



## Dissolving used rubber tires†

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Sijia Zheng, Mengchen Liao, Yang Chen and Michael A. Brook \*

Used automobile tires present an enormous environmental burden. Efficient methods for degradation of the sulfur crosslinks in organic elastomers have proven elusive. We show that the reductive silylation of RS-SR bonds to silyl thio ethers RSSiR<sup>2</sup> in up to 90% yield using a variety of hydrosilicones occurs in the presence of <1 mol% B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for model compounds. Sulfur-cured automotive rubber required 10 wt% catalyst for efficient sulfide cleavage. At temperatures ranging from room temperature to 100 °C recoveries of organic polymers as oils from tires using this one step process ranged from 56% for complex mixtures of rubber crumb from ground tires to 93% for butyl rubber (bicycle inner tubes; 87% yield at 100 °C over 30 minutes). After removal of inorganic materials by simple filtration, the recovered polymeric oils were radically or oxidatively crosslinked to generate new elastomers that can be optionally reinforced with the solids recovered in the initial reduction procedure. This mild process constitutes a facile route to reutilize the organic polymers found in automobile and other sulfur-crosslinked rubbers.

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## Introduction

The radically induced<sup>1</sup> vulcanization of alkene-containing hydrocarbon polymers, reported by Goodyear in 1844,<sup>2</sup> is a technological advancement that remains an integral part of modern life; sales of automobile tires prepared using this process are expected to reach 3 billion units in 2019.<sup>3</sup> The elastomer products, crosslinked with sulfur oligomers, are incredibly robust products, which pose a major challenge; they are far too stable to be readily recycled.

Automobile tires exemplify polymers derived from fossil fuels that are destined for single use. Used tires constitute a significant environmental burden, particularly because of the scale of production.<sup>4</sup> In large part, used tires are simply placed in stockpiles,<sup>5</sup> from which leaching into the environment of their many (toxic) constituents occurs.<sup>6</sup> Dangerous, highly polluting, difficult-to-arrest tire fires at such storage facilities are not uncommon.<sup>7</sup>

Some automotive rubber is exploited as fuel in the cement industry; capturing SO<sub>2</sub> during combustion may be problematic. Some tires are turned into crumb and used as fillers,<sup>8</sup> for example, in asphalt, cement or turf replacements from which, however, leaching of contaminants may still occur.<sup>9</sup>

There is a longstanding need to recover the organic materials from tires for sustainable reuse. Although the S-S bond strength is only ~280 kJ mol<sup>-1</sup>,<sup>10</sup> practicable processes for S-S cleavage in vulcanized tires have not been reported. Aggressive chemical approaches, for example, reactive reduction with LiAlH<sub>4</sub><sup>11,12</sup> or amines<sup>13</sup> have not proven commercially viable. Reuse strategies therefore typically involve energetically intensive, relatively inefficient pyrolytic conversion into fuel gas, low grade carbon black and other low value materials.<sup>14</sup> The world is in dire need of new efficient methods for recycling waste tire rubber, especially in ways that allow the recovery and reuse of the basic building blocks.

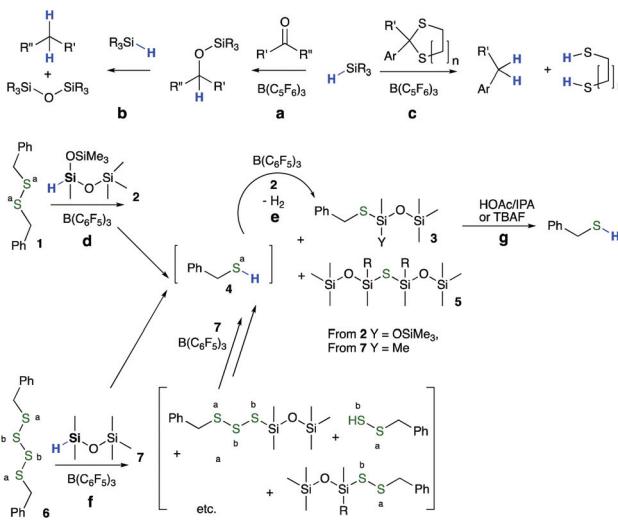
The weak Si-H bond in hydrosilanes makes them excellent reducing agents, particularly when strong Si-heteroatom bonds are formed in the process.<sup>15</sup> Thus, reductive hydrolysis/alcoholysis<sup>16</sup> and C=O hydrosilylation,<sup>17</sup> among others, are efficient processes. Key to the work described here is the Lewis acid-catalyzed (typically B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> = BCF) reduction of carbonyls (Fig. 1a), ethers, silanols, alkoxysilanes (the Piers–Rubinsztajn reaction<sup>18–20</sup> Fig. 1b), benzylic sulfides, and thioacetals (Fig. 1c) using HSi functional groups.<sup>21</sup> These reactions are normally easy to control, often work at room temperature, and the main experimental issues are associated with managing the co-products when they are flammable gases, including hydrogen or alkanes.

