ELECTRONIC SUPPORTING INFORMATION

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Additional Methods

Soxhlet extraction

Raw rubber samples may contain organic additives, including oil or other additives that could influence the reductive cleavage process. Therefore, in a control experiment, the extractable components were extracted prior to reduction. The most commonly used extraction solvent,[35] acetone, was used to remove resins, free sulfur, acetone soluble softeners and antioxidants, processing rubber additives, mineral oils, waxes, organic accelerators and their reactive products and fatty acids. The extraction procedure was as follows: 5.0 g raw truck tread-1 rubber powder was placed inside Whatman cellulose extraction thimble (33mm×118mm). The sample containing the thimble was extracted with 200mL refluxing acetone 56 °C for 72h in a standard Soxhlet apparatus. After this purification, the sample was dried in 100 °C oven overnight. The weight of collected sample was 4.48g.

Stock solutions

$B(C_6F_5)_3$: BCF was dissolved in dry toluene to prepare a stock solution (50mg mL^{-1}).
Stock solution of naphthalene in chloroform-*d*: solid naphthalene (4 mg, 0.031 mmol) was added to chloroform-*d* (2 mL, 3.0 g, 24.92 mmol) in a dried 20.0 mL glass vial.

Disulfide and Tetrasulfide Chemistry

Dibenzyl tetrasulfide titration using bis(trimethylsiloxy)methylsilane ([SiH]/[SS]=1:1)

To a dried glass NMR tube (7×5 mm) purged with dry N_2 gas, dibenzyl tetrasulfide (0.055 g, 0.185 mmol, a mix of oligosulfides, see above) and bis(trimethylsiloxy)methylsilane (0.048 g, 0.216 mmol) were added together with chloroform-*d* stock solution (0.6 mL). Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.023 mL, 0.0045 mmol) after 5 min sonication. Each point in Figure S2 was obtained by adding bis(trimethylsiloxy)methylsilane (0.048 g, 0.216 mmol) and $B(C_6F_5)_3$ stock solution (0.023 mL, 0.0045 mmol) in aliquots portion by portion with 3 h time interval between additions. The peak area of the hydrogens on the carbon adjacent to polysulfide bonds including pentasulfide (-C**H₂**SSSSS), tetrasulfide (-C**H₂**SSSS), trisulfide (-C**H₂**SSS) and disulfide (-C**H₂**SS) in ^{1}H NMR (Figure S2) were plotted against different ratio of hydrosilane (Si<u>**H**</u>) input (Figure S2, Table S2).

Table S1 Reactivity comparison using dibenzyl sulfide **1** and bis(trimethylsiloxy)methylsilane **2**

Ratio [SiH]/[SS]	**1** (g)	**2** (g)	DCM (g)	$B(C_6F_5)_3$ (mL)[a]
0.25	0.50	0.12	1.68	0.021
0.5	0.50	0.24	2.05	0.042
1	0.50	0.46	2.59	0.084
1.5	0.50	0.68	3.20	0.125
2	0.50	0.91	3.81	0.167

a: 100 mg mL^{-1} $B(C_6F_5)_3$ stock solution

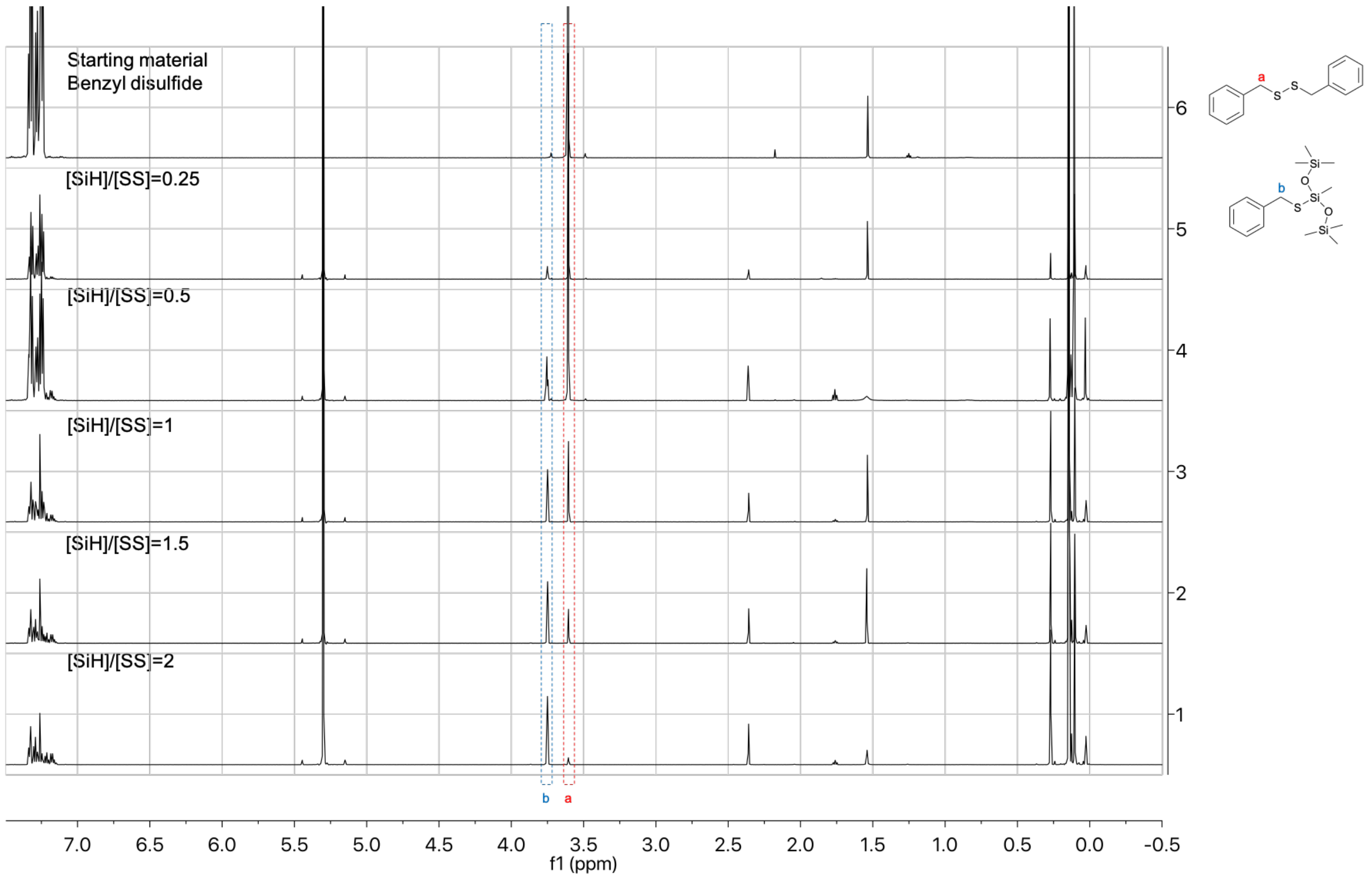


Figure S1 Benzyl disulfide reaction with MD^{H}M monitored by ^{1}H NMR (during the titration, small quantities of solvent remained in the sample; peaks at 1.5 and 2.3 ppm reflect the presence of water and toluene, respectively.)

