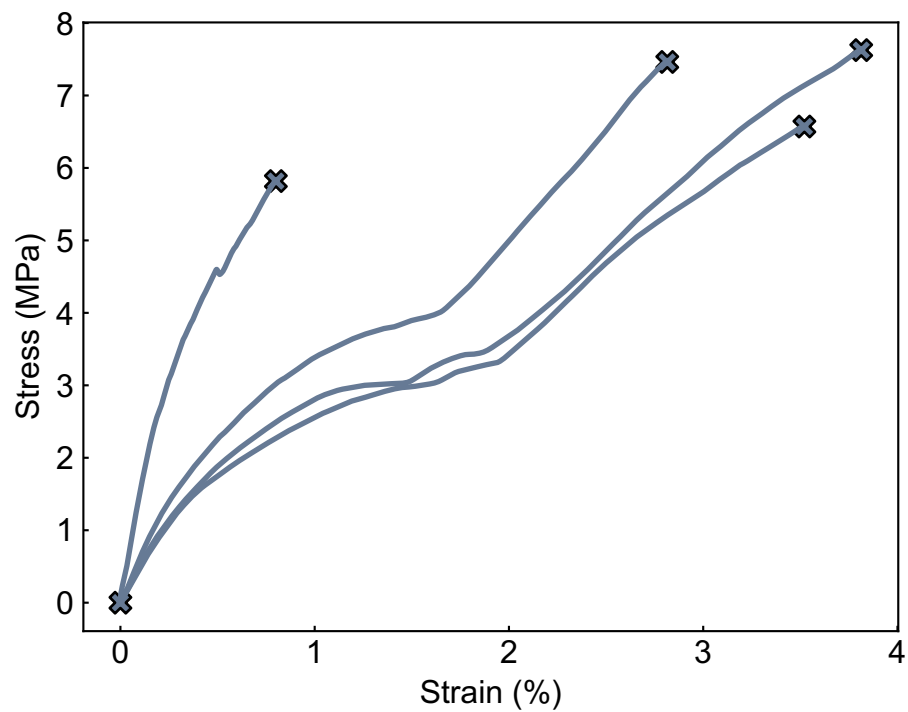
Entry	U_T (MPa)	Failure
1	1.08	Adhesive
2*	—	Adhesive
3	0.15	Adhesive
4*	—	Adhesive
5*	—	Adhesive

Fig. S56 | Glass lap-shear adhesion data for pristine HDPE (1.5 mm/min). (* = failed during pre-strain step).



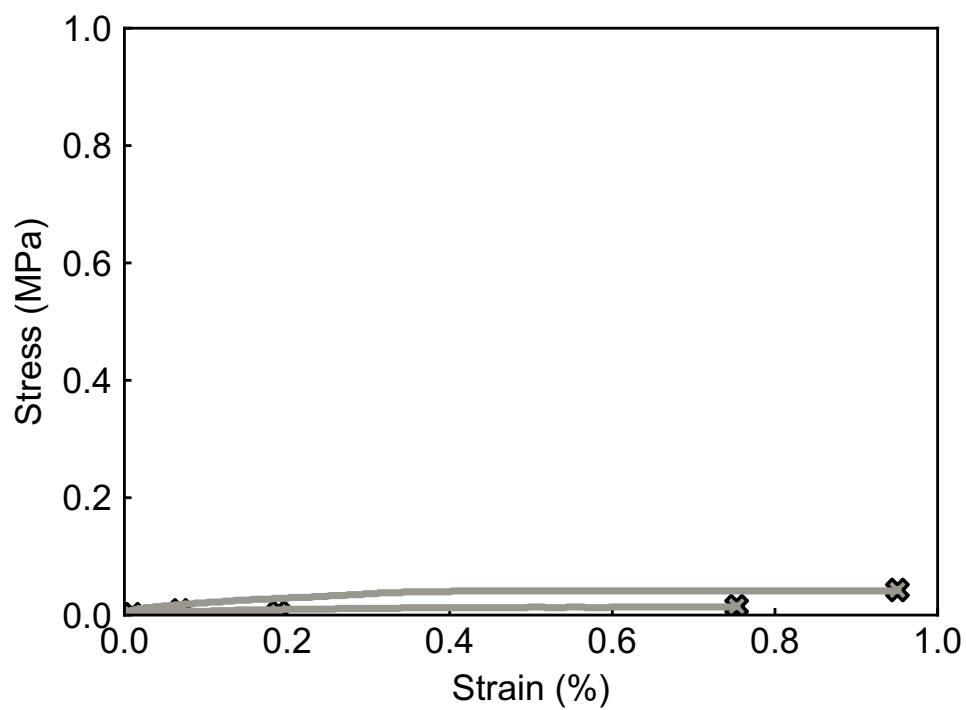
Entry	U_T (MPa)	Failure
1	2.82	Adhesive
2	3.75	Adhesive
3	4.20	Adhesive
4	4.52	Adhesive
5	2.82	Adhesive

Fig. S57 | Glass lap-shear adhesion data for solution-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min).



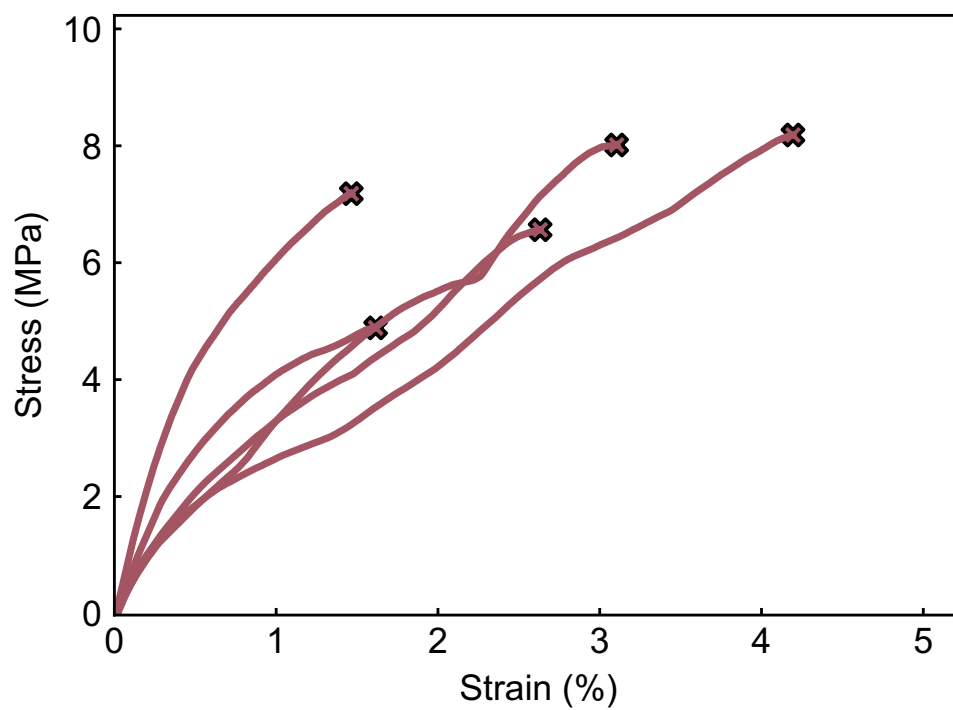
Entry	U_T (MPa)	Failure
1	5.8	Adhesive
2	7.6	Adhesive
3	7.5	Adhesive
4	6.6	Adhesive
5*	—	—

Fig. S58 | Glass lap-shear adhesion data for film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



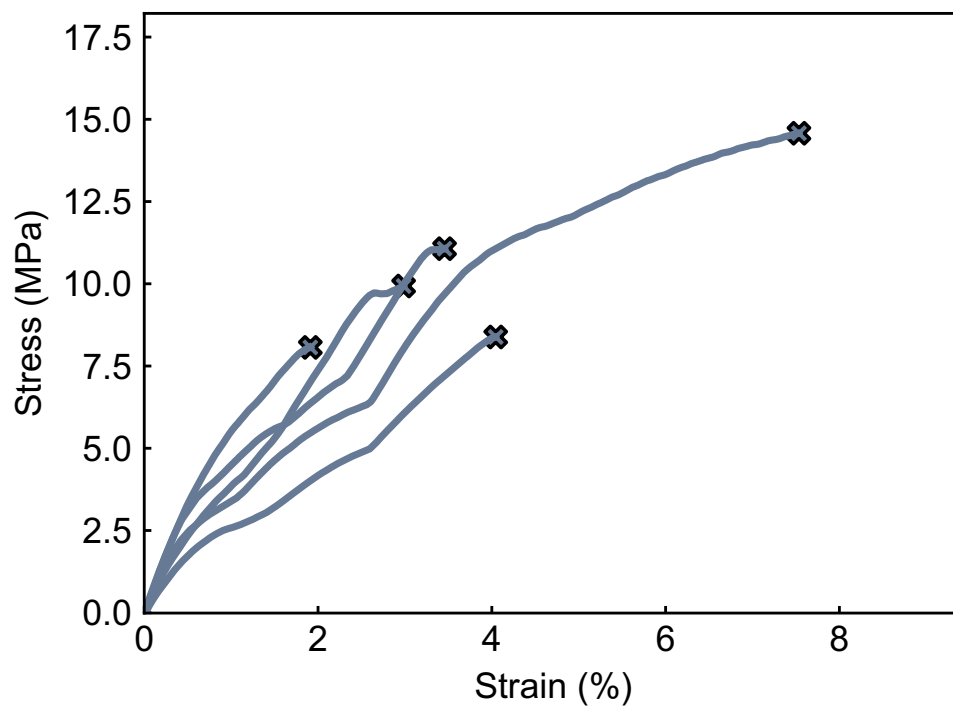
Entry	U_T (MPa)	Failure
1	0.04	Adhesive
2	0.02	Adhesive
3	0.00	Adhesive
4	0.01	Adhesive
5	0.00	Adhesive

Fig. S59 | Aluminum lap-shear adhesion data for pristine LDPE (1.5 mm/min). (* = failed during pre-strain step).



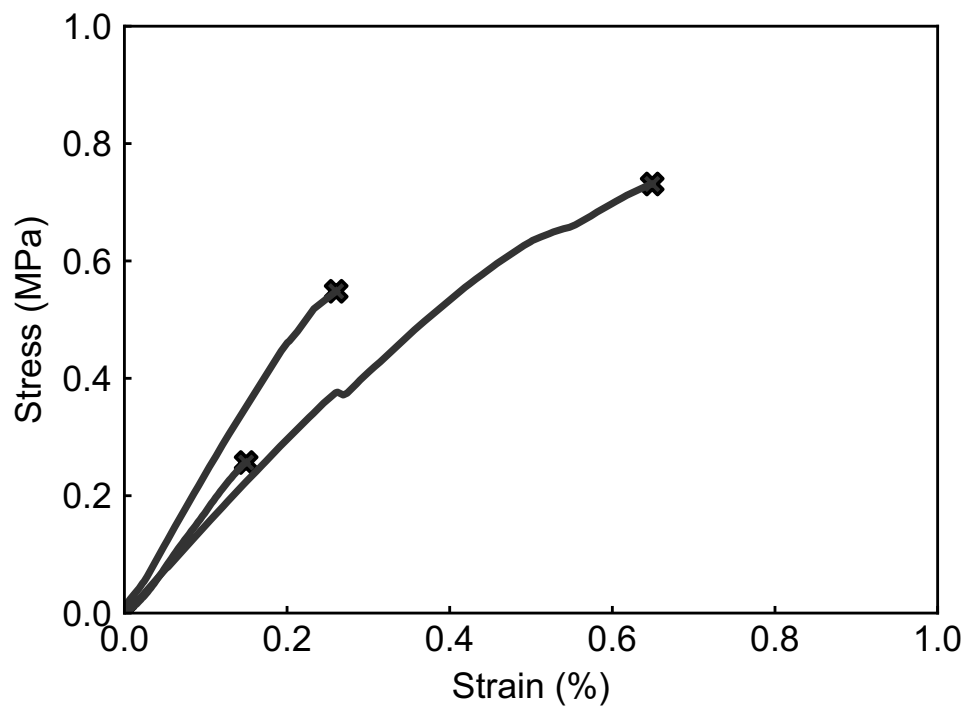
Entry	U_T (MPa)	Failure
1	6.56	Adhesive
2	8.01	Adhesive
3	4.89	Adhesive
4	7.18	Adhesive
5	8.18	Adhesive

Fig. S60 | Aluminum lap-shear adhesion data for solution-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



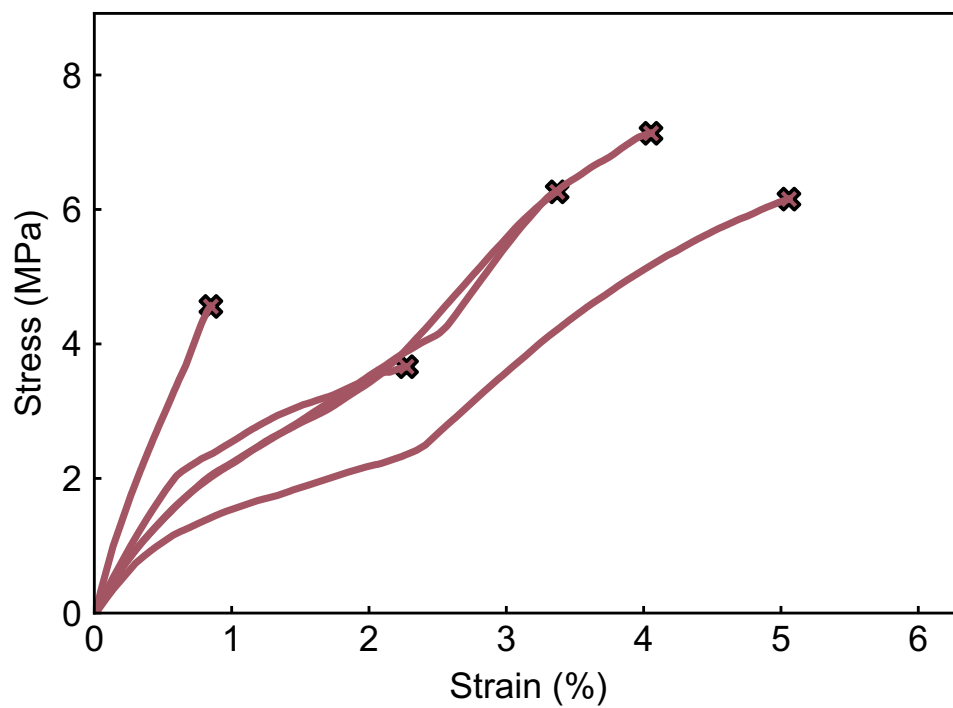
Entry	U_T (MPa)	Failure
1	8.07	Adhesive
2	14.58	Adhesive
3	9.93	Adhesive
4	8.38	Cohesive
5	11.07	Cohesive

Fig. S61 | Aluminum lap-shear adhesion data for film-oxidized LDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



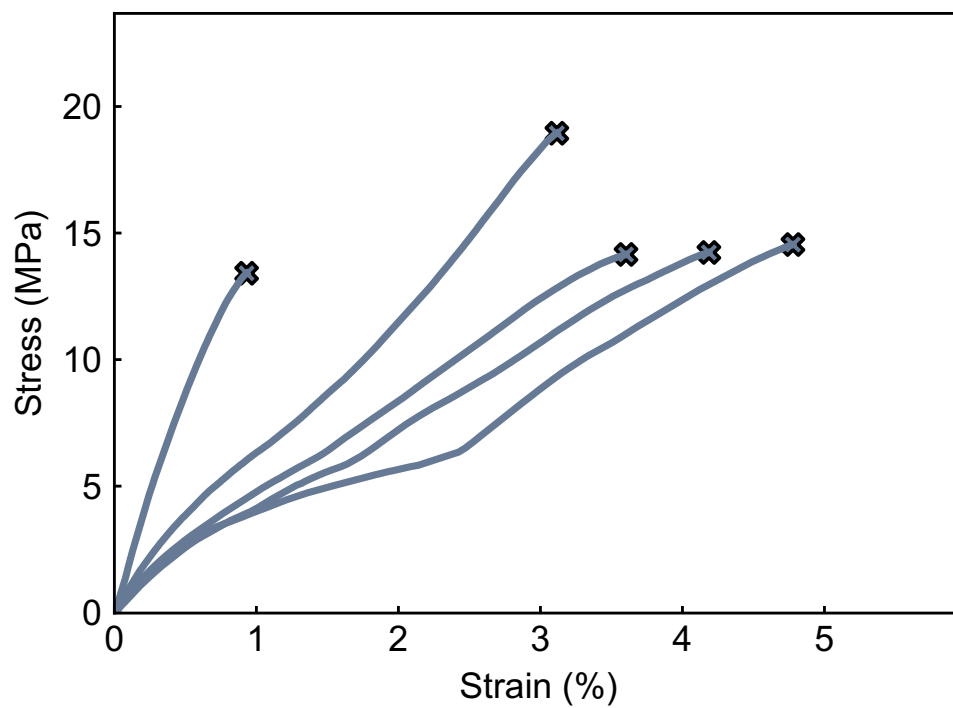
Entry	U_T (MPa)	Failure
1	0.55	Adhesive
2	0.73	Adhesive
3	0.26	Adhesive
4	0.40	Adhesive
5	0.00	Adhesive

Fig. S62 | Aluminum lap-shear adhesion data for pristine HDPE (1.5 mm/min). (* = failed during pre-strain step).