We report that, catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, hydrosilanes effectively reduce S-S bonds of model organic disulfides, tetrasulfides and, more importantly, complex sulfur-crosslinked solid automotive rubbers in the forms of bicycle inner tubes, solid tires or tire crumb in good to excellent yield. The products are polymeric, silyl-protected thiolated organic oils that are readily

Department of Chemistry and Chemical Biology, McMaster University, 1280 Main St W, Hamilton, ON, Canada L8S 4M1. E-mail: mabrook@mcmaster.ca

† Electronic supplementary information (ESI) available: Tables of reactivity of di- and tetrasulfides, rubber components, efficiency of repeated reduction and GPC data of produced oils. Figures showing NMR data of starting rubbers, product oils, TGA data or starting rubbers, and products oils, photographs showing the process from rubber to oils to new rubbers. See DOI: 10.1039/c9gc03545a





**Fig. 1** Selected examples of  $B(C_6F_5)_3$ -catalyzed reduction by SiH groups. (a) Carbonyl reduction to silyl ethers; (b) silyl ether reduction to alkanes (Piers-Rubinsztajn); (c) aromatic thioacetal cleavage to alkanes; (d) disulfide cleavage to silyl thio ethers (this work); (e) reduction of thiols to silyl thio ethers; (f) silyl thiol ether formation from oligosulfides, and, (g) Si-S cleavage using acid or fluoride catalysis.

separated from the accompanying, unreactive solids, such as fillers, fiber and metal reinforcements, pigments, *etc.* simply by filtration or centrifugation. The products, sulfur-containing polymeric oils, may be converted back into (reinforced) rubbers using simple oxidative or radical processes.

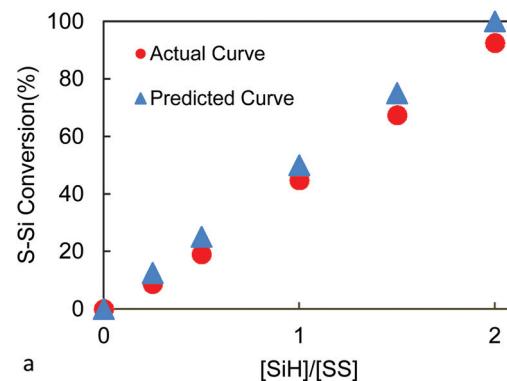
## Results

### Model reductions of dibenzyl disulfide and tetrasulfide

Model reductions of dibenzyl disulfide **1** ( $n = 1$ ) were undertaken with bis(trimethylsiloxy)methylsilane **2** ( $HSiMe(OSiMe_3)_2$ ,  $MD^H M$ ) (the common nomenclature used for silicones is Q:  $SiO_{4/2}$ ; T:  $MeSiO_{3/2}$ ; D:  $MeSiO_{2/2}$  and M:  $Me_3SiO \sim$ ) as reducing agent in the presence of BCF (Fig. 1d, e, Fig. 2, Table S1, and Fig. S1, ESI<sup>†</sup>). With less than one equivalent of hydrosiloxane, residual starting material and only product **3** were recovered, demonstrating that the reaction of SiH with S-H, *e.g.*, in compound **4**, is faster than that with S-S bonds. Complete reduction of **1** → **3** required 2 equiv. of the hydrosiloxane and occurred in 90% yield using only 0.8 mol% BCF; the other sulfur-based product **5** was removed under reduced pressure. Reduction of the analogous tetrasulfide **6** to **3** using  $HSiMe_2OSiMe_3$  **7** required five equivalents of  $MD^H M$  and demonstrated that both C-S<sup>a</sup>-S<sup>a</sup> and S<sup>a</sup>-S<sup>b</sup>-S<sup>b</sup> linkages undergo efficient reductive silylation (Fig. 1f, 2 and Fig. S2, ESI<sup>†</sup>).

### Reduction of used automotive rubbers

Automotive tires contain a complex variety of constituents, including (spent) catalysts for their formation, antioxidants, colorants, particulate reinforcing agents like carbon black and/or organosulfur-modified silica, and fibrous reinforcing agents



**Fig. 2** (a) Disulfide conversion in benzyl disulfide system versus [SiH]/[SS] using  $MD^H M$ . (b) Polysulfide conversion in benzyl tetrasulfide system versus [SiH]/[SSSS] using  $MD^H M$ . For integration data, see Table S2.†

including nylon cord and woven steel.<sup>14</sup> Holding together this complex assortment of excipients is the sulfur-crosslinked elastomer. We reasoned that the (oligo)sulfide linkages in rubber tires could be reductively cleaved using hydrosilanes in analogy to the reactions with the oligosulfide model compounds (Fig. 1d-f).

Scrap rubber from automobile tires is available in large quantity in the form of 'rubber crumb'. It is formed by shredding tires from multiple sources to remove metal wires and polyester cord and grinding the resulting product to various crumb sizes. The typical organic constituents in crumb mixtures include isobutene isoprene (IIR), butadiene rubber (BR), styrene-butadiene rubber (SBR), isoprene rubber (IR) and natural rubber (NR). Thermal degradation profiles allow one to determine the constitution of sulfur-crosslinked elastomers; depending on their structure, the polymers degrade between 300–485 °C,<sup>22,23</sup> (Fig. S5, and S6, Table S3†) while inorganic carbon (carbon black) thermally decomposes from 560–800 °C in oxygen.<sup>24</sup> In the rubbers tested, the organic rubber content was approximately 60 wt% (Table 1, Fig. S11†).

Two separate sources of commercial crumb were compared for their reactivity under the reducing silylation conditions. Much more BCF catalyst (10 wt% compared to the rubber start-

Table 1 Constituents in rubber starting materials

Rubber	Rubber constituents <sup>a</sup>	Components		
		Organic (%)	Carbon black (%)	Other solids (%)
EPDM	EPDM	55.1	26.4	18.5
Inner tube		61.1	33.0	5.9
Truck tread -1	IR/NR	62.2	28.4	9.4
Truck tread -2	IR/NR	65.0	23.0	12.0
Tread (snow tire)	IR/NR + BR	63.0	22.9	14.1
Side wall (snow tire)	IIR + IR/NR + BR	59.4	22.2	18.4
Crumb-1	BR + EPDM	47.6	44.6	8.8
Crumb-2	IIR + PBD	61.6	31.5	6.9

<sup>a</sup> EPDM terpolymer of ethylene, propylene and diene, IR/NR isoprene rubber/nature rubber, IIR isobutene isoprene rubber, BR butadiene rubber. Constituents were determined by a combination of TGA, which showed separate decomposition temperatures for IIR and IR/NR, and <sup>1</sup>H NMR.

ing material) was required to achieve reasonable yields of reduction with rubbers than with the model compounds (<1 mol%), which is not surprising given the complexity of the mixed rubber starting materials and the fact that they have been exposed to degradation and various environments during use.