Table S2 ^{1}H NMR Integration data used to plot Figure 2.[a]

Ratio [SiH]/[SS]	$C\underline{H}_2SS$	$C\underline{H}_2SSS$	$C\underline{H}_2SSSS$	$C\underline{H}_2SSSSS$	$C\underline{H}_2SSi$
Figure 2a					
0	4.00	-	-	-	0.00
0.25	3.65	-	-	-	0.35
0.5	3.24	-	-	-	0.76
1	2.21	-	-	-	1.79
1.5	1.30	-	-	-	2.70
2	0.30	-	-	-	3.70
Figure 2b					
0	0.06	1.95	1.18	0.81	0.00
1	0.00	0.85	0.89	0.86	1.40
2	0.00	0.23	0.52	0.72	2.53
3	0.00	0.02	0.23	0.51	3.24
4	0.00	0.00	0.04	0.32	3.64
5	0.00	0.00	0.00	0.00	4.00

[a] Fig. 2a: The numbers represent the relative integration of CH_2 adjacent to S (2 x CH_2, total = 4H). Fig 2b: The tetrasulfide is actually a complex mixtures oligosulfides, with the tetrasulfide as major constituent. In this case, naphthalene was used an internal standard. The total integration of the CH_2-S groups all constituents was normalized to 4H.

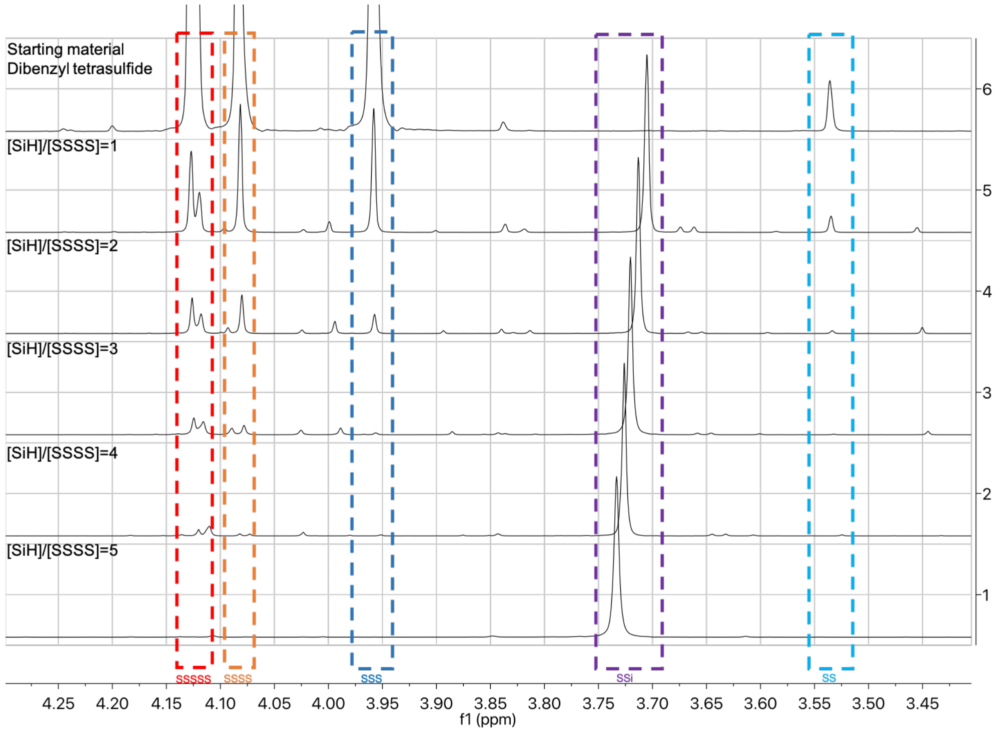


Figure S2 Benzyl tetrasulfide reaction with MD^{H}M monitored by ^{1}H NMR

Rubber Chemistry

Sample preparation

Figure S3 a: Sailun Truck tread 2. b: Sectioning the external, road contacting section with a reciprocating saw to give Truck tread 2.

Starting Material Characterization

Particle Sizes

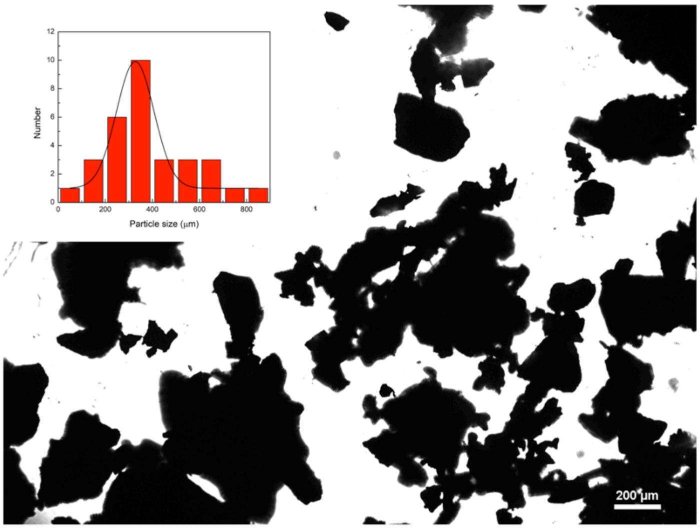


Figure S4 Particle size of ground rubber (inner tube) crumb)

^{13}C HR-MAS NMR

The polymer constituents of rubber samples were estimated from carbon high-resolution magic angle spinning (^{13}C HR-MAS) NMR spectroscopy. The dry rubber powder samples were weighed (～ 10 mg) and placed into a ^{13}C HR-MAS rotor and then inserted into the spectrometer. ^{13}C HR-MAS spectra were acquired using a Bruker Avance 850HD NMR spectrometer operating at 213.8 MHz for ^{13}C. Samples were typically spun at 8 kHz using a 4 mm ^{13}C HR-MAS probe (P/N 132955, S/N 0002) maintained at 25 °C. One-dimensional spectra were acquired using standard pulse-acquisition (Figure S5).