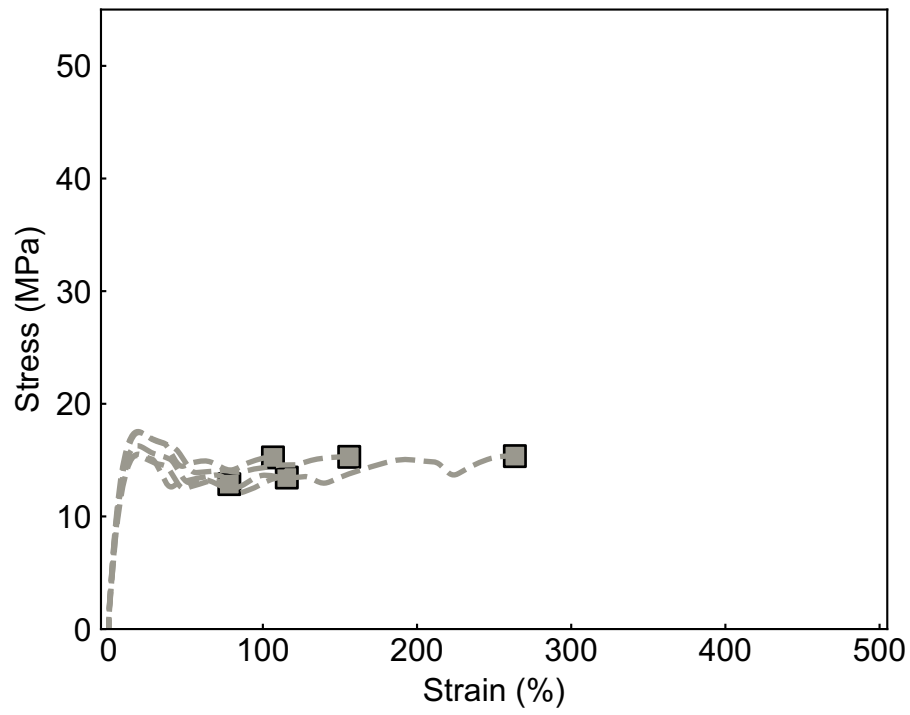
Entry	U_T (MPa)	Failure
1	4.56	Adhesive
2	3.66	Adhesive
3	6.26	Adhesive
4	7.13	Cohesive
5	6.15	Cohesive

Fig. S63 | Aluminum lap-shear adhesion data for solution-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



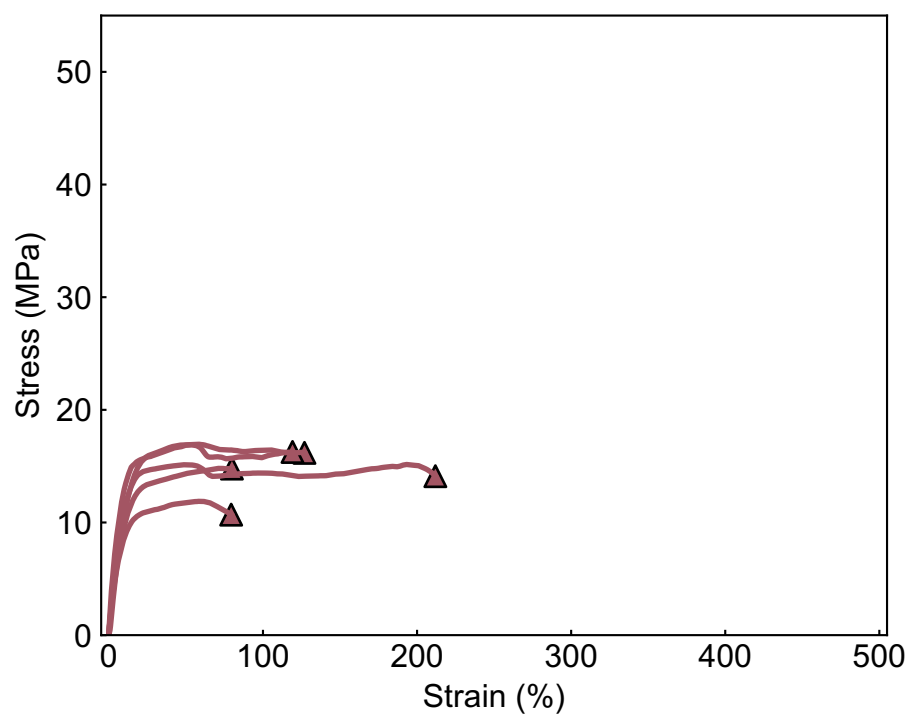
Entry	U_T (MPa)	Failure
1	14.55	Cohesive
2	14.23	Adhesive
3	13.41	Adhesive
4	14.15	Cohesive
5	18.94	Cohesive

Fig. S64 | Aluminum lap-shear adhesion data for film-oxidized HDPE (0.3 mol% ketone) (1.5 mm/min). (* = failed during pre-strain step).



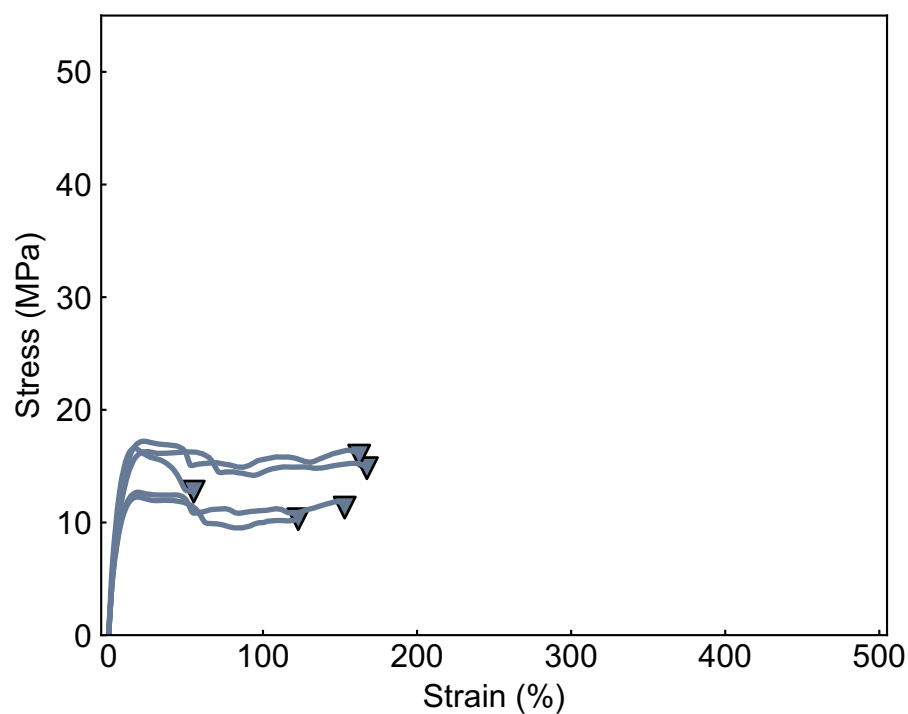
Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	263	231	16.3	15.3
2	107	220	17.5	15.2
3	78	218	15.6	12.9
4	156	247	17.6	15.2
5	116	206	15.5	13.4

Fig. S65 | Tensile data for pristine LDPE (100 μm thickness, 10 mm/min).



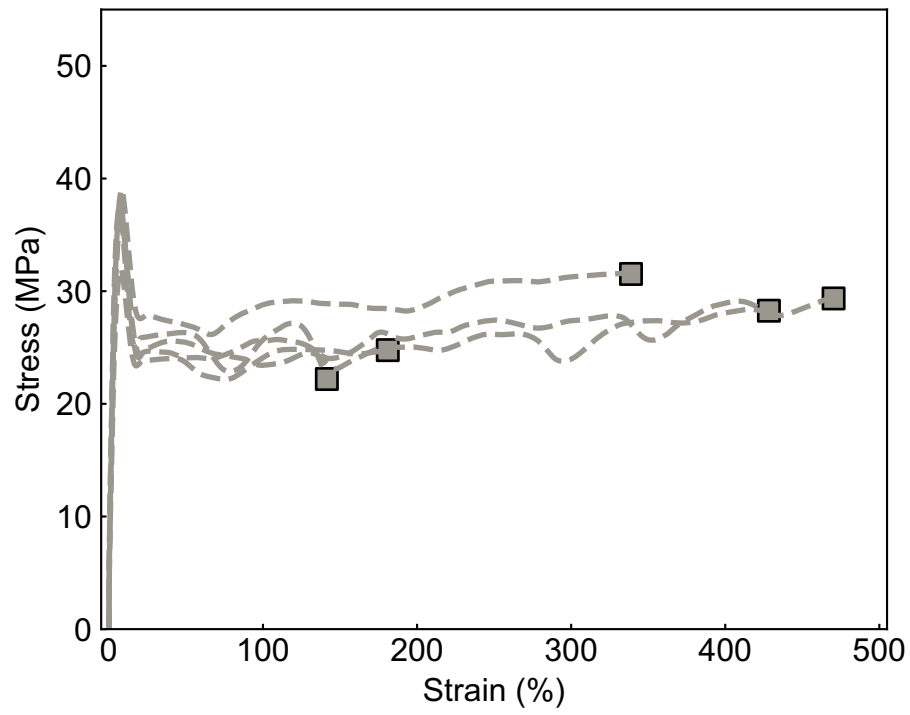
Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	80	61	14.4	14.8
2	127	67	17.0	16.1
3	212	78	15.2	14.1
4	119	162	16.9	16.2
5	79	133	11.8	10.7

Fig. S66 | Tensile data for solution-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



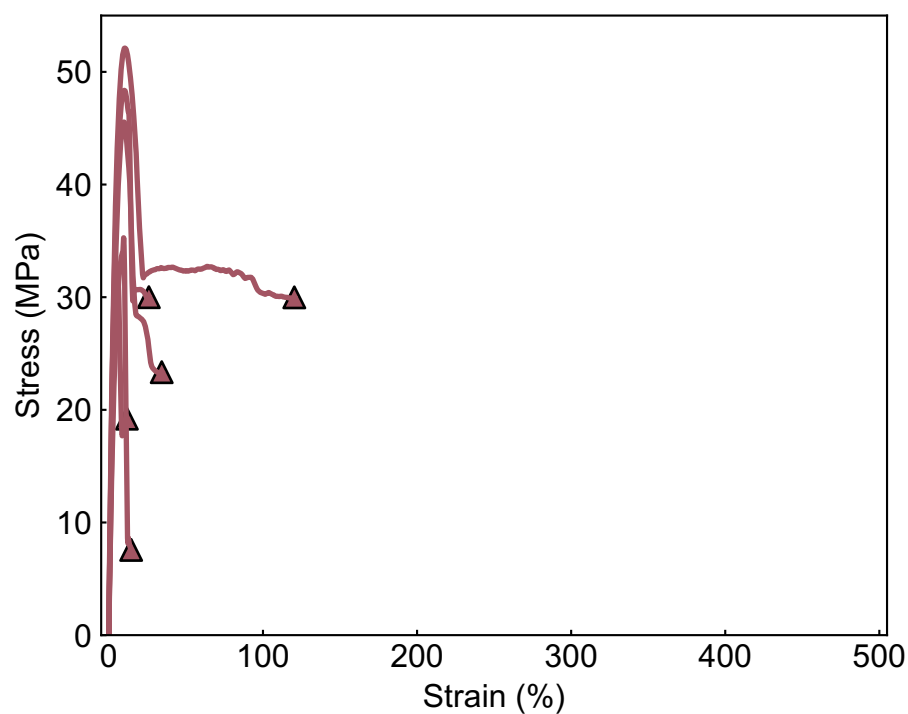
Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	123	208	12.3	10.2
2	162	288	17.3	15.9
3	167	227	16.4	14.8
4	55	313	16.6	12.7
5	153	257	12.8	11.3

Fig. S67 | Tensile data for film-oxidized LDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).



Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	141	980	38.3	22.3
2	339	928	39.2	31.5
3	181	795	32.7	24.7
4	470	898	36.4	29.3
5	428	1020	37.4	28.2

Fig. S68 | Tensile data for pristine HDPE (100 μm thickness, 10 mm/min).



Entry	ε_b (%)	E (MPa)	σ_Y (MPa)	U_T (MPa)
1	12	1486	32.3	19.1
2	34	846	45.6	23.3
3	26	1174	48.5	29.8
4	14	930	34.0	7.5
5	120	1040	52.2	29.9

Fig. S69 | Tensile data for solution-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).

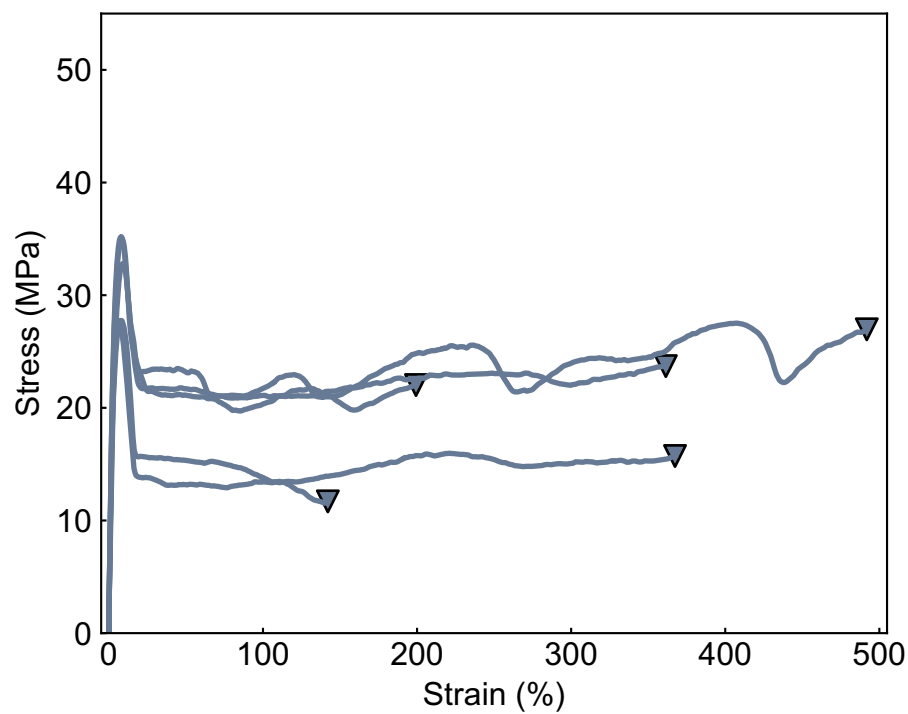


Fig. S70 | Tensile data for film-oxidized HDPE (0.3 mol% ketone) (100 μm thickness, 10 mm/min).