With 7 as reducing agent, organic oils were recovered in 36% yield from one crumb rubber source and a moderate 56% yield from another (2 lots, Fig. 3g). Use of second and third reduction steps with fresh catalyst and hydrosilane significantly improved overall conversion of elastomer to oils (steps (1) 56% → (2) +29.6% → (3) +2.5% (total 88% organic recovery) – the inorganic constituents were removed by centrifugal separation (Tables 2 and 3, Fig. S14†). In retrospect, in a practical sense, only the improvement in overall efficiency of the second step could be justified. The reduction process was readily visible by eye, as black dispersions were converted to yellow oils (Fig. 3b → f,g, Fig. S7 and S8, ESI†).

Improved recoveries of organic polymers were observed with single composition rubbers. For example, about 60% of an EPDM elastomer (ethylene propylene diene terpolymer, 'pond liner') was converted to a soluble oil using reductive silylation with 7 and  $B(C_6F_5)_3$  in toluene at 60 °C. Automotive rubbers were efficiently reduced to oils in one step in yields ranging from 52–93%. These included: IIR from a (used) bicycle inner tube; IR/NR from the outermost section of truck tire tread; a mixture of IIR, IR/NR and BR from a snow tire side wall; and IR/NR, BR from a snow tire tread (Tables 2 and 3). The process is easily seen from the reduction of a bulk section of snow tire tread (Fig. 3a). Shortly after the reduction reaction started, the reinforcing steel wires separated from the bulk rubber and were collected on the magnetic stir bar (Fig. 3c); accompanied by particulate formation to give a black dispersion (Fig. 3b) – the bulk rubber underwent shrinkage, but not complete disintegration (Fig. 3d, Fig. S19†). Filtration allowed separation of a black solid mass comprised primarily of inorganic excipients and a yellow solution of silylated organic oils in toluene (Fig. 3e, f, Fig. S7 and S18†).

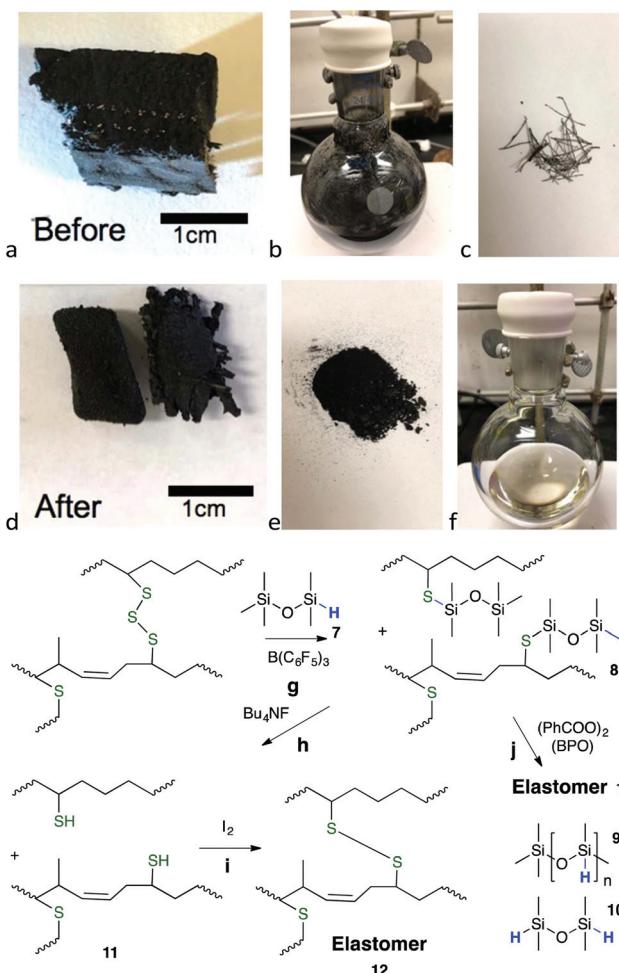


Fig. 3 (a) Section of snow tire tread cross-section, unreacted. (b) Reductive dispersion using 7 and 10 wt% BCF after 6 days. (c) Metal wires that self-affixed to the magnetic stir bar. (d) Shrunken sections after reaction. (e) Inorganic and unreacted rubber constituents isolated by gravity filtration. (f) Product silyl-protected thiolated organic oils 8 in toluene (56% yield; note: the recovered oil may be a darker color, depending on starting material and the specific reaction, Fig. S7†). (g) Reductive silylation (a → d, e, f). (h) Cleavage of SiS bonds. (i) Oxidative coupling produces elastomers crosslinked by disulfides. (j) Radicals form elastomers from alkene-containing oils. Steps i and j can optionally use recovered inorganic constituents as reinforcing agents in the elastomers.

Oligosulfides were converted into silyl thiol ethers during reduction (Fig. 3g and Fig. S7†). Therefore, the residual solids and recovered non-volatile liquids often exhibited a weight gain when compared to the starting rubber mass (Table S4†). The product oils 8 (Fig. 3, for <sup>1</sup>H NMR data, see Fig. S15†) typically exhibited a bimodal distribution of molecular weight, with a low fraction centered near 10 000 g mol<sup>-1</sup> and a broad peak centered near 1 million g mol<sup>-1</sup> (Table S5, Fig. S16†).