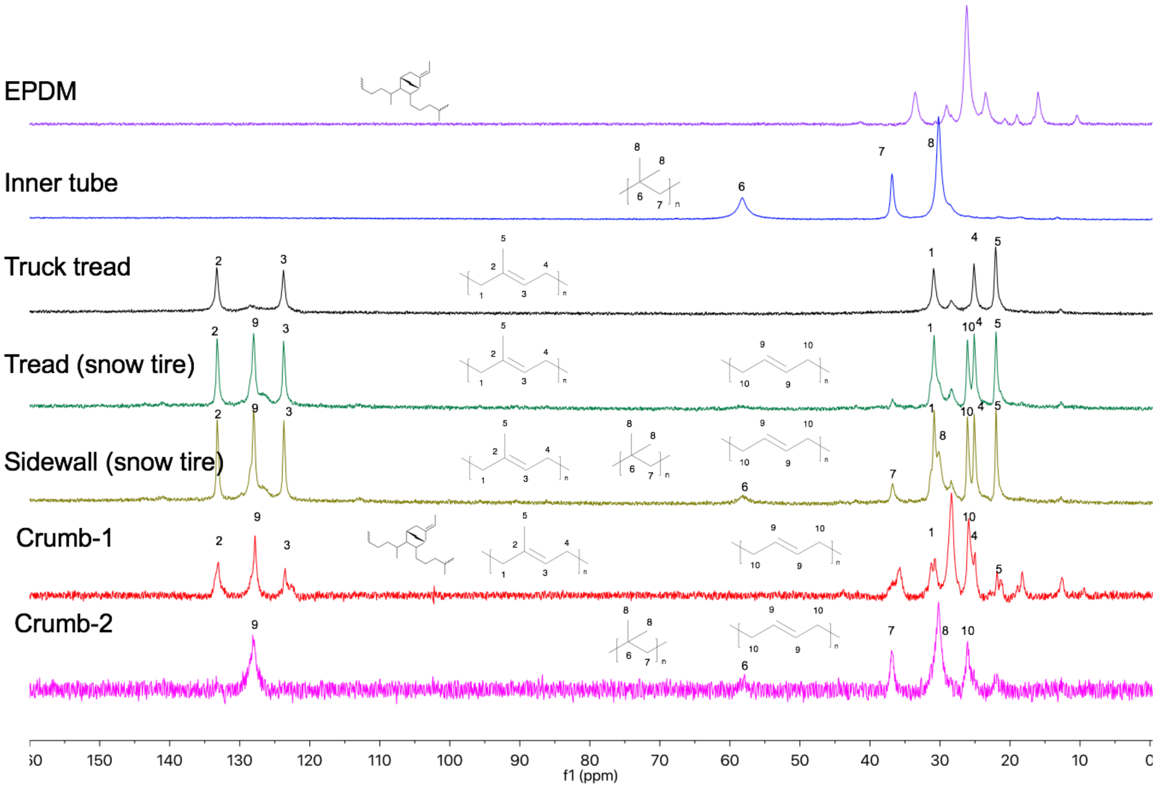


Figure S5 The ^{13}C HR-MAS NMR of different rubber samples

TGA of Starting Materials

Table S3 Rubber components characterized by TGA profile

Component	% Mass Loss
Organic materials	50 °C to 550 °C (nitrogen)
Carbon black	560 °C to 800 °C (air)
Ash	Residue at 800 °C

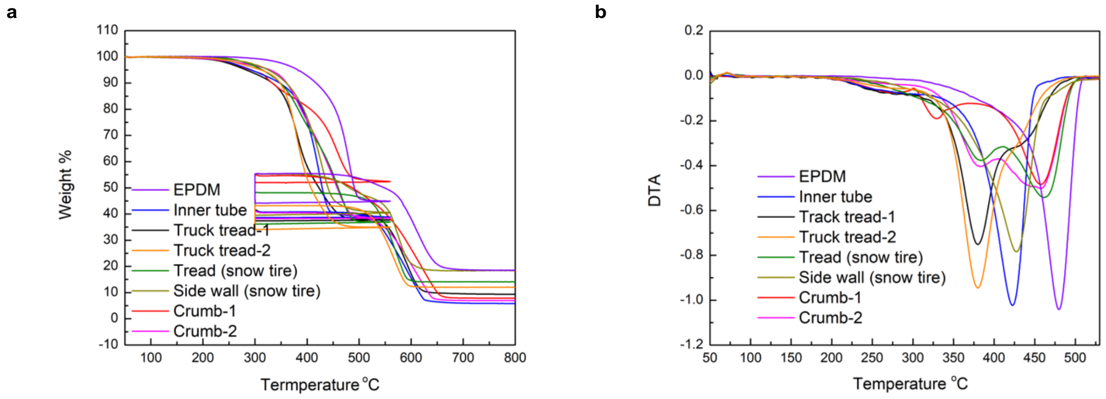


Figure S6 The thermogravimetric analysis curves (a) and differential thermal analysis curves (b) of different rubber samples.

Reduction of rubbers: General procedure (with powders or coupons)

Bulk samples

Bulk samples were cut directly from different parts of a car tire using a reciprocating saw (Figure S3). The experimental procedure for their reduction is as follows. The bulk piece of rw tread (cross-section, 2.083g, ~1.200cm × 1.519cm × 1.125cm, containing metal and fiber) was allowed to swell in dry toluene (80 mL) for 6h. Pentamethyldisiloxane (7.6g, 51.35mmol, 10 mL) was added to the reaction mixture. Several ceramic beads were added to increase shear force while stirring with a magnetic stirrer. BCF catalyst was added portion by portion each 24h (6+2+2+2 wt% $B(C_6F_5)_3$). The reaction mixture was heated in a 60 °C oil bath for 6 d (Figure S18). The residual undissolved rubber bulk was washed with toluene and dried in a 100 °C oven. The suspension was centrifuged, then washed, and re-centrifuged (repeated twice). The supernatants were mixed, and the solvent was removed by rotary evaporation. The volatile organics were removed by blowing with a stream of N_2 for 48 h. The residual (now smaller, Figure S19a) rubber bulk (0.460g, broken in two pieces: 0.675cm × 1.331cm × 0.445cm, 0.754cm × 0.937cm × 0.340 cm) and powder (0.527g) were separately examined using TGA (Figure S12a). The recovered organic liquid was characterized by NMR.
Powdered samples were reduced following the same protocol. Powders were prepared by cryogenic grinding as noted in the main text.