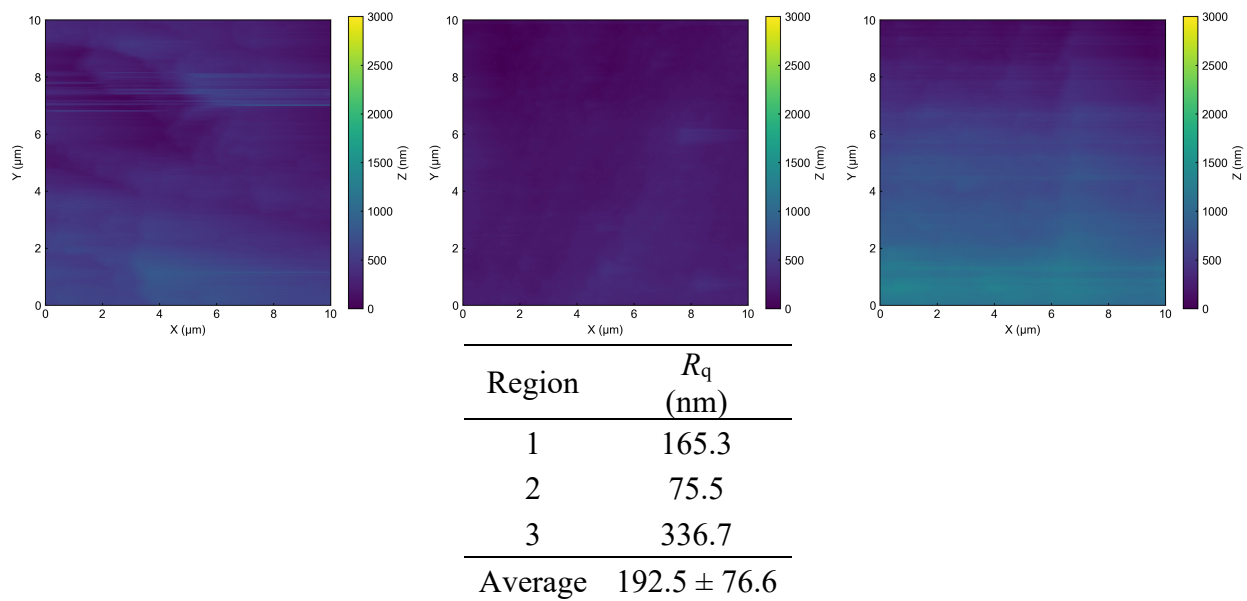


Fig. S71 | Atomic force microscopy height maps of pristine LDPE film (3 regions).

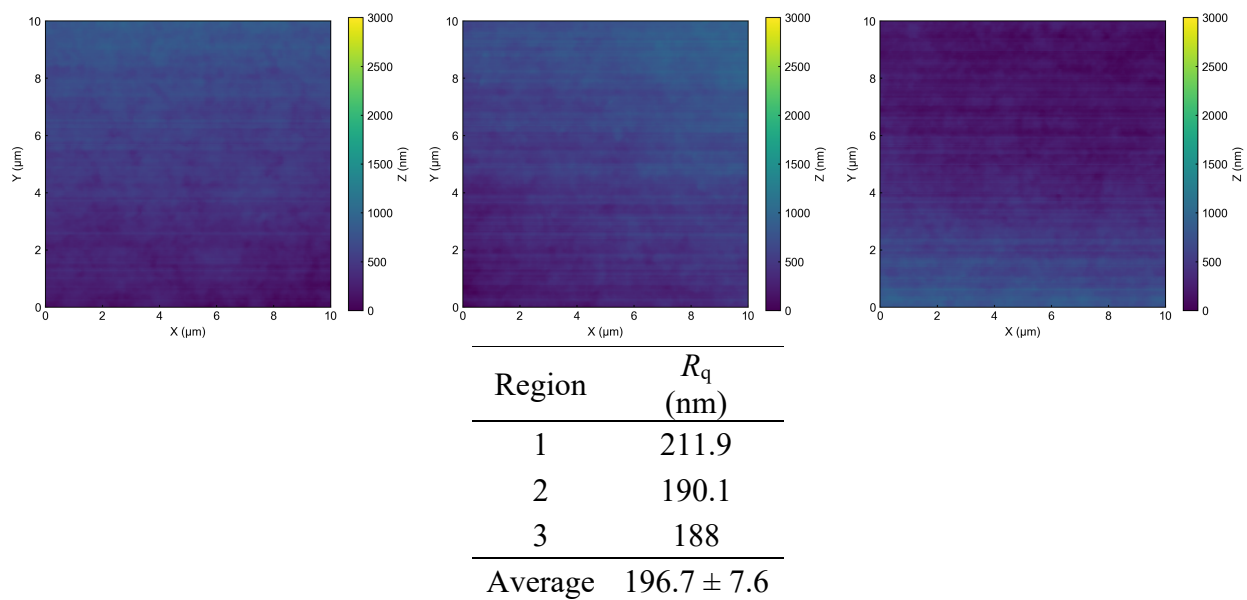


Fig. S72 | Atomic force microscopy height maps of LDPE oxidized in solution before melt-pressing into a film (**4a**) (3 regions).

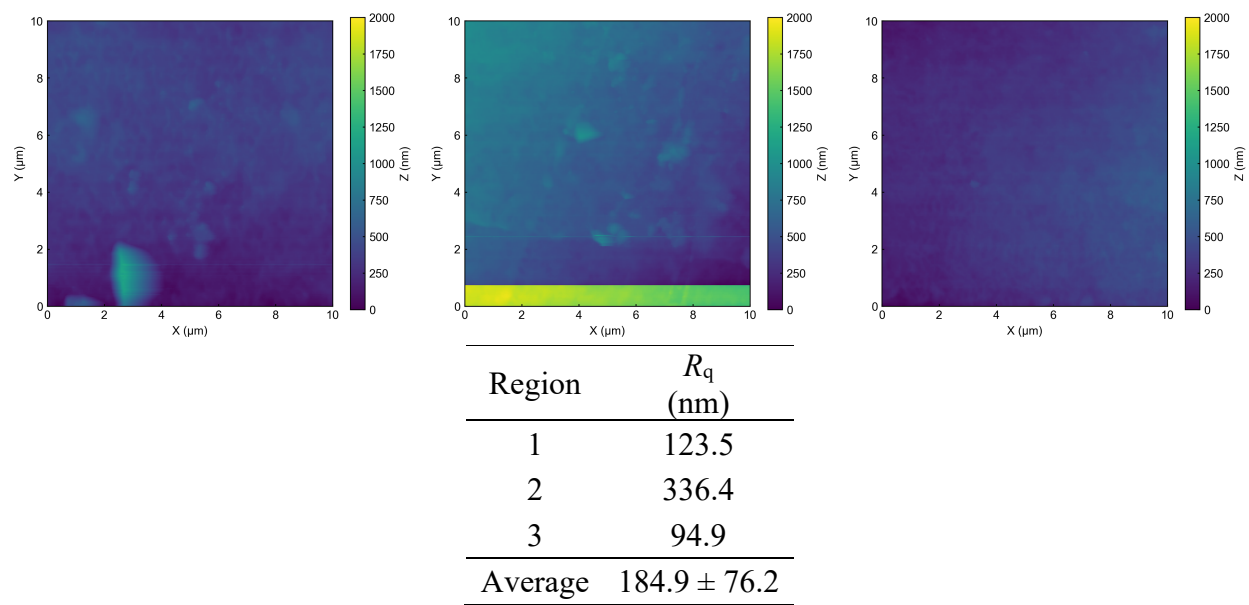


Fig. S73 | Atomic force microscopy height maps of LDPE oxidized as a film (**4b**) (3 regions).

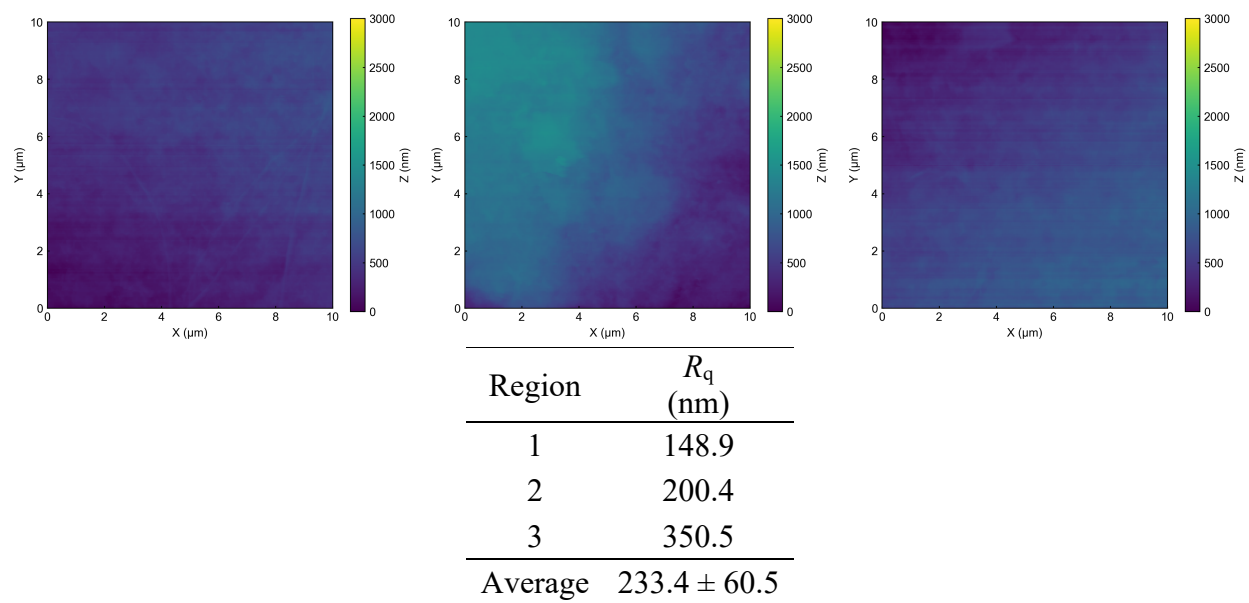


Fig. S74 | Atomic force microscopy height maps of pristine HDPE film (3 regions).

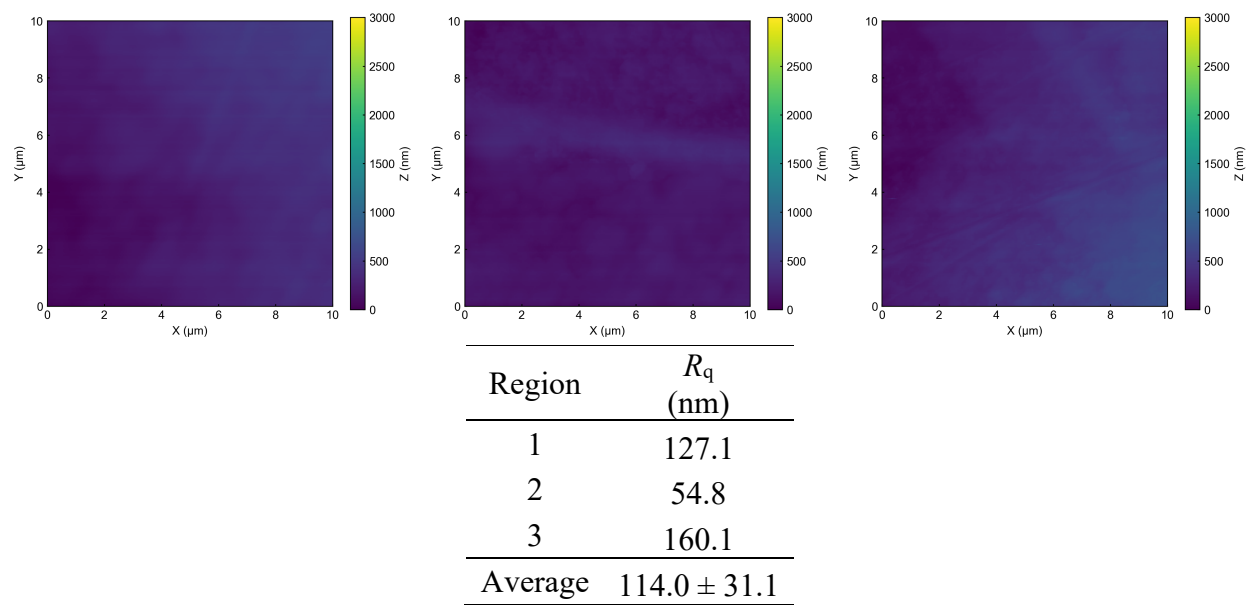


Fig. S75 | Atomic force microscopy height maps of HDPE oxidized in solution before melt-pressing into a film (**4c**) (3 regions).

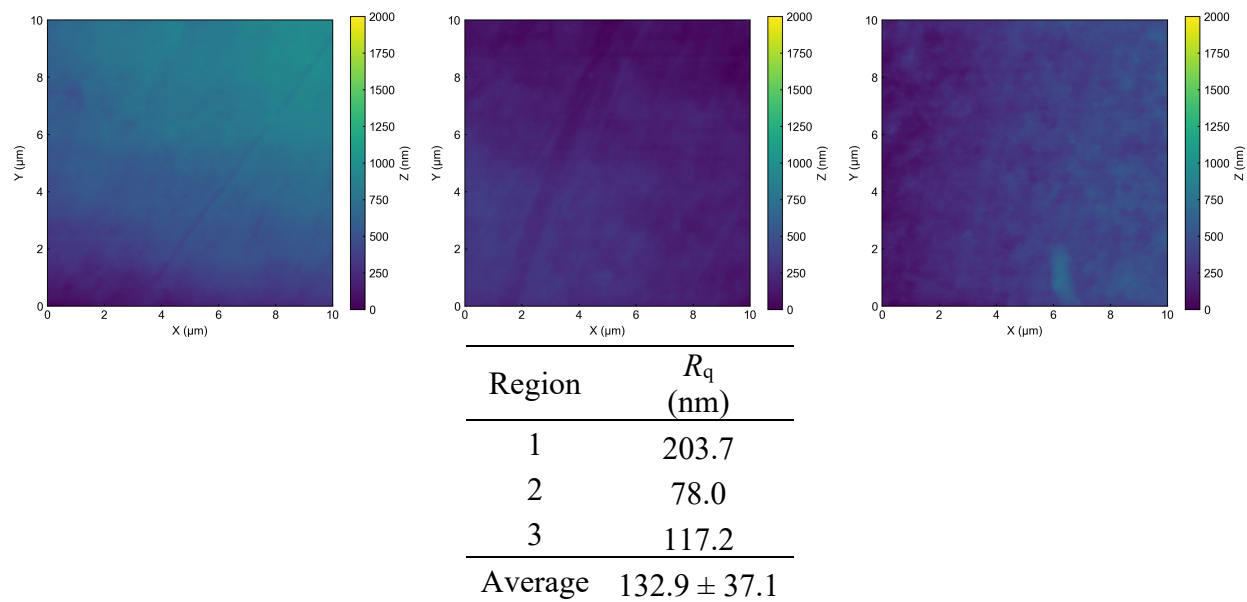


Fig. S76 | Atomic force microscopy height maps of HDPE oxidized as a film (**4d**) (3 regions).