Several factors were manipulated to improve the efficiency of the reduction process. A variety of hydrosilicones are commercially available that vary in the density of SiH groups. Model studies on the reduction of the organic sulfides or auto-



Table 2 Efficiency of reductive silylation of sulfur-crosslinked rubbers<sup>a</sup>

Rubber	Rubber constituents <sup>b</sup>	Starting components			Yield <sup>c</sup> (%)
		Organic (%)	Carbon black (%)	Other solids (%)	
Crumb-1	BR + IR/NR + EPDM	47.6	44.6	8.8	35.8
Crumb-2	IIR + BR	61.6	31.5	6.9	56.2
Repeat process with 1 <sup>st</sup> product					85.8
Repeat process with 2 <sup>nd</sup> product					88.3 <sup>d</sup>
EPDM	EPDM	55.1	26.4	18.5	60.4
Inner tube	IIR	61.1	33.0	5.9	92.9
	100 °C 30 min <sup>e</sup>				87.0
Truck tread <sup>f</sup>	IR/NR	65.0	23.0	12.0	89.8
Tread (snow tire) <sup>g</sup>	IR/NR + BR	63.0	22.9	14.1	51.8
Side wall (snow tire)	IIR + IR/NR + BR	59.4	22.2	18.4	53.8

<sup>a</sup> Experimental conditions: Rubber (300 mg); B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (30 mg, 10 wt%), 12 mL toluene 7 (1.5 mL) at 60 °C for 48 h. <sup>b</sup> Constituents were determined by a combination of TGA, which showed separate decomposition temperatures for IIR and IR/NR, and <sup>1</sup>H NMR. EPDM = terpolymer of ethylene, propylene and diene, IR/NR isoprene rubber or natural rubber, IIR isobutene isoprene rubber, BR butadiene rubber. <sup>c</sup> Organic yield = (total organic-recovered organic)/total organic × 100. Organic composition established using TGA (Fig. S6, S9, S11, Table S3,† and Table 1). <sup>d</sup> Cumulative yield for 3 process steps. <sup>e</sup> Process utilized hydrosilicone 10 (1.5 mL) at 100 °C for 30 min. <sup>f</sup> External road contacting component only. <sup>g</sup> Cross-section of entire tread from core to external surface.

Table 3 Depolymerization efficiency of organic elastomers by hydrosilanes<sup>a</sup>

Starting rubber components <sup>b</sup>		Parameters				Results	
Sample (mg)	Form	Organic (mg)	Inorganic <sup>c</sup> (mg)	Hydrosilanes (mL)	Temperature (°C) & Time (h)	Organic yield <sup>d</sup> (%)	Residual solid <sup>e</sup> (mg)
Crumb 1 (300)	Powder	143	157	7 (1.5)	60/48	35.8	206.7
Crumb 2	First <sup>g</sup>	185	115	7 (1.5)	60/48	56.2	182.9
	Second <sup>g</sup>	80.9	102	7 (1.5)	60/48	85.8	74.0
	Third <sup>g</sup>	26.3	47.7	7 (1.5)	60/48	88.3	64.0
EPDM (300)	Powder	165	135	7 (1.5)	60/48	60.4	162.0
Inner Tube (300)	Coupon	183	117	7 (1.5)	60/48	62.4	49.0 + 118.0 <sup>f</sup>
Inner Tube (300)	Powder	183	117	7 (1.5)	60/48	92.9	112.7
Inner Tube (2000)	Powder	1222	778	7 (10.0)	60/48	89.1	821.0
Inner tube (300)	Powder <sup>h</sup>	183	117	7 (1.5)	100/0.5	79.0	150.0
Inner tube (300)	Powder <sup>h</sup>	183	117	7 (1.5)	100/2	80.3	143.4
Inner tube (300)	Powder <sup>h</sup>	183	117	7 (1.5)	100/4	81.5	142.3
Inner tube (300)	Powder <sup>h</sup>	183	117	7 (1.5)	100/10	85.0	122.0
Inner tube (300)	Powder <sup>h</sup>	183	117	M <sup>H</sup> M <sup>H</sup> (1.5)	100/0.5	87.0	151.0
Inner tube (300)	Powder <sup>i</sup>	183	117	M <sup>H</sup> M <sup>H</sup> (1.5)	100/0.5	85.0	151.0
Truck Tread 1 (300)	Powder	187	113	MM <sup>H</sup> (1.5)	60/48	88.3	109.5
Truck Tread 1 (300)	Powder (Soxhlet)	175	125	MM <sup>H</sup> (1.5)	60/48	87.6	115.1
Truck Tread 1(2000)	Powder	1244	756	MM <sup>H</sup> (10.0)	60/48	84.6	861.0
Truck Tread 2 (300)	Powder	195	105	7 (1.5)	60/48	89.8	109.0
Tread (snow tire) (300)	Powder	189	111	7 (1.5)	60/48	51.8	180.0
Side wall (snow tire) (300)	Powder	178	122	7 (1.5)	60/48	53.8	183.0

<sup>a</sup> Experimental conditions: B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/rubber = 10 wt%, 12 mL toluene. <sup>b</sup> Based on TGA. <sup>c</sup> Includes carbon black and thermally stable inorganic moieties. <sup>d</sup> Fraction of available elastomer converted into organic soluble oils. <sup>e</sup> Residual solid contains carbon black, inorganics and residual polymeric rubber. <sup>f</sup> 49.0 mg of residual powder and 188 mg of residual coupon still containing elastomer (Fig. S10†). <sup>g</sup> Process for degradation of Crumb-2 using multiple reduction cycles; 169.0 mg of starting material were used in the 2<sup>nd</sup> reduction and 65.0 mg in the 3<sup>rd</sup> (Fig. S14b†). <sup>h</sup> The rubber powder was allowed to swell in reaction mixture for 3 h before adding B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst. <sup>i</sup> Catalyst solution was added immediately after addition of hydrosilane.

motive rubbers were undertaken with 2 or 7, respectively, because the use of small molecules facilitated characterization of the reaction products. Either compound is too expensive for practical use. Attempts to facilitate reduction of rubbers with the inexpensive, high SiH density polymer Me<sub>3</sub>Si(OSiMe<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub> 9 were unsuccessful (Fig. S17†) because the

silicone product of the reduction is a network polymer, which led to the formation of intractable tars. By contrast, the use of inexpensive, high SiH density HMe<sub>2</sub>SiOSiMe<sub>2</sub>H 10 led to efficacious, rapid reduction of rubbers (Tables 2 and 3, Fig. S17†).