The calculations of yield and the appearance of the materials are shown in Figure S8 and Figure S9. The TGA data before and after reduction for the different rubbers may be found in (Figure S11). Increasing the scale from 300 to 2000 mg did not significantly change the efficiency of the process (Figure S13). The effect of Soxhlet extraction was minor. Multiple reductions led to additional material, but with decreasing fractions of soluble oil produced (Figure S14, Table 2, Table 3).
The organic yields were calculated from TGA profiles:

$$\text{Organic Yield } \% = \frac{m_0 \times W_0 - m_i \times W_i}{m_0 \times W_0} \times 100$$

i.e., (Organic yield = (Total Organic-Recovered Organic)/Total Organic * 100)
Where m_0 is the mass of starting rubber and m_i is the mass of residual solid. W_0 is the organic weight % in starting rubber. W_i is the organic weight% in residual solid. Both W_0 and W_i is got from TGA.

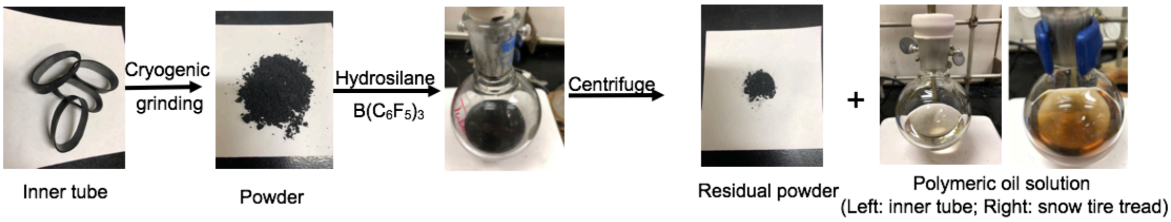


Figure S7 Sequence of conversion of starting rubber samples to organic oils and residual powers (shown for inner tube rubber). Note: the turbidity of the recovered oil can vary depending on batch and on starting material; oil on the right is from a batch of car snow tire tread.

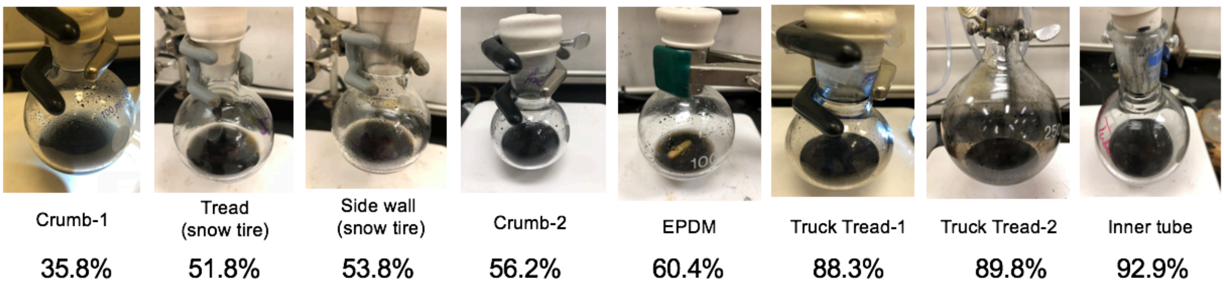


Figure S8 Visible differences in the reaction processes as a function of reduction efficiency

Product Characterization

TGA of Reduced Products

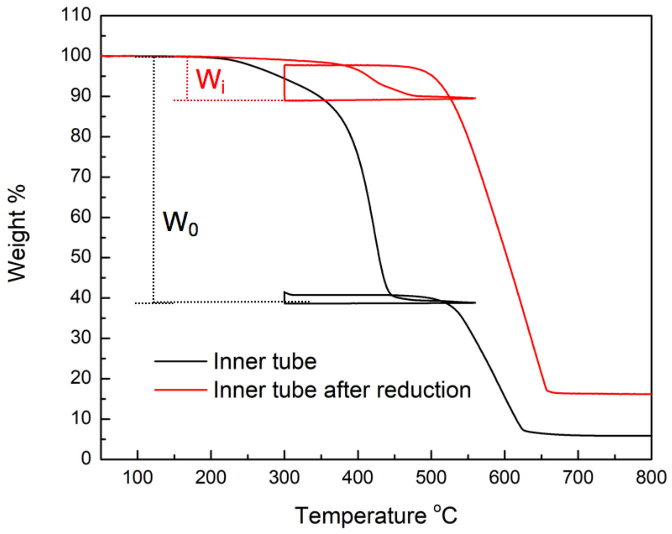


Figure S9 Determination of organic polymer fraction using TGA, shown for the inner tube.

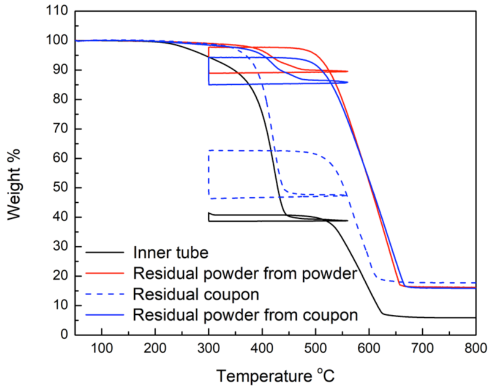
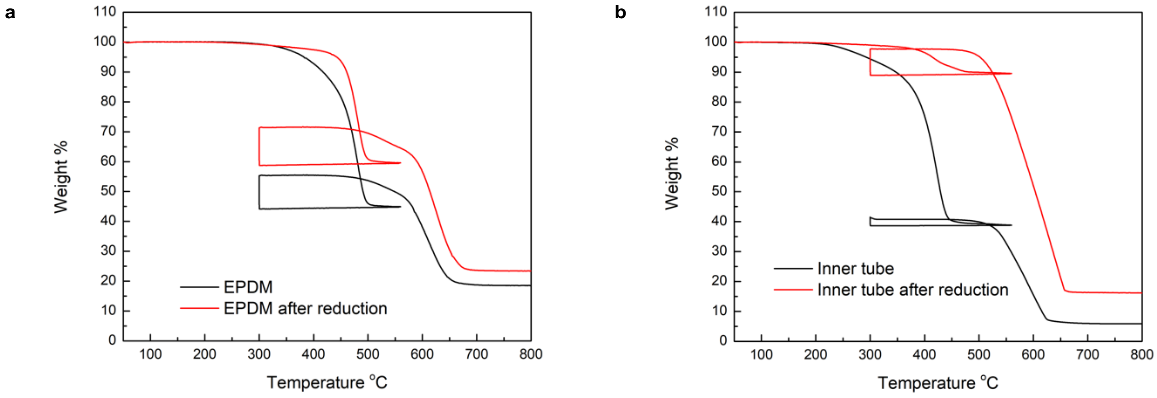