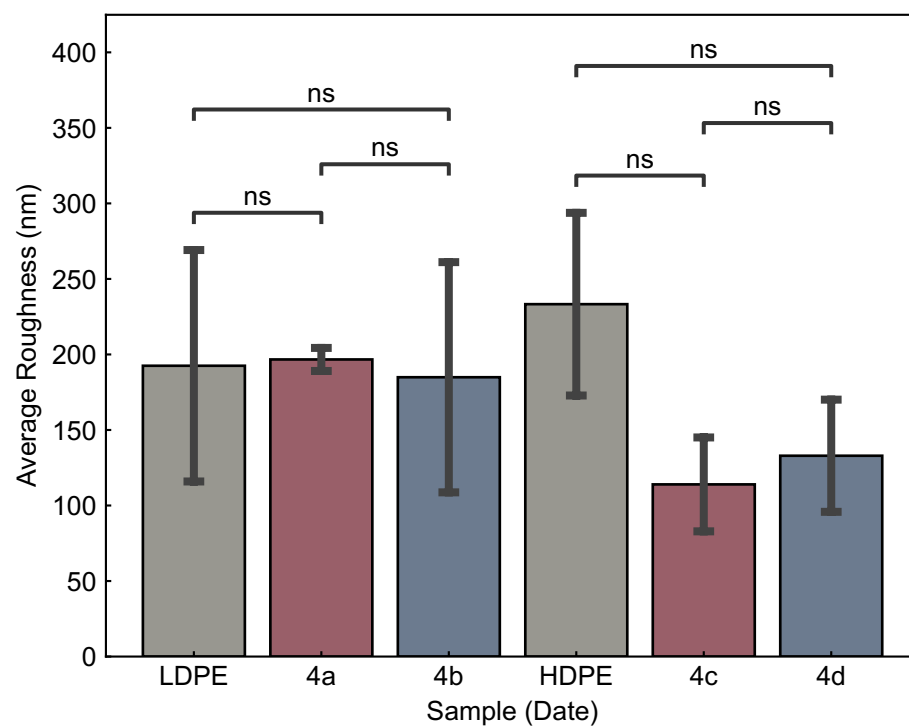


Fig. S77 | Root-mean-square surface roughness of pristine and oxidized PE samples as measured by atomic force microscopy.

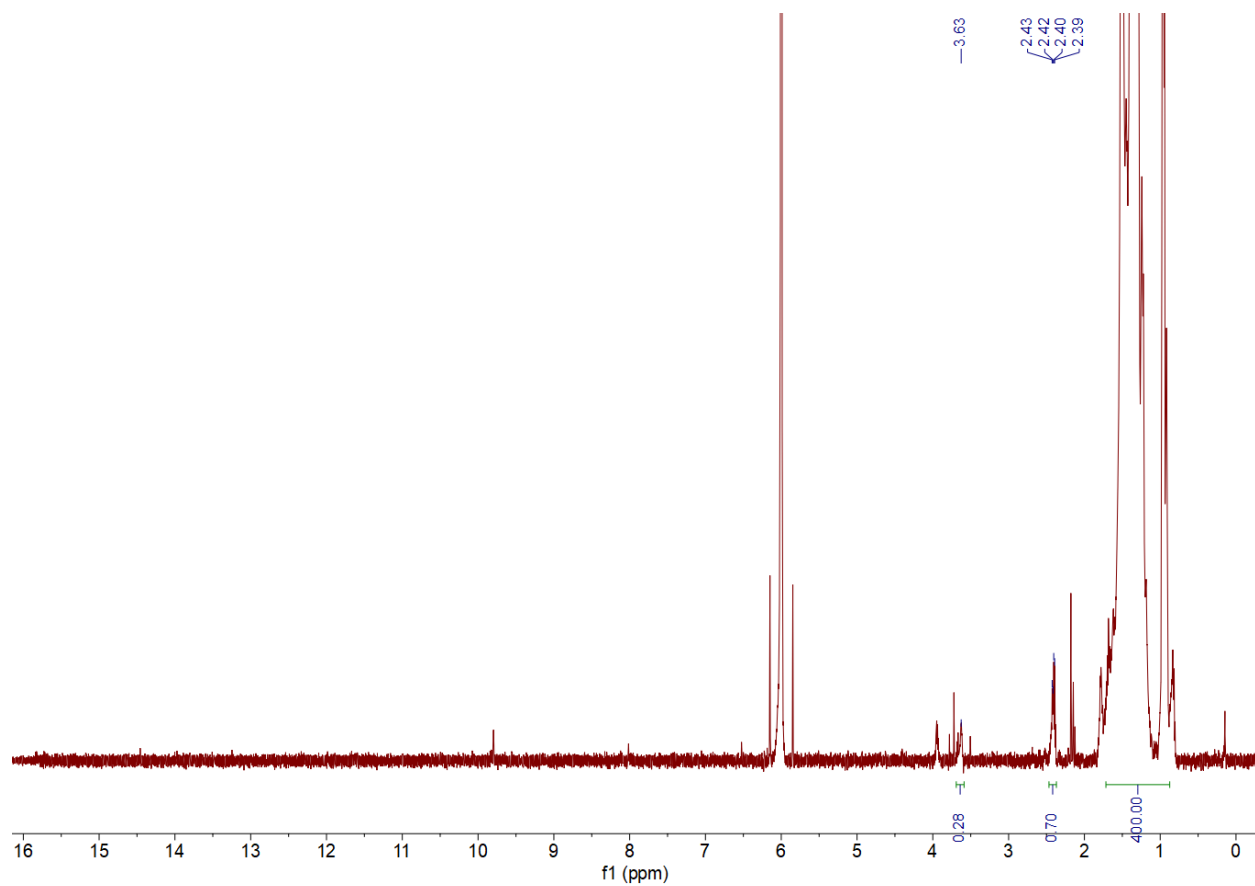


Fig. S78 | Representative ^1H NMR of hydroxyl-functionalized LDPE (Table S14, entry 8) (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 $^\circ\text{C}$).

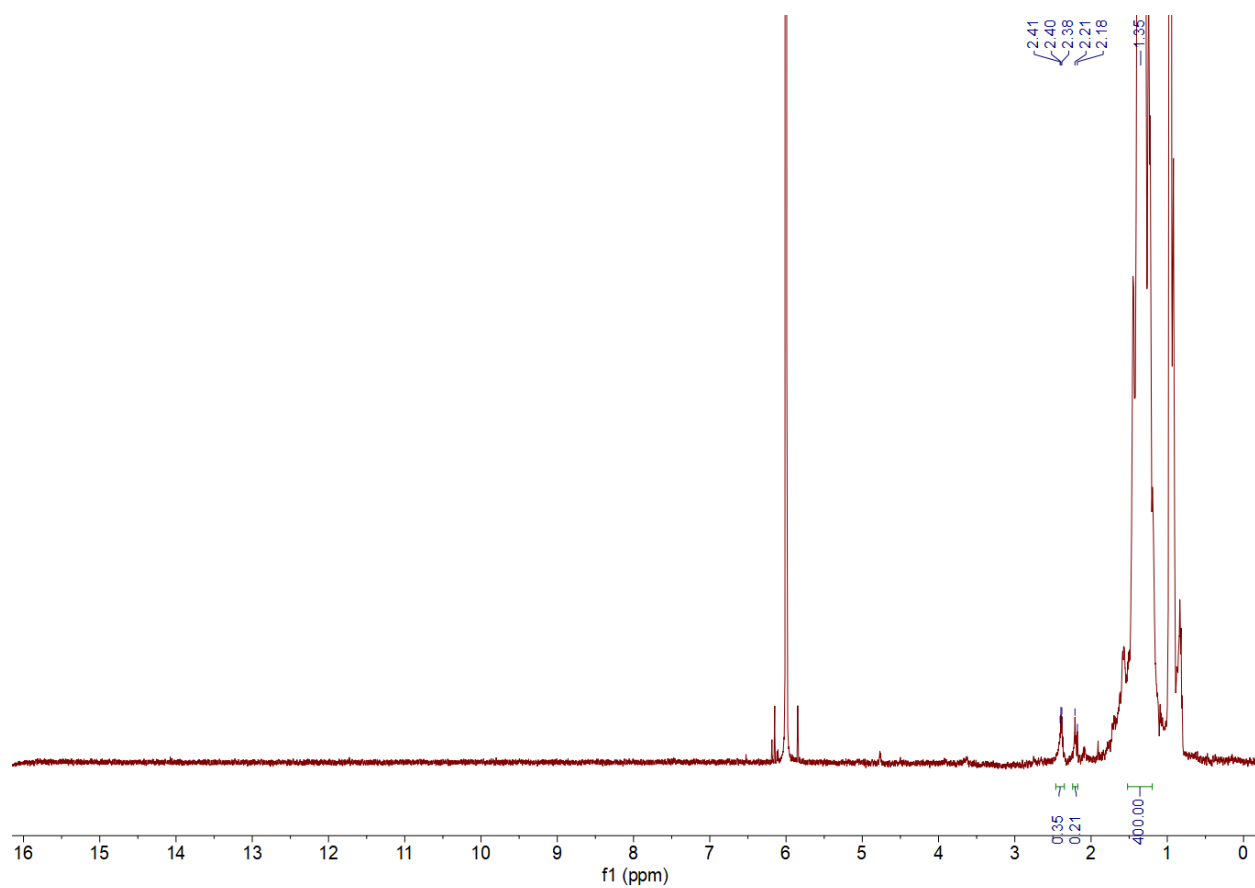


Fig. S79 | Representative ^1H NMR of oxime-functionalized LDPE (**Table S16**, entry 2) (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 $^\circ\text{C}$).

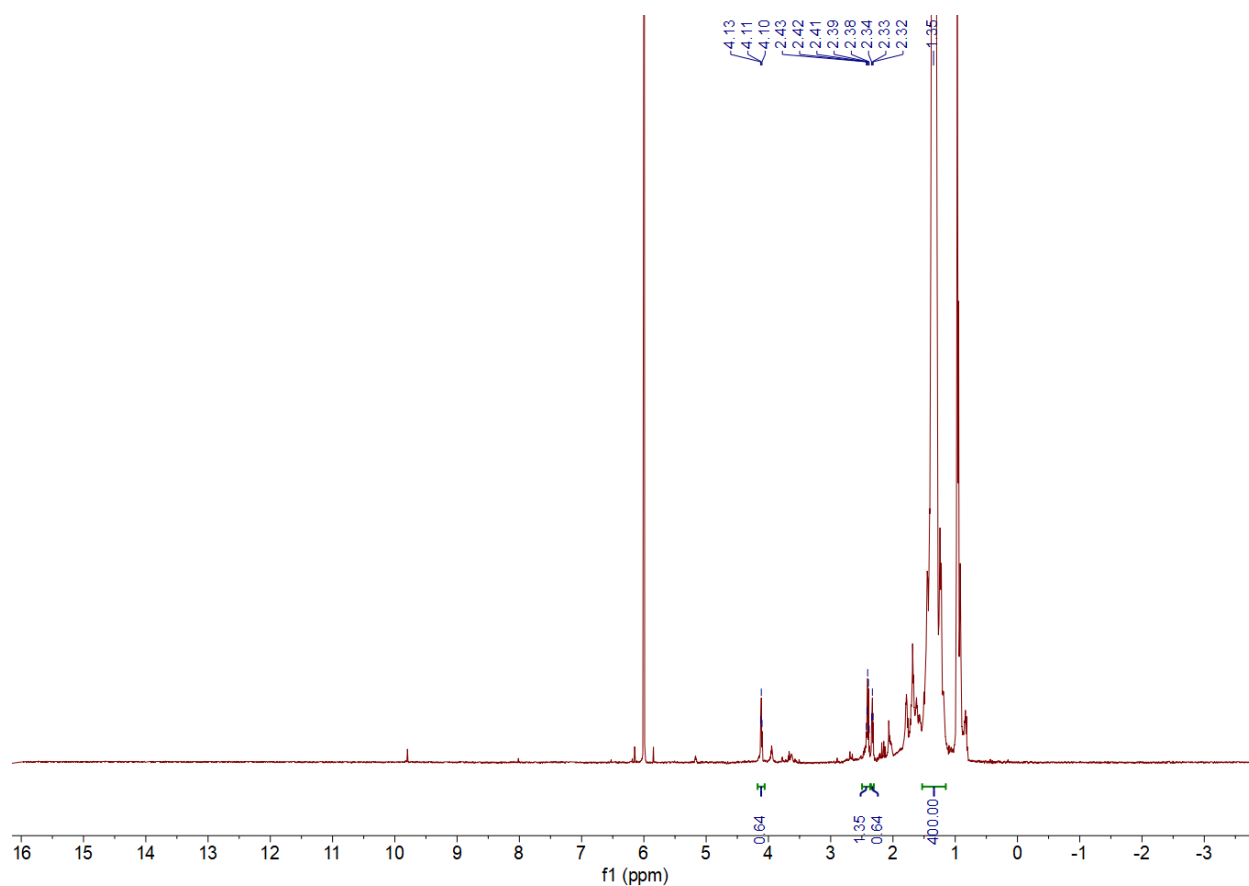


Fig. S80 | Representative ^1H NMR of ester-functionalized LDPE (Table S15, entry 7) (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 $^\circ\text{C}$).

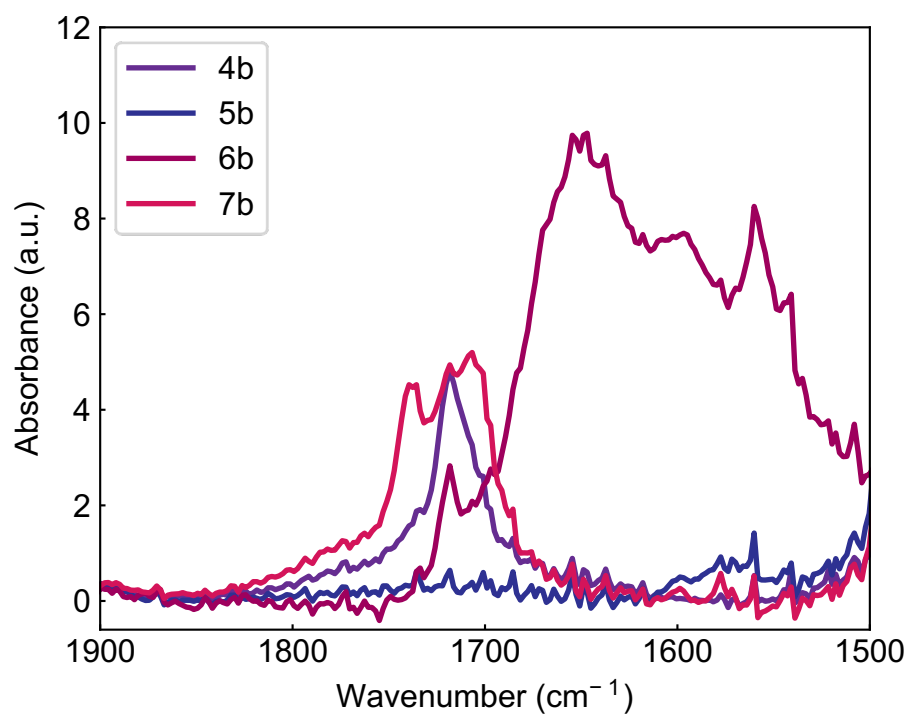


Fig. S81 | FTIR spectroscopy of derivatized LDPE highlighting 1900–1500 cm^{-1} .