Unlike the model compounds above, relatively large quantities of the BCF catalyst, 10 wt% against the rubber, were



required for the reduction of rubbers to occur efficiently. Pre-swelling the rubber in commonly used organic solvents like acetone,<sup>25</sup> or an initial Soxhlet extraction using acetone to remove potential catalyst inhibitors, *e.g.*, amines, free sulfur, acetone soluble colorants, antioxidants, processing rubber additives, *etc.*, did not appreciably increase either the rate or yield of the reduction (Table 3, Fig. S14†). We continue to work on process optimization to reduce the quantities of catalyst required.

Several other factors were found to affect the efficiency of the reduction of rubbers, including surface area, process temperature and reducing agent. Unsurprisingly, the reduction of bulk elastomers, including cylindrical sections of bicycle inner tube (diameter ~16.9 mm, thickness ~0.82 mm, IIR, Fig. S7†), and a cross-section of an automobile snow tire (IR/NR + BR, Fig. 3), were slow to occur and low yielding at 60 °C using 7 (Fig. S6†). In both cases, the objects underwent significant shrinkage (Fig. S19†), and increased crosslink density as shown by an increase in Young's modulus (Table S4†), but maintained their shape. Cryogenic grinding of the starting rubbers to increase rubber surface area (to particle size ~330 µm, Fig. 4) led to significant enhancements in yield;

an increase from 52 to 93% was observed in the case of the inner tube (IIR, Table 3).

The tire reductive silylation studies were initially undertaken using relatively mild temperatures because literature suggests that the  $B(C_6F_5)_3$  catalyst undergoes degradation at temperatures above 80 °C in the presence of moisture.<sup>26</sup> Current studies with rubber reduction, however, showed this not to be problematic. A 93% yield of recovered organic polymer (IIR from inner tube) was achieved at 100 °C after 18 hours using 10, but an 87% yield had already been achieved in the first 30 minutes (Table 3). This result suggests that reduction processes at 100 °C or higher could be adapted to a continuous process.

Initial studies for reusing/re-crosslinking the recovered oil focused initially on the regeneration of thiols from silyl thio ethers. There are few reports of the reactivity of Si-S compounds.  $Me_3Si-SiMe_3$  is very labile, undergoing rapid degradation simply in the presence of water (vapor) to form  $H_2S$  and  $Me_3SiOH$ .<sup>27</sup> By contrast, the hydrolysis of silicone-based thio ethers was much less facile. Alcoholysis of 3 (Fig. 1g) yielded 12% product only once acetic acid was added to isopropanol solutions (the less sterically hindered thio ether  $PhCH_2SSiMe_2OSiMe_3$  underwent rapid, quantitative cleavage under the same conditions). The silylated polymeric oils derived from elastomers 8 were yet less reactive. It was necessary to use more aggressive nucleophiles for silicon, such as  $Bu_4NF$ <sup>28</sup> to regenerate the silyl free thiols 11 (Fig. 3h and Fig. S20†).

Once cleaved, the freed thiols on the organic polymers could be crosslinked into a new elastomer 12 by oxidative coupling using iodine in isopropyl alcohol<sup>29</sup> (Fig. 3i and Fig. S21†). However, it was also discovered that, if silylated polymers 8 were derived from IR/NR or BR and possessed residual alkenes, re-crosslinking did not require removal of the silyl groups; simply adding a radical initiator such as benzoyl peroxide (BPO) and heating led to new elastomers 13 (Fig. 3j).

The ability to create new elastomers from the recovered polymeric oils was demonstrated by creating a new automotive tire (for a child's toy) using 8. A mold of the tire was made in silicone rubber (Fig. 4a and b). Silylated oil 8 derived from IR/NR (tire tread) was placed in the mold in the presence of BPO and heated to give a new, soft elastomer (Fig. 4b + c → e,f durometer Shore OO 68, Table S6†). Adding to 8 the inorganic excipients (recovered from the production of 8, Fig. 4h), and then curing oxidatively, led to harder, more brittle elastomers (Shore A 91; original rubber Shore A 60).

Reductive silylation processes have shown synthetic merit in many arenas. The relatively weak SiH bond,<sup>30</sup> particularly in the presence of  $B(C_6F_5)_3$  and related Lewis acids, readily reduces a variety of bonds<sup>15</sup> driven, in large part, by the thermodynamic benefit of forming Si-heteroatom bonds (heteroatom=O, N, S, *etc.*).<sup>31</sup> We have demonstrated that this type of process works effectively with S-S bonds to form thio silyl ethers. The key finding of this work is that, in addition to clean model compounds, the process works with complex and dirty samples – used automotive tires – to convert sulfur-cured



**Fig. 4** (a) The right front tire was removed from a toy car. (b) A silicone mold of the tire. (c) Organic oil 8 was prepared by reduction of truck tire tread (Sailun, IR/NR) with hydrosilane 7. (d) Silicone mold filled with 0.707 g 8 + 1 wt% BPO + 0.3010 g residual solid. (e) New tire after curing. (f) Tire replacement. (g) The residual solid during the preparation of 8 could be included in the pre-elastomer formulation. (h) Close up showing: (i) the original tire, (ii) tire made without additional inorganic excipients 13, and (iii) tire including inorganic excipients.



elastomers into polymeric oils, in up to ~90% yield. The process can be rendered practicable at temperatures as low as 100 °C and the product oils can find new utility in elastomeric objects using at least two different cure modes. We are currently establishing the quality of elastomers that can be produced from different used tire feedstocks. The recovered inorganic mass can also be repurposed as a filler in those new elastomers. Thus, reductive silylation provides a new opportunity to find commercial value in materials that are environmentally problematic. It is not possible to effectively 'reuse' automotive rubber, but reductive silylation is worthy of consideration as a strategy for recycling and reuse.