Figure S10 Thermogravimetric analysis (TGA) of powder (red) or coupon (blue) inner tube after reduction.



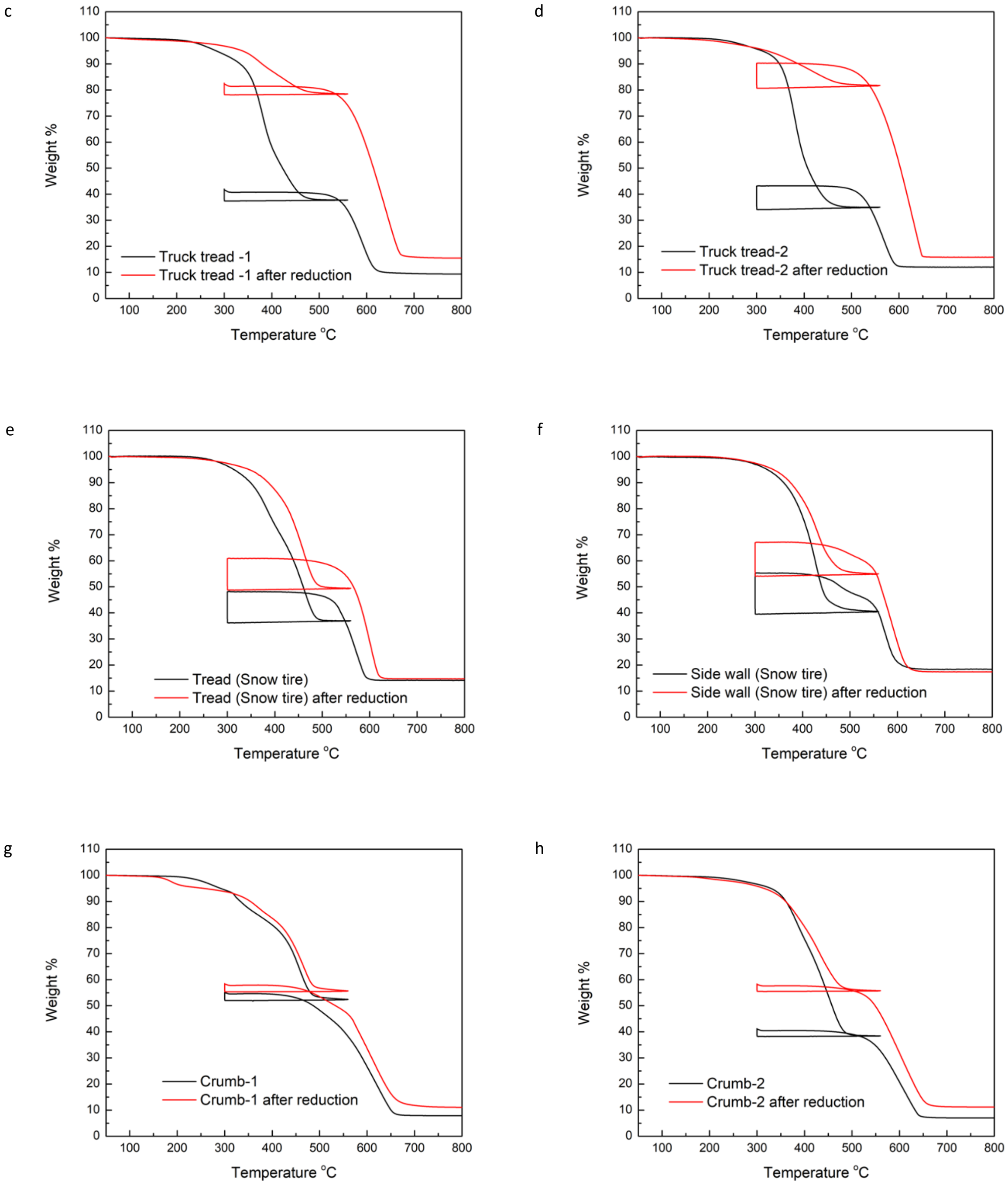


Figure S11 Thermogravimetric analysis (TGA) of different rubber samples. Before (black line) and after reduction (red line)

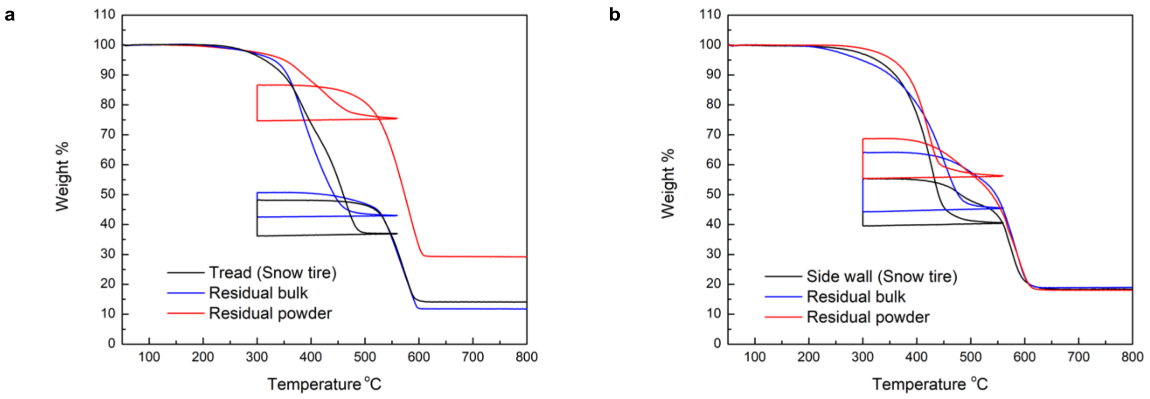


Figure S12 Thermogravimetric analysis (TGA) of a: tread (snow tire) and b: Side wall (snow tire). Original starting bulk rubber (black, Figure 3a), residual bulk rubber (Figure 3d) after reduction (blue), and residual powder (Figure 3e)) collected after reduction (red).