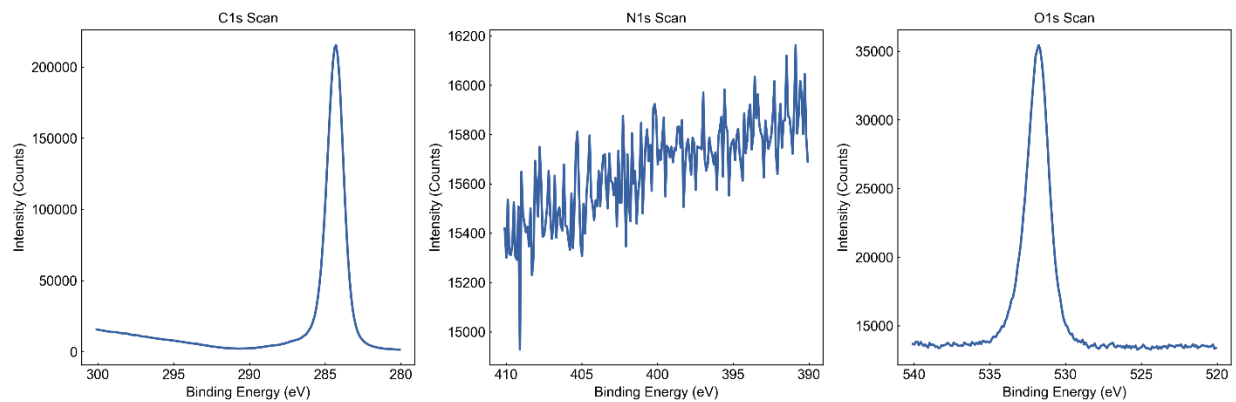


Fig. S82 | X-ray photoelectron spectroscopy measurements of **4b** examining the C(1s), N(1s), and O(1s) regions.

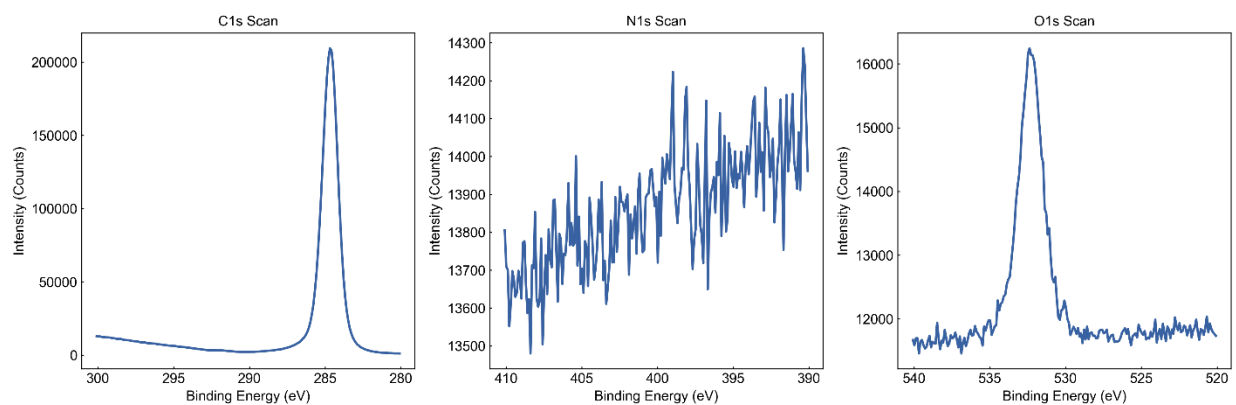


Fig. S83 | X-ray photoelectron spectroscopy measurements of **5b** examining the C(1s), N(1s), and O(1s) regions.

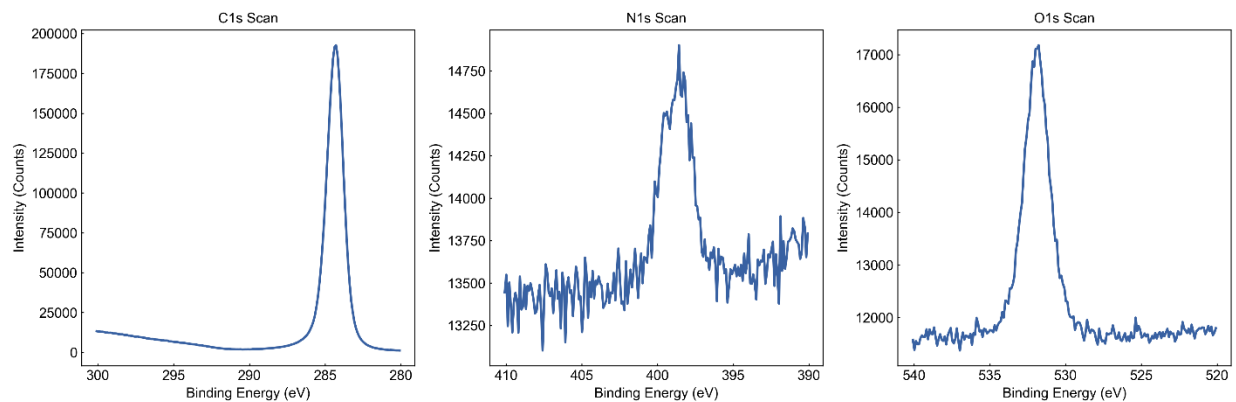


Fig. S84 | X-ray photoelectron spectroscopy measurements of **6b** examining the C(1s), N(1s), and O(1s) regions.

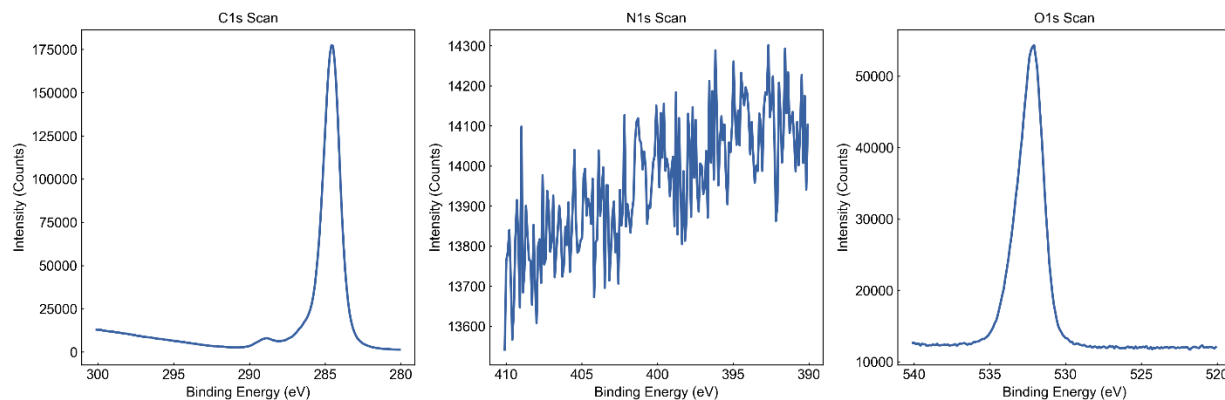


Fig. S85 | X-ray photoelectron spectroscopy measurements of **7b** examining the C(1s), N(1s), and O(1s) regions.

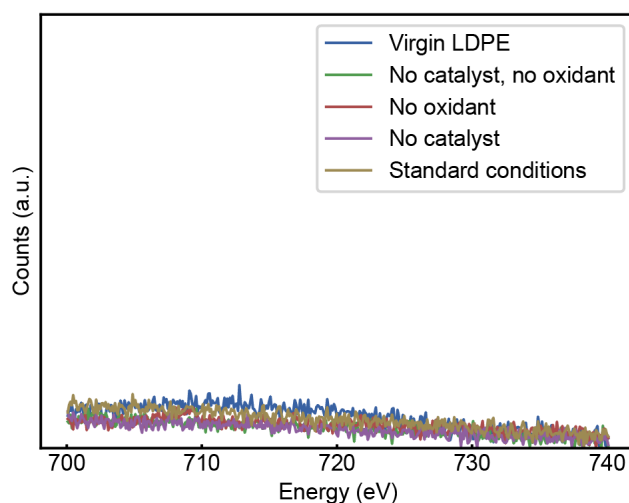
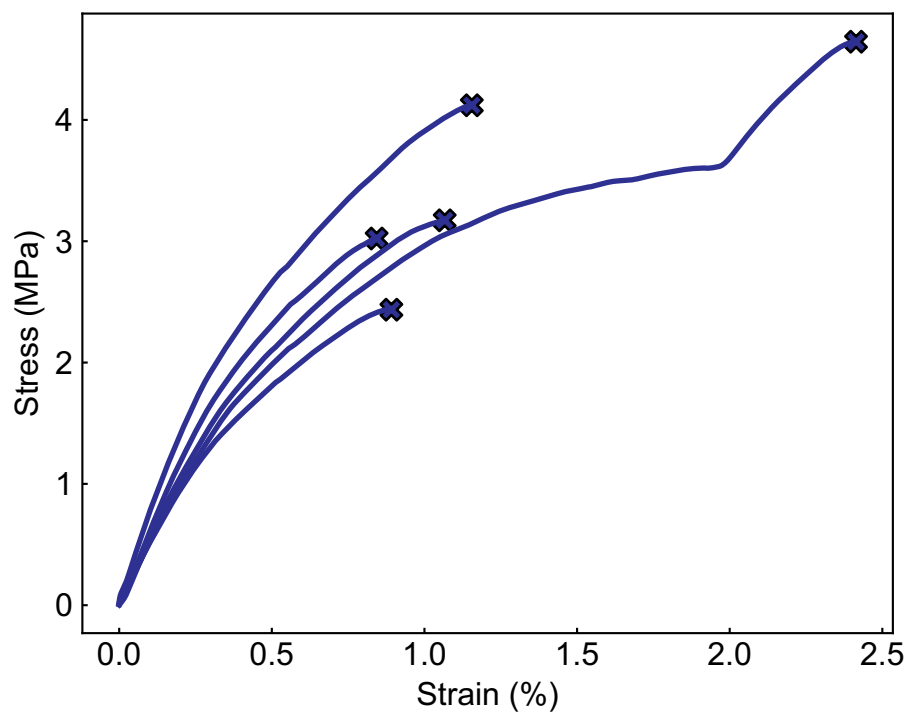
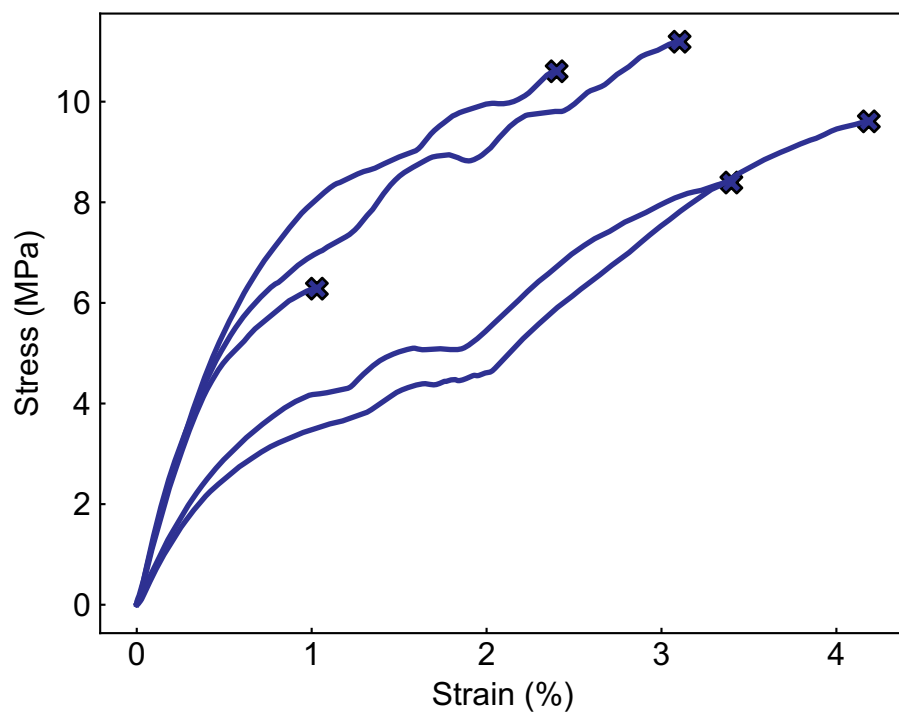


Fig. S86 | X-ray photoelectron spectroscopy (Fe 2p region) of LDPE in pristine form and LDPE after reactions conducted under a series of conditions, including conditions without catalyst or oxidant ('BuPh, 65 °C, 24 h), without oxidant (0.001 mol% **1**, 'BuPh, 65 °C, 24 h), without catalyst (0.3 equiv 'BuOOH, 'BuPh, 65 °C, 24 h), or under standard conditions for oxidation that form oxo-LDPE (0.001 mol% **1**, 0.3 equiv 'BuOOH, 'BuPh, 65 °C, 24 h).



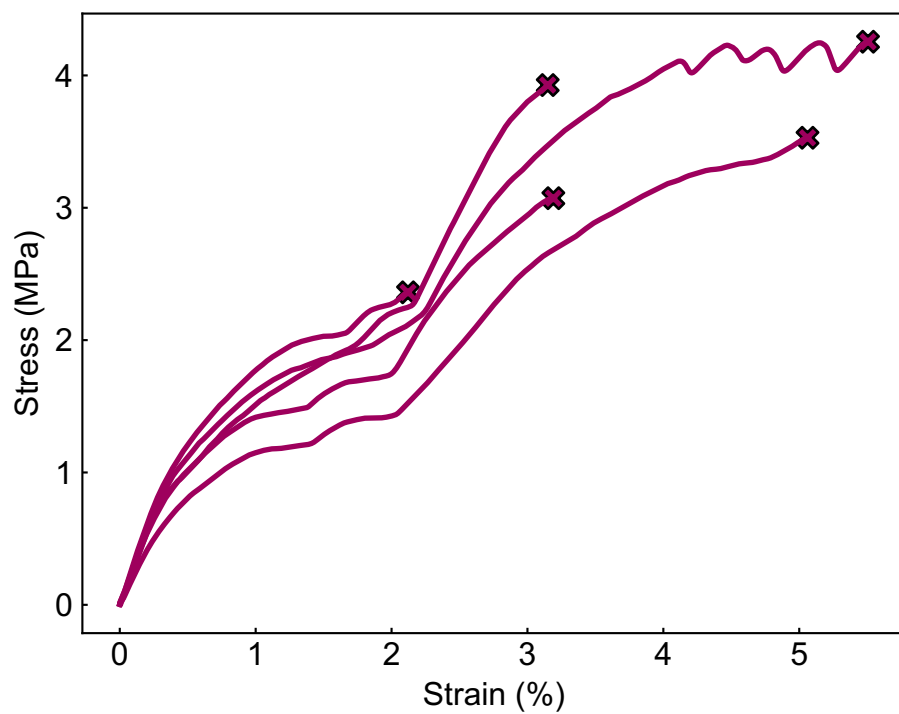
Entry	U_T (MPa)	Failure
1	3.02	Adhesive
2	3.17	Adhesive
3	2.44	Adhesive
4	4.64	Adhesive
5	4.12	Cohesive

Fig. S87 | Glass lap-shear adhesion data for alcohol-containing LDPE derivatized as a solution (**5a**) (1.5 mm/min).