## Experimental

### Materials

Pentamethyldisiloxane **7**, bis(trimethylsiloxy)methylsilane **2**, ( $\text{HMe}_2\text{SiOSiMe}_2\text{H}$ ,  $\text{MD}^{\text{H}}\text{M}$ ) **10**, ( $\text{Me}_3\text{Si}(\text{OSiMeH})_n\text{OSiMe}_3$ ,  $\text{MD}^{\text{H}}_n\text{M}$ ) **9**, were purchased from Gelest and used after drying over molecular sieves overnight. Dibenzyl disulfide, benzyl bromide, tetrabutylammonium fluoride trihydrate (TBAF), and iodine ( $\text{I}_2$ ) were obtained from Sigma Aldrich and used as received. Benzoyl peroxide (BPO) was purchased from BDH. Sodium tetrasulfide was purchased from Dojindo.  $\text{B}(\text{C}_6\text{F}_5)_3$  (BCF) was prepared by Grignard reaction following a literature procedure;<sup>32</sup> we acknowledge with gratitude Prof. David Emslie, McMaster University, for providing this sample. Rubber samples: bicycle inner tube (Chaoyang 700 × 38/45C bicycle inner tube, China), EPDM (pond liner, purchased at a local garden centre, producer unknown), Crumb-1 (Als-RC, Amazon, Canada), Crumb-2 (Canadian Eco Rubber Ltd, Emterra, Canada), were used as received. Truck tread 1: a piece of truck tread, not part of a complete tire, was found at a local garbage dump (origin unknown). Truck tread 2: (Sailun 225/70R19.5). In both cases, samples were cut only from the external, road contacting tread part (Fig. S3†); both rubbers were based on polyisoprene. The tread and side wall samples – cross-sections – were cut from different parts of a used car tire (snow tire, Cooper 185/65R4, Fig. 5). Naphthalene (internal standard) was purchased from Fisher. Toluene (solvent) received from Caledon (HPLC grade) was dried over activated alumina before use. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories. Glass apparatus were dried overnight at 120 °C and cooled under a dry nitrogen atmosphere for 30 min prior to use.

### Methods

**NMR.**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using deuterated solvents chloroform-*d* and acetone-*d*<sub>6</sub>. For  $^{29}\text{Si}$  NMR, chromium(III) acetylacetone was used as paramagnetic relaxation agent.

**GC-MS.** Analyses were performed using an Agilent 6890N gas chromatograph (Santa Clara, CA, USA), equipped with a DB-17ht column (30 m × 0.25 mm i.d. × 0.15 µm film, J&W



Fig. 5 (a–c) A commercial snow tire was cut into (d) sidewall and tread sections using a reciprocating saw with blade designed for cutting metal. (e) Tread 1.200 × 1.519 × 1.125 cm. (f) Sidewall cut into 1.595 × 1.427 × 0.6096 cm. These samples were subjected to 'bulk reduction' of their as-cut shape. (g) For other reductions, the rubbers were chopped into fine pieces after cooling with liquid nitrogen and ground to powder using coffee grinder (KitchenAid). (h) sidewall. (i) Tread.

Scientific) and a retention gap (deactivated fused silica, 5 m × 0.53 mm i.d.), and coupled to an Agilent 5973 MSD single quadrupole mass spectrometer. One microliter of sample was injected using an Agilent 7683 autosampler in splitless mode. The injector temperature was 250 °C and carrier gas (helium) flow was 1.1 mL min<sup>-1</sup>. The transfer line was 280 °C and the MS source temperature was 230 °C. The column temperature started at 50 °C and was increased to 300 °C at 8 °C min<sup>-1</sup>, then held at 300 °C for 15 min to give a total run time of 46.25 min. Full scan mass spectra between *m/z* 50 and 800 mass units were acquired after a solvent delay of 8 min.

**LC-MS.** Analyses were undertaken using an Agilent Technologies 1200 LC coupled to an Agilent 6550 QTOF mass spectrometer. An injection volume of 2 µL was separated on a Phenomenex Luna C18(2) (150 mm × 2.0 mm, 3 µm) column with 100 Å pore size (Phenomenex, CA, USA). The mobile phases were LC-MS-grade 45/55 water/methanol with 0.5% acetic acid (A) and methanol with 0.5% acetic acid (B) at a flow rate of 300 µL min<sup>-1</sup>. The column temperature was maintained at 40 °C, and the autosampler storage tray was set at 10 °C. The mobile phase gradient eluted isocratically with 10% B for 1.0 min followed by a gradient to 100% B over 17 min. The gradient was maintained at 100% B for 2 min and decreased to 10% B over 0.1 min. The gradient was then followed by a 5 min re-equilibration prior to the next injection. The total time for an HPLC run was 25 min.



The MS parameters (for LC-MS) chosen were as follows: ESI, gas temperature at 225 °C, drying gas at 13 L min<sup>-1</sup>, nebulizer pressure at 20 psi, sheath gas temperature at 400 °C, sheath gas flow at 12 L min<sup>-1</sup>, VCap at 3500 V, nozzle voltage at 1000 V, fragmentor at 375 V, and Oct 1 RF Vpp at 750 V. The data were acquired in electrospray positive mode from *m/z* 50 to 1000 at a scan rate of 1.5 Hz. The mass was auto recalibrated using reference lock mass from Agilent ESI-T Tuning Mix (for Ion Trap).