Effect of Reaction Scale

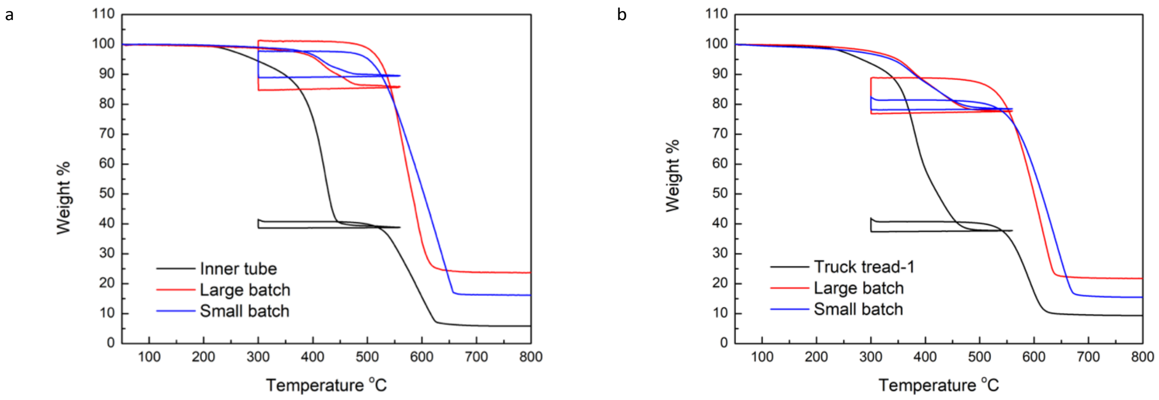


Figure S13 Thermogravimetric analysis (TGA) of a: inner tube and b: truck tread-1 (right) samples with different scales (small = 300 mg; large = 2000 mg).

Extraction Efficiency During Repetitions

Table S4 Decrosslinking of bulk rubber; effect of multiple repetitions

Rubber type	Starting material Character-istics	Start-ing mass (mg)	**7** (mL)	Constitution of Residue				Recover-ed volatile liquid (mg)	Young's modulus of bulk Before/After (MPa)
				Bulk (mg)	Powder (mg)	Metal[d] (mg)	Total mass (mg)		
Side Wall	First (Bulk with fiber)[a]	1475	7.4	1197	48	0	1245	142	5.52±1.21/ 16.86±1.36
Side Wall[b]	Second (Powder, no metal or fiber)[c]	300	1.5	-	204	-	204	221	-
Tread	First (Bulk with metal and fiber)[a]	2083	10.0	460	527	294	1281	830	22.28±1.62/ 57.78±2.40
Tread[b]	Second (Powder, no metal or fiber)[c]	300	1.5	-	214	-	214	183	-

[a] Experimental conditions for the first reduction: BCF/ Rubber = 12wt% (added portion by portion: 6+2+2+2), 6 days, 60 ºC. [b] The residual bulk materials from the first reduction were ground into a powder prior to the second reduction. [c] Experimental conditions for the second reduction: BCF/ Rubber = 10wt% (added all at once), 48h, 60 °C. [d] Note: Only metal was removed from the elastomer matrix in step 1; polymeric fiber; remained bound to the residual bulk solid.

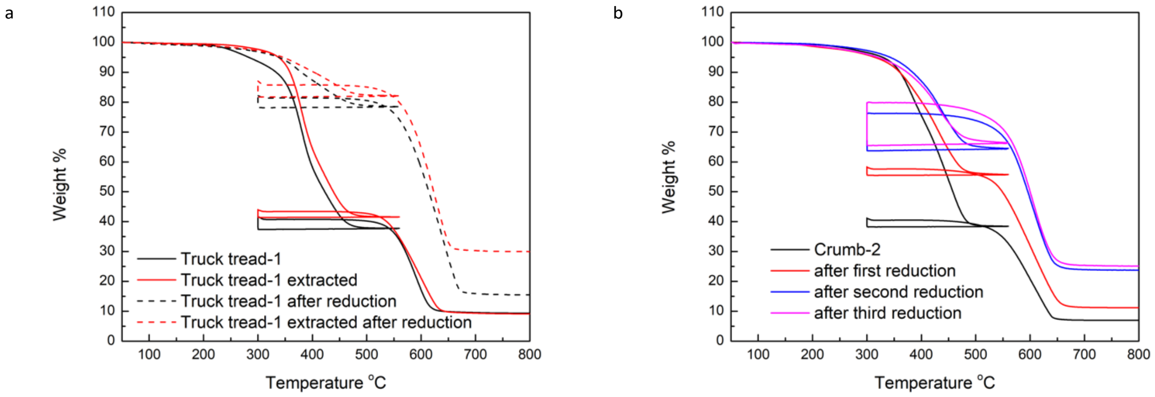


Figure S14 Thermogravimetric analysis (TGA) of a: truck tread samples with (red) or without (black) Soxhlet extraction. b: Crumb-2 sample after multiple reduction steps

NMR Characterization of Product Polymer Oils

The oils produced by the silylating reductions were characterized primarily by NMR. The signatures of the constituent polymers were readily identified. The geminal dimethyl groups on the backbone of polyisobutylene is particularly characteristic (Figure S15), as are backbone methyl groups from propylene and isoprene units. The constituent rubber components, as shown by NMR, are consistent with the TGA data on the starting elastomers (Figure S6). The molecular weights of these oils were in the 10000 g mol^{-1} range, with much higher fractions in some cases (Figure S16).