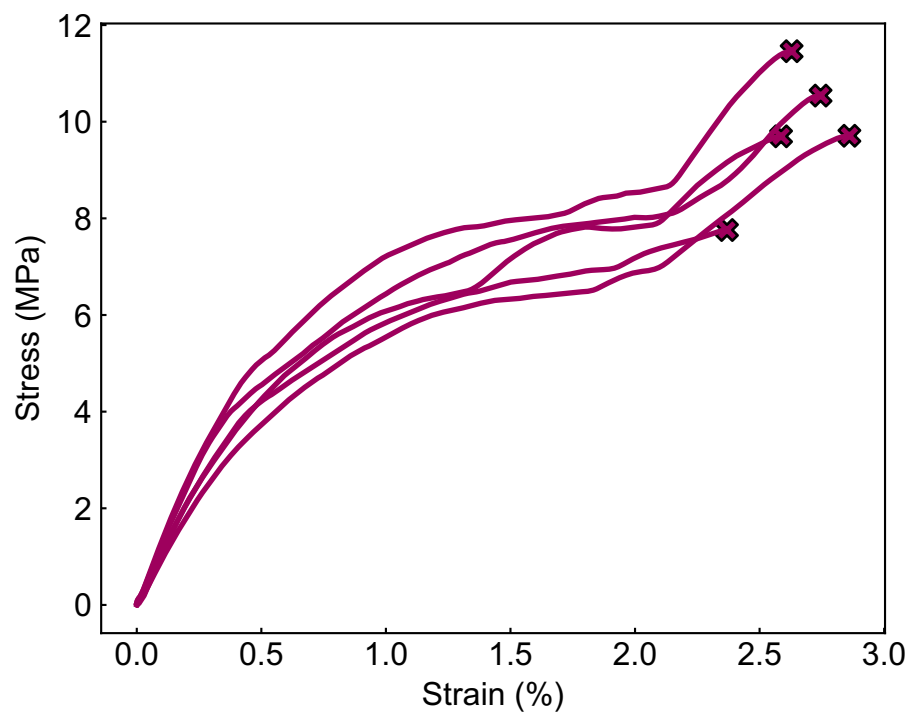
Entry	U_T (MPa)	Failure
1	8.39	Adhesive
2	9.61	Adhesive
3	6.28	Adhesive
4	11.19	Adhesive
5	10.60	Adhesive

Fig. S88 | Glass lap-shear adhesion data for alcohol-containing LDPE derivatized as a film (**5b**) (1.5 mm/min).



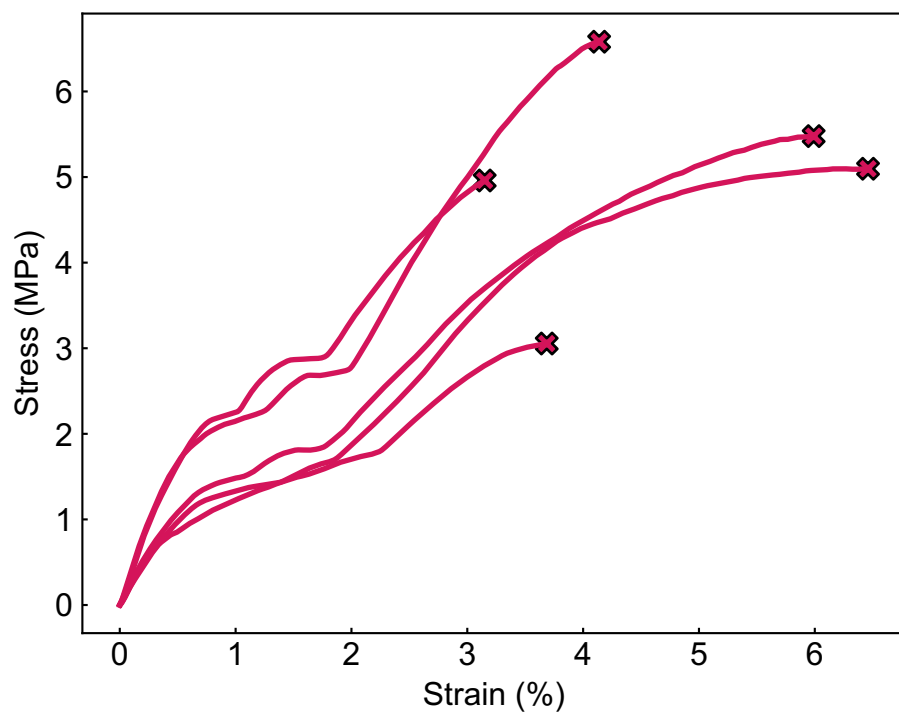
Entry	U_T (MPa)	Failure
1	2.36	Adhesive
2	3.53	Adhesive
3	3.93	Adhesive
4	4.25	Adhesive
5	3.07	Adhesive

Fig. S89 | Glass lap-shear adhesion data for oxime-containing LDPE derivatized as a solution (**6a**) (1.5 mm/min).



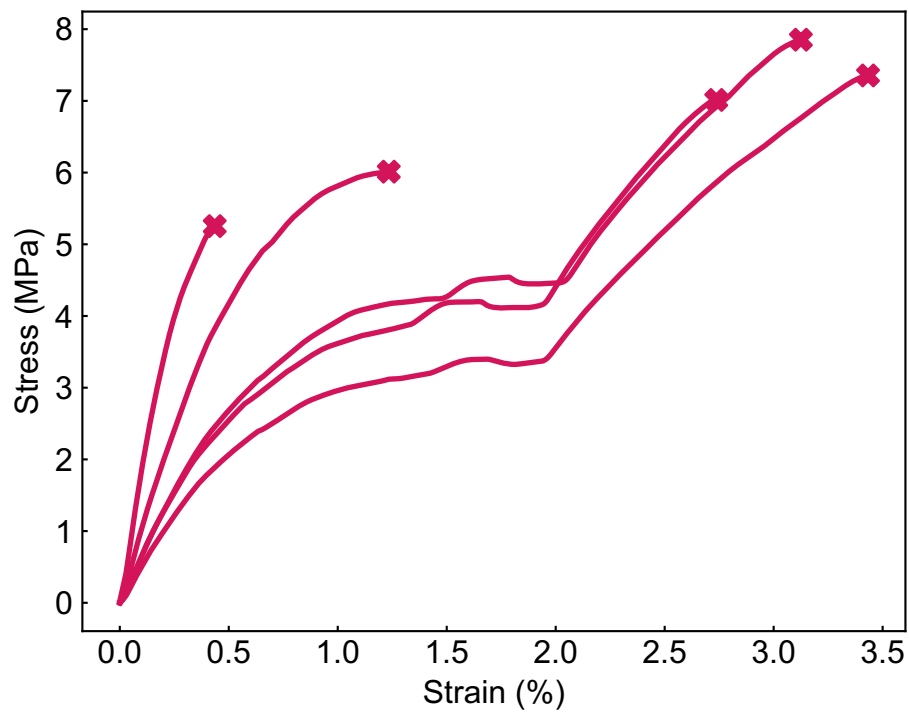
Entry	U_T (MPa)	Failure
1	9.70	Adhesive
2	11.46	Adhesive
3	9.71	Cohesive
4	10.54	Adhesive
5	7.76	Adhesive

Fig. S90 | Glass lap-shear adhesion data for oxime-containing LDPE derivatized as a film (**6b**) (1.5 mm/min).



Entry	U_T (MPa)	Failure
1	6.58	Adhesive
2	5.10	Cohesive
3	3.06	Adhesive
4	4.96	Cohesive
5	5.48	Adhesive

Fig. S91 | Glass lap-shear adhesion data for ester-containing LDPE derivatized as a solution (**7a**) (1.5 mm/min).



Entry	U_T (MPa)	Failure
1	5.25	Adhesive
2	7.85	Adhesive
3	6.01	Cohesive
4	7.01	Adhesive
5	7.35	Adhesive

Fig. S92 | Glass lap-shear adhesion data for ester-containing LDPE derivatized as a film (**7b**) (1.5 mm/min).

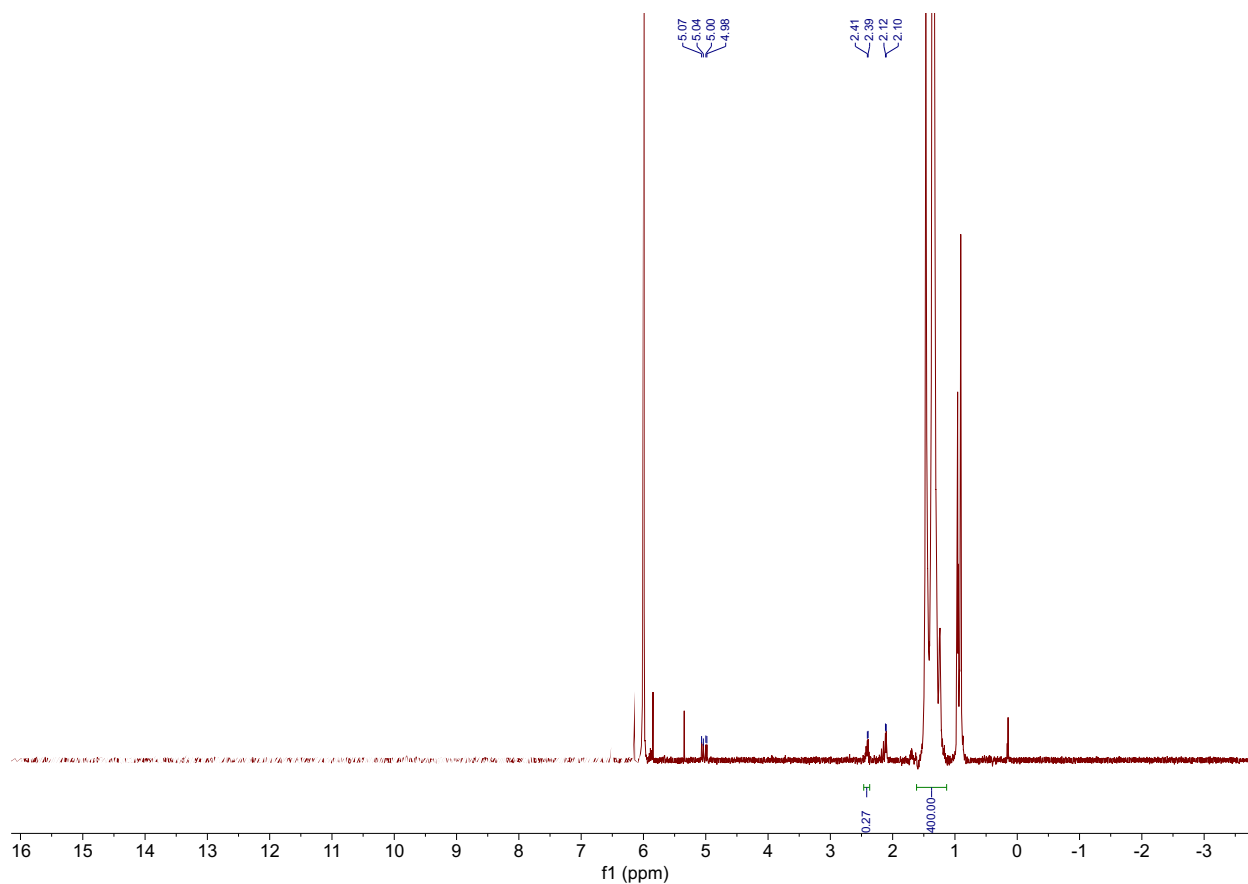


Fig. S93 | Representative ^1H NMR of chemically oxidized PE **8b** (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 $^\circ\text{C}$).

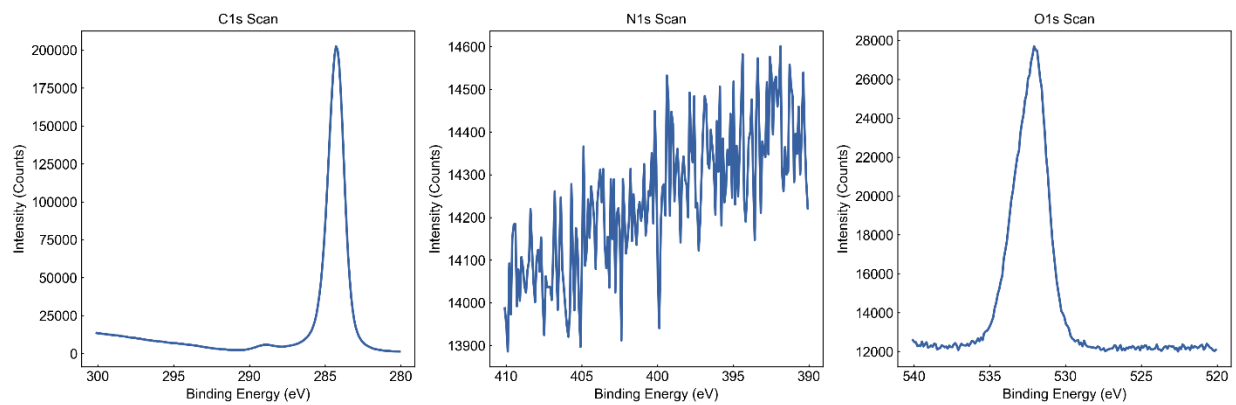


Fig. S94 | X-ray photoelectron spectroscopy measurements of **8b** examining the C(1s), N(1s), and O(1s) regions.

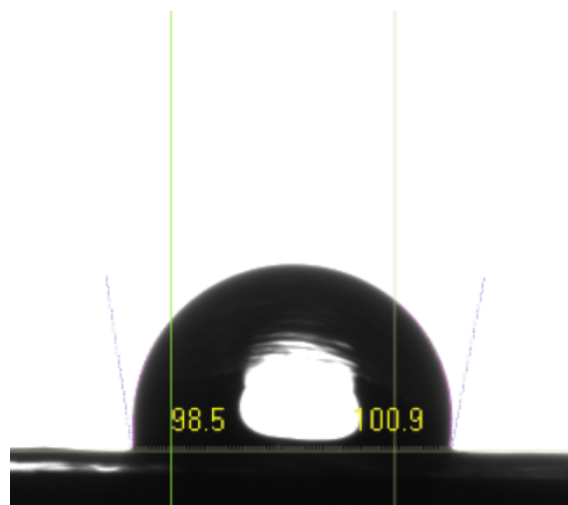


Fig. S95 | Representative water contact angle measurement of LDPE.

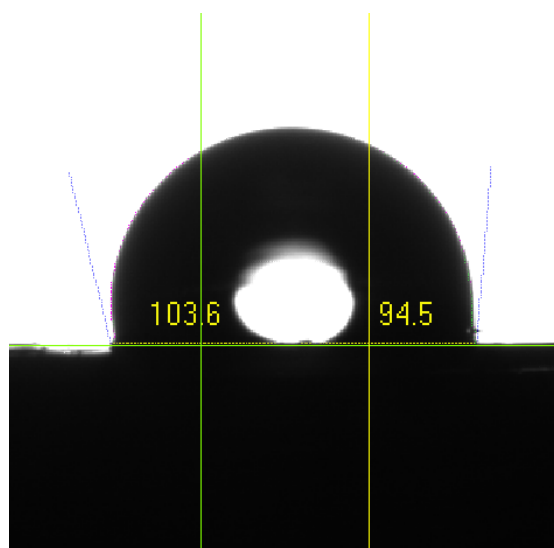


Fig. S96 | Representative water contact angle measurement of HDPE.