**GPC.** Molecular weight of recovered organic oil and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup>.

The polymer constituents of rubber samples were estimated from carbon high-resolution magic angle spinning (<sup>13</sup>C HR-MAS) NMR spectroscopy (Fig. S5†). **TGA:** Thermogravimetric analysis (TGA) according to ASTM D 6370-99 (American Society for Testing and Materials) was used to measure the organic carbon (polymer), carbon black content and inorganic residue of the component.<sup>24</sup> A small amount of test sample (2 to 5 mg) was placed into the alumina pan of the calibrated Thermogravimetric Analyzer (Mettler Toledo TGA/DSC 3+). A 100 cm<sup>3</sup> min<sup>-1</sup> argon purge was applied and the furnace was heated from 50 °C to 560 °C at 10 °C min<sup>-1</sup>. Then, the furnace was cooled to 300 °C and the purge gas was changed to air at 100 cm<sup>3</sup> min<sup>-1</sup>. The temperature was allowed to equilibrate for 2 min before the furnace was heated to 800 °C at 10 °C min<sup>-1</sup>.

The constituents of sulfur-cured rubbers have well-defined thermal decomposition profiles (Table S3†). Within the thermal decomposition range of the organic polymers, there are further distinctions. TGA and DTA data (Fig. S6†) show the constituents of the rubber samples tested (Table 1).

**Young's modulus.** The Young's moduli of rubber samples were determined using a MACH-1 micromechanical system (Biomomentum Instruments) with a 0.500 mm hemispherical indenter radius, and Poisson ratio of 0.3. All measurements were conducted at 22 °C and in triplicate, with error bars representing the standard deviation of the replicate measurements.

**Preparation of powdered rubber.** Raw rubber samples of different shapes and sizes were obtained. The rubber crumb samples were of broad dispersity, with average particles sizes of 1.30 ± 0.09 mm for Crumb-1 and 2.14 ± 0.06 mm for Crumb-2. As noted above, more efficient reduction occurred with higher surface area samples. A cryogenic grinding progress was used to obtain rubber powder samples with homogeneous particle sizes for comparable experiments. Liquid nitrogen was employed to cool the rubber samples below their glass transition temperature before they were pulverized with a coffee grinder (KitchenAid) to give powders with an average particle size of ~330 nm (Fig. 5g, i and Fig. S4†).

## Preparation of dibenzyl tetrasulfide

To a pre-dried 200 mL round-bottomed flask purged with dry N<sub>2</sub> were added sodium tetrasulfide (0.098 g, 0.562 mmol), benzyl bromide (0.209 g, 1.22 mmol) and dry THF (50 mL, 44.45 g, 0.616 mol) as solvent. The mixture was stirred for 23 d and collected by vacuum filtration. The mixture was purified using column chromatography; the low polarity impurity (S<sub>8</sub>) was removed using hexanes, after which the elution solvent was switched to dichloromethane, to give a yield of 77% (137 mg, based on the different sulfides found in the product. Note: it was not possible to detect tetrasulfide or higher polysulfide linkages in the GC-MS, which may be due to thermal degradation of polysulfide bond (when *n* > 3).<sup>33,34</sup>

<sup>1</sup>H NMR (600 MHz, acetone-*d*<sub>6</sub>):  $\delta$  3.72 (s, 0.11H), 4.11 (s, 2.02H), 4.24 (s, 1.20H), 4.30 (s, 0.67H), 7.28–7.40 (m, 9.21H) ppm. <sup>13</sup>C NMR (600 MHz, acetone-*d*<sub>6</sub>):  $\delta$  29.85, 43.55, 43.99, 44.54, 128.36, 129.42, 130.33, 137.54, 137.80 ppm. GC-MS C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>, MW: 246: [M<sup>+</sup> – 1] = 65.2 (18), 77.2 (8), 91.1 (90), 121.1 (5), 181.2 (18), 246.1 (20); S<sub>8</sub>, MW: 256: [M<sup>+</sup> – 1] = 64.1 (100), 77.1 (7), 91.1 (66), 127.9 (60), 160.0 (66), 191.9 (53), 207.1 (5), 223.9 (7), 255.8 (98), 315.1 (5). C<sub>14</sub>H<sub>14</sub>S<sub>3</sub>, MW: 278: [M<sup>+</sup> – 1] = 65.2 (13), 77.1 (3), 91.2 (100), 123.1 (3), 181.2 (2), 213.1 (56), 278.1 (13).

## Dibenzyl disulfide reduction using bis(trimethylsiloxy)methylsilane ([SiH]/[SS] = 2 : 1, molar ratio between hydrosilane and disulfide)

To a pre-dried 200 mL round-bottomed flask purged with dry N<sub>2</sub> gas, was added dibenzyl disulfide (0.50 g, 2.04 mmol) and bis(trimethylsiloxy)methylsilane (0.91 g, 4.09 mmol) together with dry DCM (3.81 g, 44.86 mmol) as solvent. Freshly prepared B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> stock solution was added (0.167 mL, 0.0326 mmol) after 5 min stirring. The total reaction time was 3 h, then the reaction was quenched by adding neutral alumina. Each datapoint in Fig. 2 was obtained using the identical reaction protocol, only changing the ratio of hydrosilane to disulfide [SiH]/[SS] (Table S1†).

## Titration of disulfides to establish relative reactivity of functional groups

Conversion in the reaction was shown by peak area of the hydrogens on the carbon adjacent to the disulfide bond ( $-\text{CH}_2\text{SS}$ ) in <sup>1</sup>H NMR, which was plotted against different ratios of hydrosilane (SiH) to disulphide. Analogous techniques were used to follow the reduction of the tetrasulfide (Fig. 2).