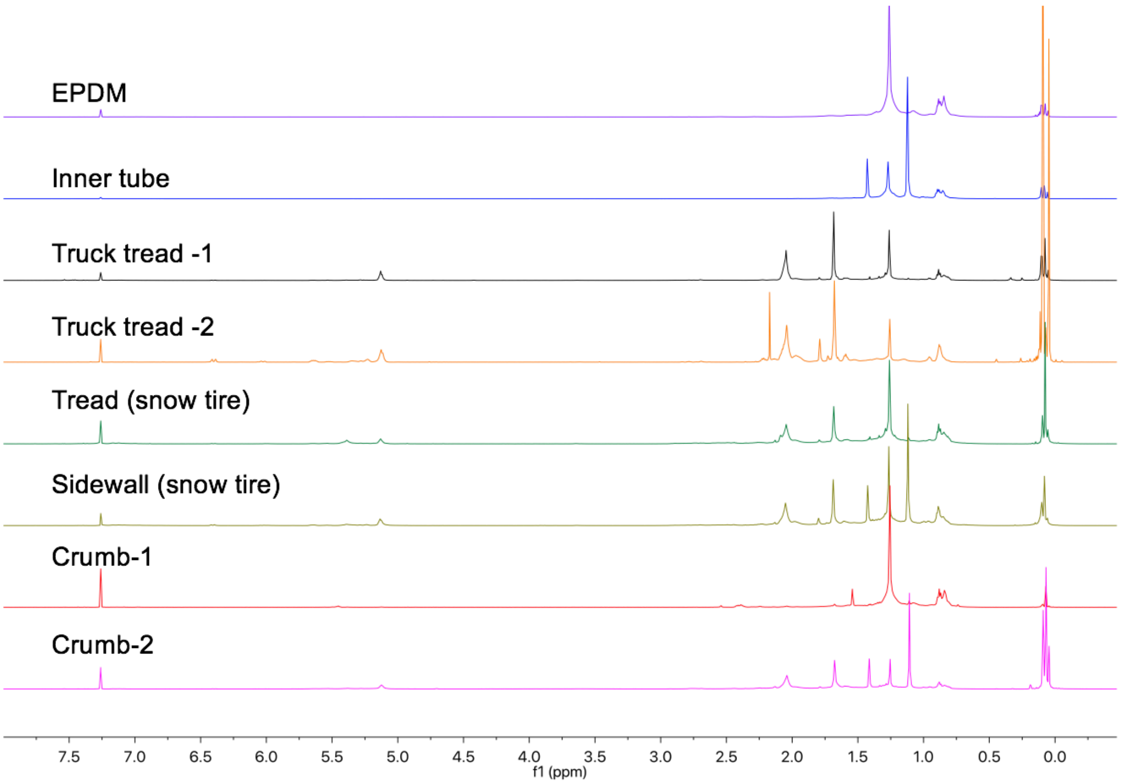
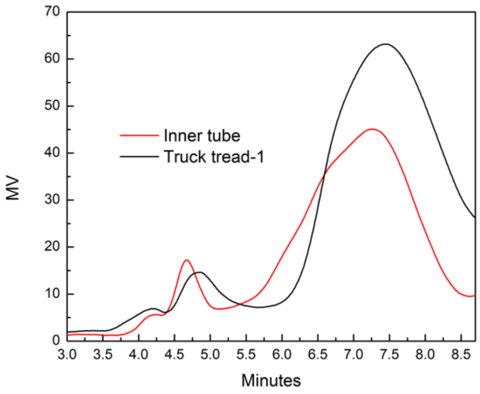


Figure S15 ^{1}H NMR of recovered organic liquids.

GPC (MW) Characterization of Product Polymer Oils

Table S5 GPC data of recovered organic oil

Rubber sample	Components	Peak 1		Peak 2	
		Mw	PDI	Mw	PDI
EPDM	EPDM	-	-	6.54×10^{4}	1.39
Inner tube	PIB	1.1×10^{7}	1.12	7.9×10^{4}	2.50
Truck tread-1	IR/NR	0.8×10^{7}	1.25	2.02×10^{4}	2.05
Truck tread-2	IR/NR	-	-	6.63×10^{4}	1.95
Tread (snow tire)	IR/NR+BR	-	-	2.18×10^{4}	1.63
Side wall (snow tie)	IR/NR+IIR+BR	-	-	4.66×10^{4}	1.84
Crumb-1	BR+IR/NR+EPDM	-	-	6.13×10^{4}	2.11
Crumb-2	IIR+BR	1.42×10^{6}	1.18	4.18×10^{4}	2.39



Figures S16 GPC data of recovered organic oil with two molecular populations.

Efficiency of Reduction Using Other Hydrosilicones

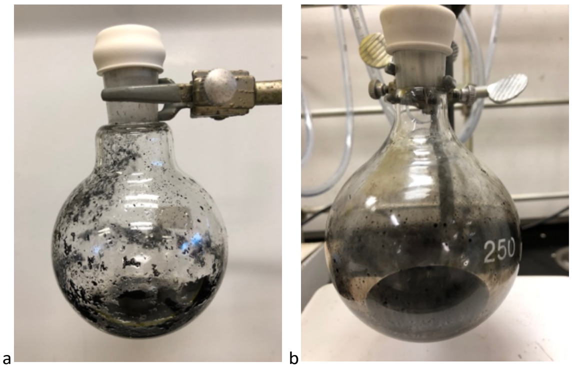


Figure S17 Inner tube reduction after 18h at 100 °C with different hydrosilanes. a: $Me_3Si(OSiMeH)_nSiMe_3$ **9**; b: $HMe_2SiOSiMe_2H$ **10**.

Multiple reductions with bulk rubber (analogous to the inner tube experiments shown in Table 2, Table 3)

It can be seen that shrinkage of the bulk elastomer occurs during the first reduction (Figure S18). The residual solid (300mg) was ground cryogenically (under liq. N_2) and subjected to a secondary reduction using fresh catalyst (30mg) and pentamethyldisiloxane (1.14g, 1.5mL). The reduction was carried out for 48 h in a 60 °C oil bath, followed with an additional wash sequence. The relative efficiency of reducing a powder vs bulk rubber (see previous section) is shown for the inner tube in Table 3.

A similar protocol was followed using a piece of sidewall (cross-section, 1.595 × 1.427 × 0.6096 cm, 1.475 g), which led to 1.427 × 1.409 × 0.549 cm). Sequential reactions showed that it was possible to capture additional depolymerized material in a second step, but it was not particularly efficient in bulk form (Table S4, Figure S12b).