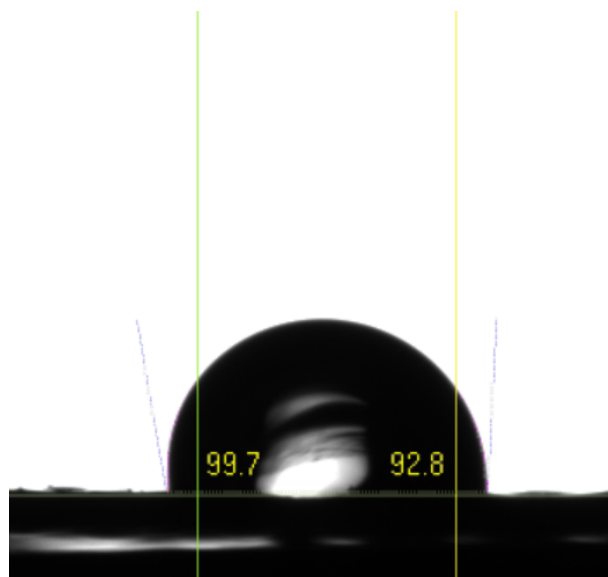


Fig. S97 | Representative water contact angle measurement of **4b**.

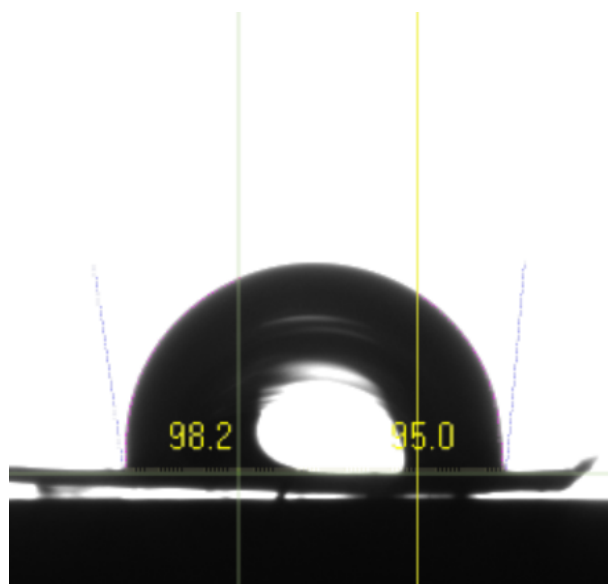


Fig. S98 | Representative water contact angle measurement of **4d**.

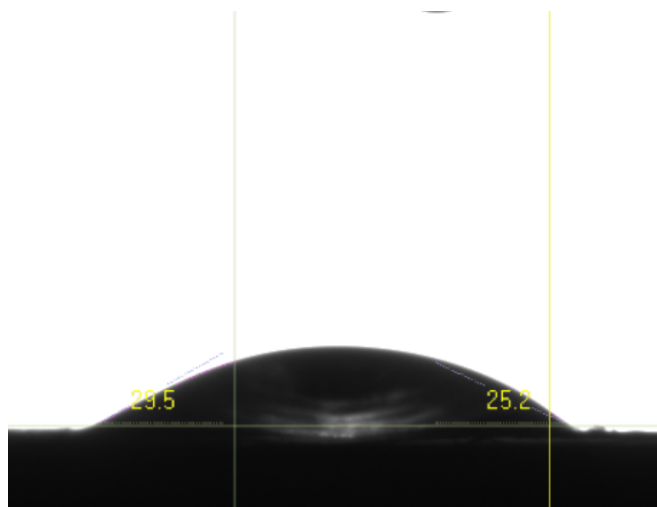


Fig. S99 | Representative water contact angle measurement of **8a**.

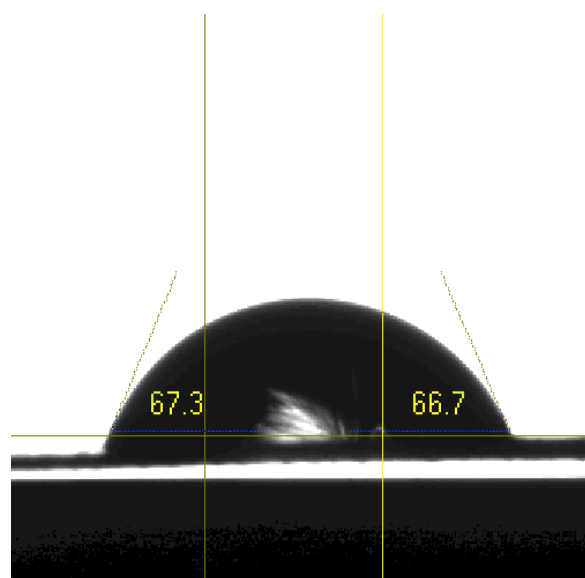


Fig. S100 | Representative water contact angle measurement of **8b**.

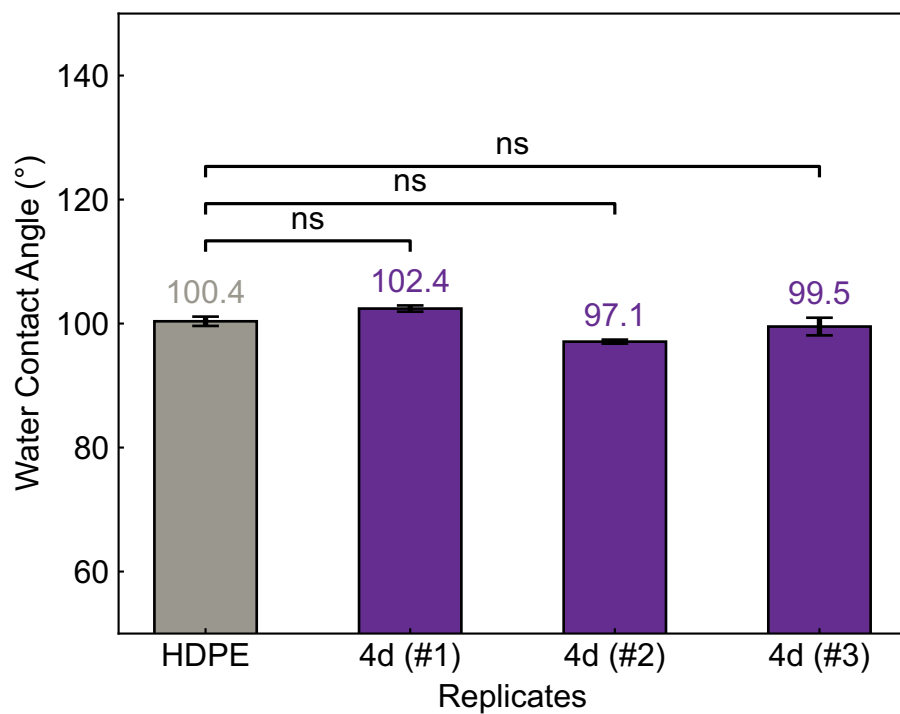
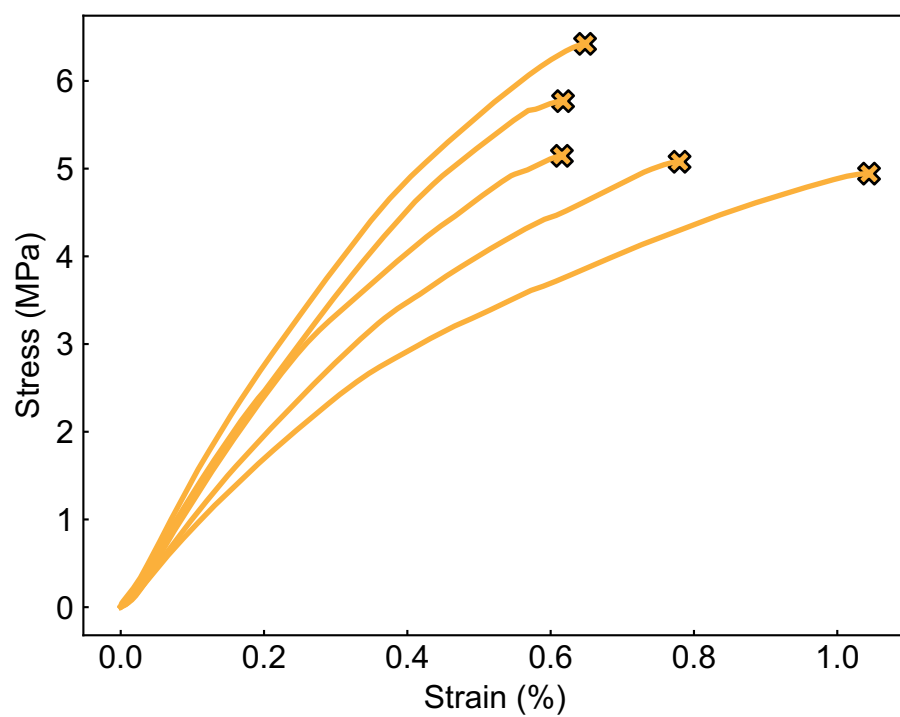
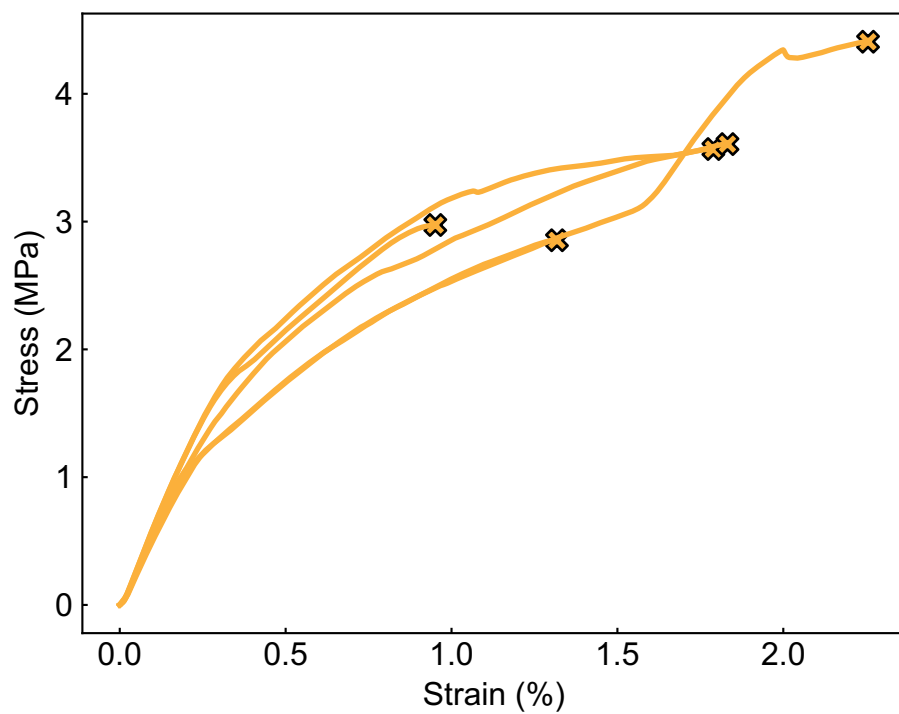


Fig. S101 | Average water contact angle of pristine HDPE and HDPE oxidized as a film with 0.3 mol% ketones from three different experiments (each bar is the average of six angle measurements per sample).



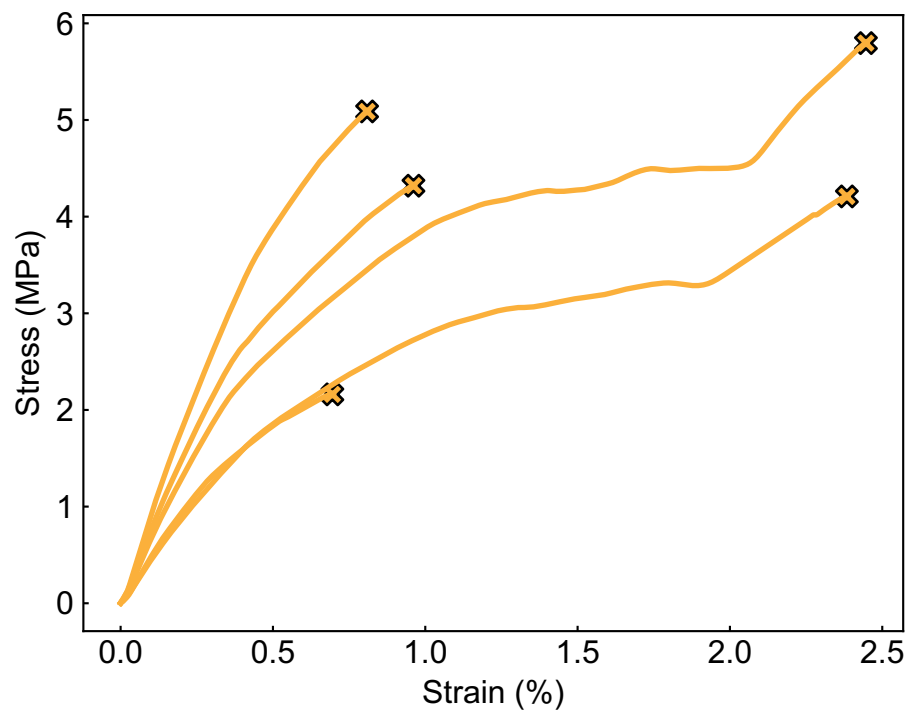
Entry	U_T (MPa)	Failure
1	6.42	Cohesive
2	5.77	Cohesive
3	5.08	Cohesive
4	5.15	Cohesive
5	4.49	Adhesive

Fig. S102 | Glass lap-shear adhesion data for chemically oxidized LDPE (**8a**) (1.5 mm/min).



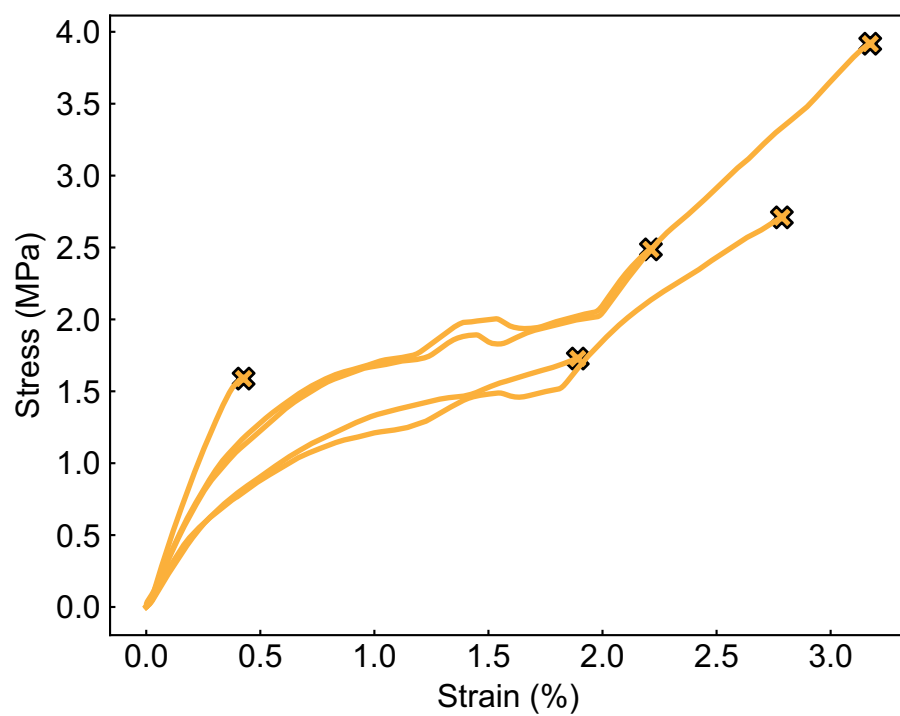
Entry	U_T (MPa)	Failure
1	3.57	Cohesive
2	2.85	Cohesive
3	2.97	Cohesive
4	3.61	Cohesive
5	4.41	Cohesive

Fig. S103 | Glass lap-shear adhesion data for chemically oxidized LDPE (**8a**) after 2 weeks of aging (1.5 mm/min).