## Reduction of rubbers: general procedure

The reaction conditions for the reduction of rubber powder are given in Tables 2 and 3. The general experimental procedure is as follows. The cryogenically ground rubber powder was allowed to swell in dry toluene (12 mL) for 30 min.

Pentamethyldisiloxane 7 was added to the reaction mixture. The stock catalyst solution was added to initiate the reaction. The suspension was heated in a 60 °C oil bath for 48 h. The residual undissolved rubber powder was washed with toluene



and separated by centrifugation (Eppendorf, Centrifuge 5424, at 12 000 rpm for 20 min). The extraction process was repeated twice to completely remove soluble compounds. The supernatants were mixed, and the solvents were removed by rotary evaporation. Any residual (organic) volatiles were removed under a stream of  $N_2$  over 24 h. The recovered organic liquid was characterized by NMR. The recovered rubber powders were dried at 100 °C overnight and then examined by TGA. The bulk sample were reduced by the similar protocol and more details were provided in ESI.†

### Reduction with inexpensive tetramethyldisiloxane $M^H M^H$

Cryogenically ground inner tube powder (300 mg) was placed in dry toluene (12 mL), followed by tetramethyldisiloxane  $M^H M^H$  (1.5 mL, 8.5 mmol). The stock catalyst solution (600  $\mu$ L, stock catalyst concentration: 50 mg  $mL^{-1}$  in toluene, catalyst concentration in reaction: 10 wt%/inner tube) was added immediately afterwards to initiate the reaction. The suspension was heated in a preheated 100 °C oil bath for 30 min. The reaction flask was put into a room temperature water bath to quench the reaction and followed by a separation process using the same protocol stated in the former paragraph. The organic yield was 87%.

### Desilylation of product polymeric oils to give 11

The silylated organic oil 8 (based tire tread, derived from IR/NR, 0.50 g) was desilylated by treatment with TBAF solution (0.5 g TBAF, 1.92 mmol TBAF, dissolved in 10 mL THF containing 0.1 mL methanol) for 24 h at 80 °C. The solvent and siloxane fragments were removed by using a rotary evaporator, followed by kugelrohr distillation; loss of silicone was clearly seen in the  $^1H$  NMR (200 °C, 3 h, Fig. S20†).

### Crosslinking of recovered oils

**Oxidative coupling of thiols using iodine.** The desilylated organic oil 11 (derived from truck tread IR/NR, 0.2 g) was allowed to react with an iodine solution (50 mM dissolved in 1/1 v/v toluene/isopropanol) for 12 h at room temperature. Solvents associated with the resulting elastomer 12 were removed under a stream of  $N_2$  over 12 h (Fig. S21a†). Crosslinking was confirmed using a swelling test. Compound 12 (0.1 g) was swelled in 10 mL of hexane; the degree of swelling was 209 wt%. The precursor oil 8 dissolved readily in hexane easily while 12 remained an elastomeric solid even after 1 h sonication (Fig. S21b†).

### Preparation of toy tire using a peroxide initiator (Fig. 4)

A silicone mold was prepared with a two-part liquid component kit (Sylgard 184). Two components were mixed at the recommended ratio of 10 parts (10.0 g) base to 1 part curing agent (1.0 g). The mixing process was performed using a planetary centrifugal mixer (FlackTek Inc.) with a duration of 5 min at a speed of 3000 rpm. In order to fabricate bubble free elastomer, the mixed uncured PDMS was thoroughly degassed in a vacuum desiccator at low pressure for 30 min.

The right front tire of a toy car was removed from the toy and placed in the degassed, uncured mixture. The mixture was cured in an 80 °C oven overnight. The tire was removed from the cured mold.

Used rubber powder from the truck tread (Sailun) (2.0 g) was reduced by pentamethyldisiloxane 7 in a 100 °C oil bath for 18 h to give a polymeric oil 8 (81.5% yield). Solvents in the supernatants, after centrifugation, were removed by rotary evaporation; any residual volatiles and silicone by-products were removed using a stream of  $N_2$  over 24 h. The oil was accompanied by residual undissolved rubber powder that was washed with toluene and separated by centrifugation (Eppendorf, Centrifuge 5424, at 12 000 rpm for 20 min), dried an 80 °C oven for 18 h, and ground into powder using a mortar and pestle (Fig. 4d).

The silylated organic oil 8 from the former step (comprised of IR/NR derivatives, 0.707 g) was dissolved in hexanes (10 mL), benzoyl peroxide (BPO, 0.01 g, 1 wt%, 0.0413 mmol) and, optionally, ground residual inorganic solids (from the preparation of 8, 0.3010 g), were added sequentially and mixed to give a homogeneous dispersion. After the solvent was removed by rotary evaporation, the mixture was placed in the silicone mold and degassed under vacuum in a desiccator for 30 min. The curing process was performed at 100 °C for 18 h. The formulations for rubber with different residual solid are listed in Table S6.†

## Conclusions

Utilization of the reactions described here to create polymeric oils by the reductive silylation of used automotive rubbers, and subsequent oxidation to new elastomers, permits the completion of a full cycle of use for these organic materials. Mild, efficient reduction of S-S bonds of organic disulfides, including those found in used, sulfur-cured rubbers permits the formation of silylated polymers 8 – already in 87% yield at 100 °C within 30 minutes – that can be separated from the inorganic constituents. Radical cure of the oils if alkenes are present, or following desilylation, oxidative cure of thiolated polymers leads to new elastomers 12, 13 that, optionally, can be reinforced by the inorganic constituents recovered during the reduction process. The practice of this recycling process has the potential to reduce the environmental impact of used, sulfur-crosslinked elastomers.

## Conflicts of interest

There are no conflicts to declare.

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