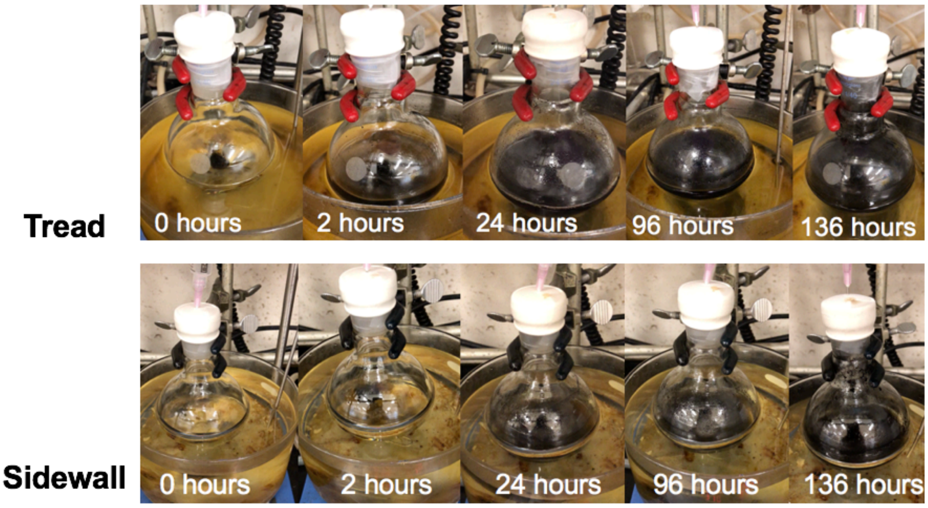


Figure S18 Time lapse photos of rubber reduction and dissolution.

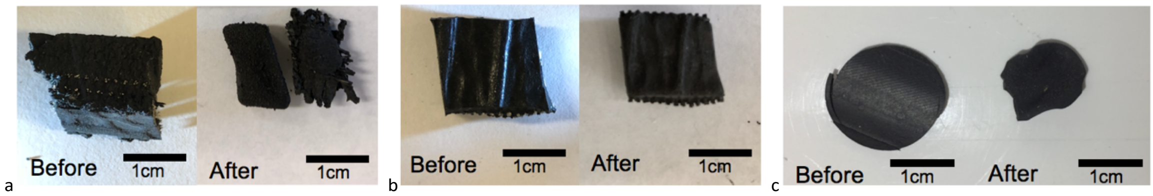


Figure S19 Shrinkage of bulk rubber after 1 reduction cycle a: snow tire tread; b: snow tire sidewall; c: bulk rubber bicycle tire.

Reduction of rubbers: General procedure (with powders or coupons)

Desilylation

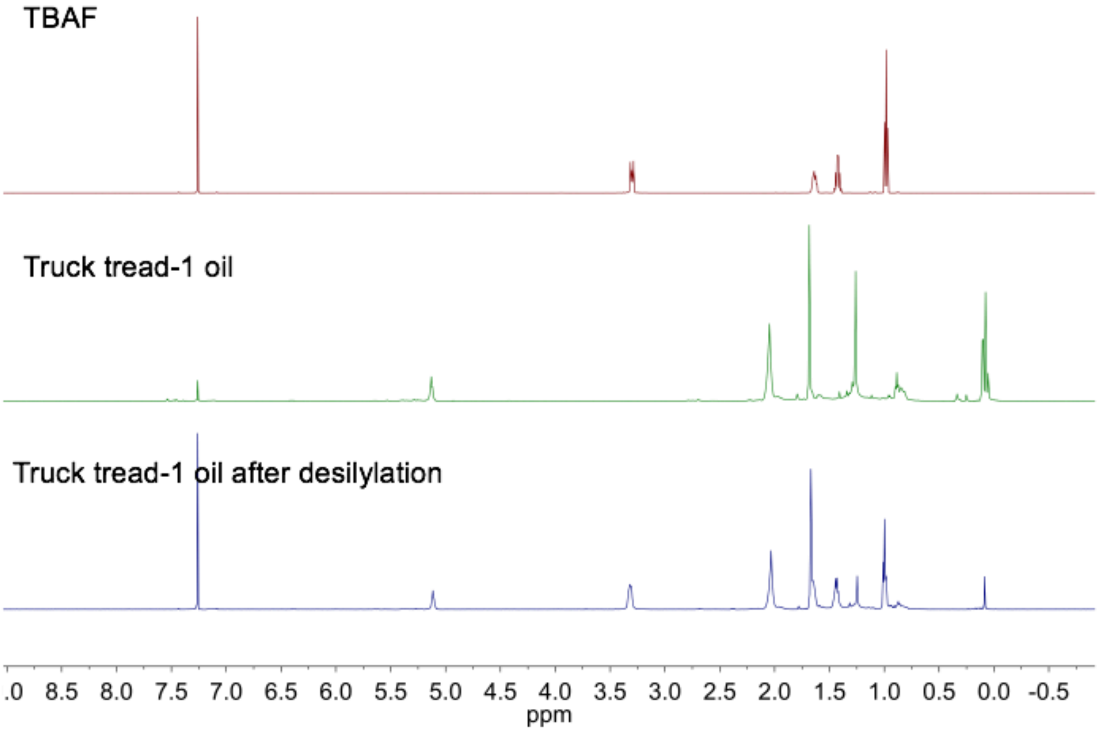


Figure S20 ^{1}H NMR showing loss of silicone groups from the organic polymers after utilizing TBAF.

Preparation of New Elastomers: A toy tire from recovered organic oil with peroxide initiator (Figure 4)

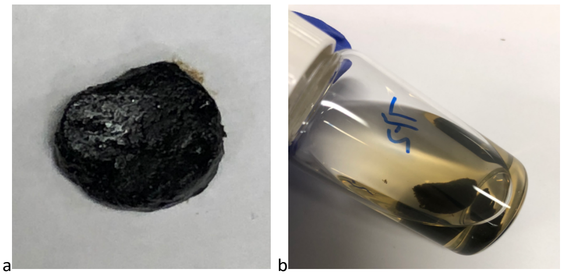


Figure S21 a: The crosslinked elastomer **1** formed by iodine reoxidation of thiols in **8**. b: The picture of 0.1g **2**, swollen in 10 mL hexane after 1h sonication.

Table S6 Recrosslinking of recovered organic oil **8** with residual solid as reinforcing agent

Organic oil **8** (Truck tire Sailun, g)	Ground residual solid (g)	BPO (g)	Hardness
1.000	0.000	0.010	68±3 (Shore OO)
0.700	0.300	0.010	91±4 (Shore A)