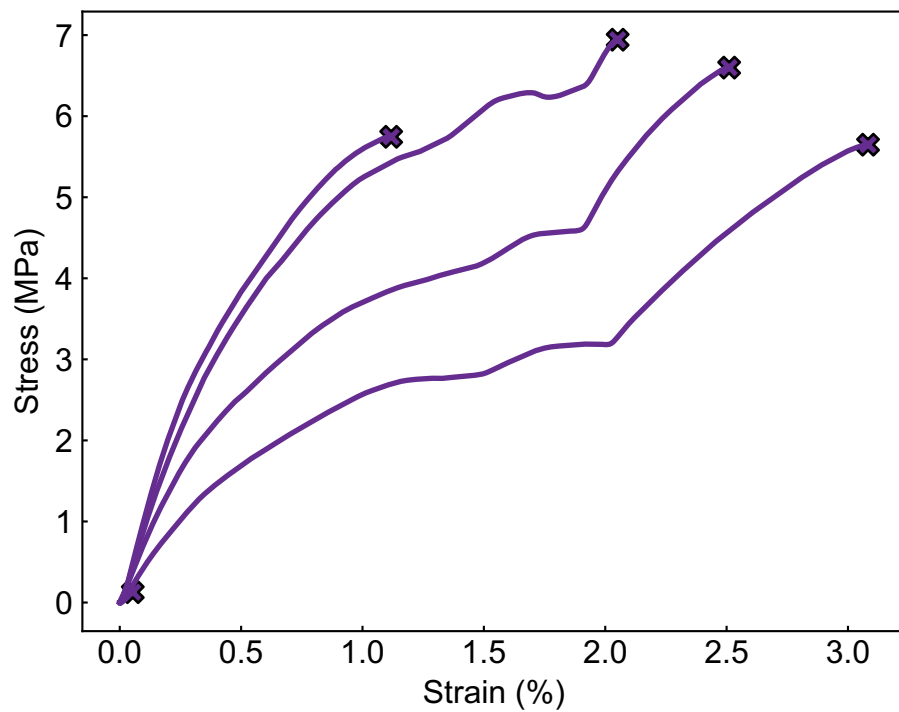
Entry	U_T (MPa)	Failure
1	4.21	Cohesive
2	2.16	Adhesive
3	5.80	Adhesive
4	5.09	Cohesive
5	4.32	Cohesive

Fig. S104 | Glass lap-shear adhesion data for chemically oxidized HDPE (**8b**) (1.5 mm/min).



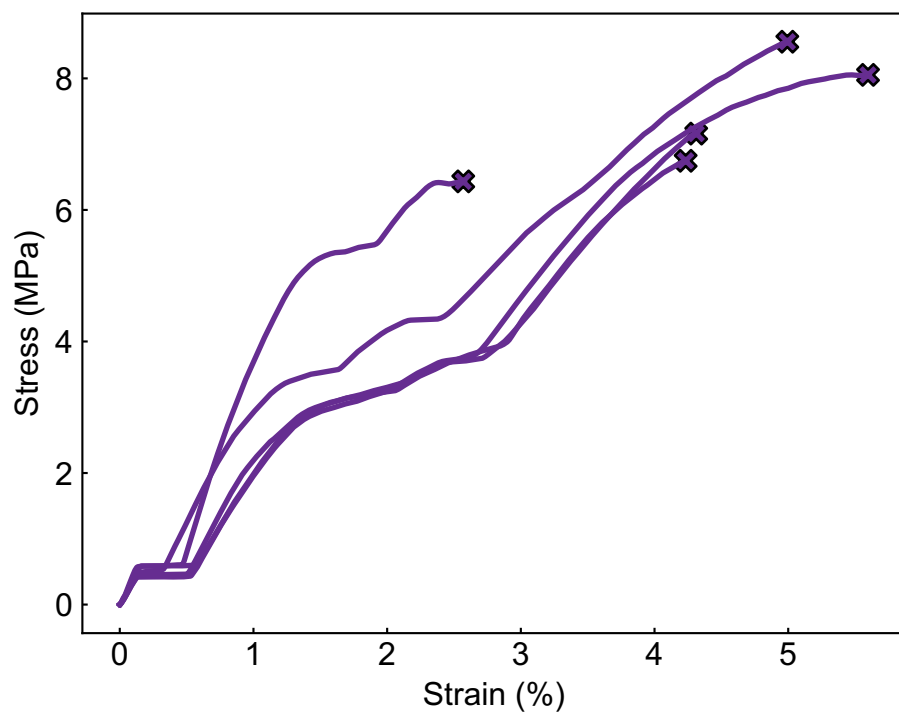
Entry	U_T (MPa)	Failure
1	2.49	Adhesive
2	1.73	Cohesive
3	2.71	Cohesive
4	1.59	Cohesive
5	3.92	Cohesive

Fig. S105 | Glass lap-shear adhesion data for chemically oxidized HDPE (**8b**) after 2 weeks of aging (1.5 mm/min).



Entry	U_T (MPa)	Failure
1	6.94	Adhesive
2*	—	—
3	6.60	Adhesive
4	5.75	Adhesive
5	5.65	Adhesive

Fig. S106 | Glass lap-shear adhesion data for catalytically oxidized LDPE (**4b**) after 2 weeks of aging (1.5 mm/min).
(* = failed during pre-strain step).



Entry	U_T (MPa)	Failure
1	6.75	Adhesive
2	8.56	Adhesive
3	6.43	Adhesive
4	7.16	Adhesive
5	8.05	Adhesive

Fig. S107 | Glass lap-shear adhesion data for catalytically oxidized HDPE (**4d**) after 2 weeks of aging (1.5 mm/min).

4. Supplemental Tables

Table S10. Swelling ratio of an HDPE film.

Entry	Solvent	Swelling ratio
1	Water	1.02
2	Acetonitrile	1.02
3	Ethanol	1.06
4	Hexane	1.07
5	Ethyl acetate	1.07
6	Tetrahydrofuran	1.09
7	Dioxane	1.10
8	Dimethyl sulfoxide	1.22
9	Toluene	1.26
10	<i>Tert</i> -butyl benzene	1.37
11	Trichlorobenzene	1.44
12	1,1,2,2-Tetrachloroethane	1.49

Conditions: HDPE film (15 mg, 100 μ m), solvent (4 mL), 65 $^{\circ}$ C, 24 h. ^a Swelling ratio calculated from the ratio of the film weight before and after incubation in the selected solvent.

Table S11. Solubility of PE in *t*BuPh (5 mg/mL). (+ = soluble, – = insoluble)

Temp. ($^{\circ}$ C)	LDPE	HDPE
50	–	–
65	–	–
80	+	–
100	+	+
120	+	+

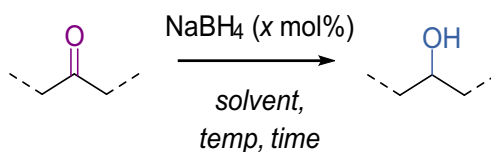
Table S12. Quantification of oxidized functional groups in post-consumer plastic materials by NMR spectroscopy prior to oxidation (subtracted from total observed oxidation after treatment).

Sample	Type	Object	Ketone (mol%)
1a	LDPE	Solvent bottle	0.3%
1b	LDPE	Ziplock	0.0%
1c	LDPE	Plastic wrap	0.1%
2a	HDPE	Bottle cap	0.0%
2b	HDPE	Milk jug	0.0%
2c	HDPE	Air bag	0.1%

Table S13. Oxidation of LDPE with ^tBuOOH and **1** with varying catalyst and oxidant loadings.

LDPE film (70 μm) $\xrightarrow[\text{tBuPh, 65 °C, 24 h}]{\text{1 (x mol%), tBuOOH (y equiv)}}$ Ketone

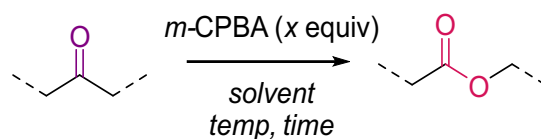
Entry	x (mol%)	y (equiv.)	Ketone (mol%)
1	0.001%	0.1	0.22%
2	0.001%	0.2	0.26%
3	0.001%	0.3	0.32%
4	0.001%	0.5	0.22%
5	0.001%	1	0.17%
6	0.002%	0.3	0.30%
7	0.010%	0.3	0.20%

Table S14. Reduction of PE films oxidized with ketones by sodium borohydride.

Entry	Method	Temp (°C)	Time (h)	x (equiv.)	Solvent	Conc. (mg/mL)	Conv. (%) ^a
1	Solution	80 ^b	24	0.10	THF	150	>99%
2	Film	20	24	0.10	THF	50	28%
3	Film	65	24	0.10	THF	25	31%
4	Film	65	24	0.10	^t BuPh	25	15%
5	Film	65	24	0.10	EtOH	25	26%
6	Film	65	24	0.10	THF	50	76%
7	Film	65	24	0.10	THF	150	64%
8	Film	65	24	0.30	THF	50	62%

^a Conversion determined by quantitative ¹H NMR spectroscopy (600 MHz, C₂D₂Cl₄, 100 °C) by integration of the ketone and alcohol regions. ^b Solution-based method adapted from ref ⁵.

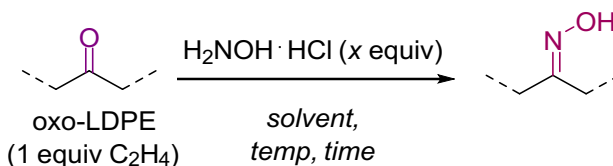
Table S15. Oxidation of PE films oxidized with ketones by *meta*-chloroperoxybenzoic acid.



Entry	Method	Temp (°C)	<i>x</i> (equiv.)	Solvent	Conc. (mg/mL)	Conv. (%) ^a
1 ^b	Solution	80	0.75	PhCl	5	74%
2	Film	65	0.75	PhCl	5	49%
3	Film	65	0.75	^t BuPh	5	15%
4	Film	65	0.75	H ₂ O	5	41%
5	Film	65	0.9	H ₂ O	23	62%
6	Film	65	2.0	H ₂ O	26	71%
7	Film	65	0.1	H ₂ O	43	51%
8	Film	65	0.1	H ₂ O	104	64%

^a Conversion determined by quantitative ¹H NMR spectroscopy (600 MHz, C₂D₂Cl₄, 100 °C) by integration of the ketone and ester regions. ^b Solution-based method adapted from ref ⁴⁷.

Table S16. Oxidation of PE films oxidized with ketones by hydroxylamine hydrochloride.



Entry	Method	Temp (°C)	Time (h)	<i>x</i> (equiv.)	Solvent	Conc. (mg/mL)	Conv. (%) ^a
1 ^b	Solution	100	4	1.40	Pyridine	25	79%
2	Film	65	16	0.10	Pyridine	50	39%
3	Film	65	24	0.05	Pyridine	50	33%
4	Film	65	24	0.10	THF	50	19%
5	Film	65	24	0.10	EtOH	50	21%
6	Film	65	24	0.10	H ₂ O	50	14%
7	Film	65	24	1.00	Pyridine	100	40%
8	Film	80	24	0.11	Pyridine	100	47%

^a Conversion determined by quantitative ¹H NMR spectroscopy (600 MHz, C₂D₂Cl₄, 100 °C) by integration of the ketone and oxime regions. ^b Solution-based method adapted from ref ⁵.

Table S17. Water contact angle measurements for pristine LDPE and oxidized PE immediately after treatment.

Sample	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Average	+/-
LDPE	100.7	100.5	97.8	97.7	95.5	95.7	98.0	0.8
HDPE	102.3	102.5	100.2	100.6	98.1	98.5	100.4	0.8
4b	97.5	94.3	94.4	97.0	97.1	90.7	95.2	1.0
4d	104.1	103.3	97.6	98.9	98.1	95.1	99.5	0.5
8a	26.5	33.3	59.2	39.5	48.3	60.9	44.6	5.2
8b	67.3	66.7	46.4	46.4	93.5	92.4	68.8	8.5

5. Supplementary References

54. Tobolsky, A. V., Metz, D. J. & Mesrobian, R. B. Low Temperature Autoxidation of Hydrocarbons: the Phenomenon of Maximum Rates. *J. Am. Chem. Soc.* **72**, 1942–1952 (1950).
55. Smith, L. M., Aitken, H. M. & Coote, M. L. The Fate of the Peroxyl Radical in Autoxidation: How Does Polymer Degradation Really Occur? *Acc. Chem. Res.* **51**, 2006–2013 (2018).
56. Walling, C. & Jacknow, B. B. Positive Halogen Compounds. I. The Radical Chain Halogenation of Hydrocarbons by t-Butyl Hypochlorite. *J. Am. Chem. Soc.* **82**, 6108–6112 (1960).
57. Müller, A. J., Hernández, Z. H., Arnal, M. L. & Sánchez, J. J. Successive self-nucleation/annealing (SSA): A novel technique to study molecular segregation during crystallization. *Polym. Bull.* **39**, 465–472 (1997).
58. Müller, A. J., Michell, R. M., Pérez, R. A. & Lorenzo, A. T. Successive Self-nucleation and Annealing (SSA): Correct design of thermal protocol and applications. *Eur. Polym. J.* **65**, 132–154 (2015).
59. Müller, A. J. & Arnal, M. L. Thermal fractionation of polymers. *Prog. Polym. Sci.* **30**, 559–603 (2005).

60. Arnal, M. L., Sánchez, J. J. & Müller, A. J. Miscibility of linear and branched polyethylene blends by thermal fractionation: use of the successive self-nucleation and annealing (SSA) technique. *Polymer* **42**, 6877–6890 (2001).
61. Kong, J., Fan, X., Xie, Y. & Qiao, W. Study on molecular chain heterogeneity of linear low-density polyethylene by cross-fractionation of temperature rising elution fractionation and successive self-nucleation/annealing thermal fractionation. *J. Appl. Polym. Sci.* **94**, 1710–1718 (2004).
62. Starck, P. Studies of the comonomer distributions in low density polyethylenes using temperature rising elution fractionation and stepwise crystallization by DSC. *Polym. Int.* **40**, 111–122 (1996).
63. Keating, M., Lee, I.-H. & Wong, C. S. Thermal fractionation of ethylene polymers in packaging applications. *Thermochim. Acta* **284**, 47–56 (1996).
64. Zhang, F. *et al.* Polydispersity of ethylene sequence length in metallocene ethylene/ α -olefin copolymers. I. Characterized by thermal-fractionation technique. *J. Polym. Sci. Part B Polym. Phys.* **40**, 813–821 (2002).
65. Table of Thermal Properties of Linear Macromolecules. in *Thermal Analysis* (ed. Wunderlich, B.) 417–431 (Academic Press, 1990). doi:10.1016/B978-0-12-765605-2.50012-1.
66. Kissin, Y. V. Polyethylene. in *Polyethylene (Second Edition)* I–XIV (Hanser, 2020). doi:10.3139/9781569908327.fm.
67. Nozue, Y. *et al.* Unusual Crystallization Behavior of Polyethylene Having Precisely Spaced Branches. *Macromolecules* **44**, 4030–4034 (2011).
68. Andrady, A. L. The plastic in microplastics: A review. *Mar. Pollut. Bull.* **119**, 12–22 (2017).

69. Chu, B. & Hsiao, B. S. Small-Angle X-ray Scattering of Polymers. *Chem. Rev.* **101**, 1727–1762 (2001).
70. Kasai, N. & Kakudo, M. *X-Ray Diffraction by Macromolecules*. vol. 80 (Springer, Berlin, Heidelberg, 2005).