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# Porous inverse vulcanised polymers for mercury capture†

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Supercritical carbon dioxide is used to generate macroporosity in an inverse vulcanised polymer, which shows excellent promise for enhanced mercury capture and filtration from water.

Heavy metal contamination exists in the waste streams of many industries, such as chemical manufacturing, mining operations, waste incineration, and fossil fuel fired power stations. The emitted heavy metals are extremely harmful environmental pollutants as they are widely distributed in the air, water and soil. Mercury is of particular concern for human health because of its relative solubility in water and tendency to bioaccumulate and cause severe toxic effects.<sup>1</sup> Sulfur is known as one of the most active sites for Hg adsorption.<sup>2</sup> Sulfur is an industrial by-product, removed as an impurity in oil-refining. This has led to vast unwanted stockpiles of sulfur, as supply greatly outweighs demand, and resulted in low bulk prices. Sulfur is therefore a promising alternative feedstock to carbon for polymeric materials.<sup>3</sup> However, elemental sulfur itself has poor physical properties for forming functional filters, and would be gradually removed in water streams, forming harmful sulfides and impurities in the water. Inverse vulcanisation,<sup>4</sup> first reported by Pyun *et al.* in 2013,<sup>5</sup> has made possible the production of high-sulfur polymers, stabilised against depolymerisation by crosslinking with small molecule dienes, such as 1,3-diisopropenyl benzene (DIB) (Fig. 1a). More recently, Chalker *et al.* were able to demonstrate a limonene based inverse vulcanised polymer for potential applications in mercury remediation.<sup>6</sup> While their results were promising, and show excellent potential for some applications, the sulfur-limonene forms a lower molecular weight polysulfide, rather than crosslinked polymer, resulting

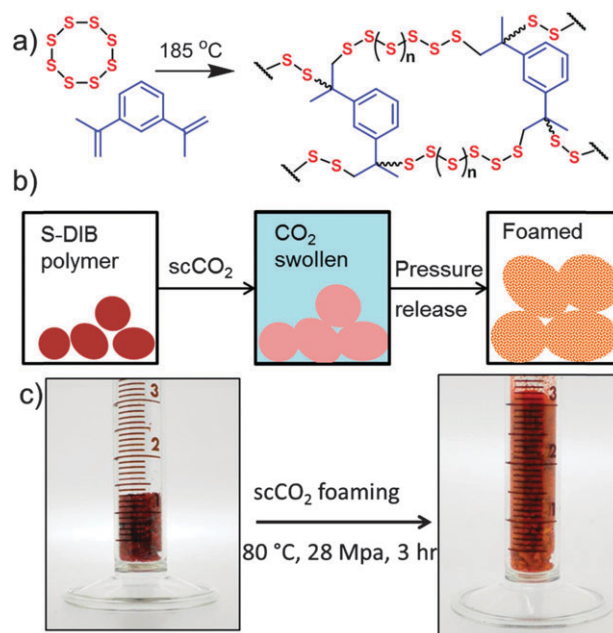


Fig. 1 (a) Reaction of elemental sulfur and 1,3-diisopropenyl benzene (DIB) produces a stable high sulfur polymer (b)  $\text{scCO}_2$  processing method to foam the polymer, (c) photographs of S-DIB (50% DIB) polymer powder (1 g) before and after  $\text{scCO}_2$  foaming.

in a waxy substance that is not shape persistent (Fig. S1, ESI†), and could be challenging to form into a functional filter.

By foaming sulfur-diisopropenyl benzene (S-DIB) polymers, to increase the available surface area, we show they gain superior performance in mercury capture compared to sulfur-limonene polysulfide. This is achieved quickly and efficiently by processing the polymer with supercritical carbon dioxide ( $\text{scCO}_2$ ), an environmentally friendly foaming agent.<sup>7</sup> Above its critical points of 31.06 °C and 7.38 MPa,  $\text{scCO}_2$  has zero surface tension, tuneable density, and high diffusivity.<sup>8</sup>  $\text{CO}_2$  is non-combustible and non-toxic as well as being relatively environmentally benign,<sup>9</sup> and as it is a gas at ambient temperatures and pressures it can be easily removed after reaction,

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1 leaving no solvent residues in the processed material.<sup>7</sup> Super-  
critical CO<sub>2</sub> is typically a poor solvent for high molecular weight  
polymers, but conversely, the solubility of scCO<sub>2</sub> in polymers is  
usually substantial.<sup>10</sup> The permeation of scCO<sub>2</sub> into a polymer  
5 causes it to plasticise and swell in volume.<sup>11</sup> On release of  
pressure the dissolved CO<sub>2</sub> expands rapidly, foaming the poly-  
mer and creating pores.<sup>12</sup>

10 Exposure to trace mercury is a very real current health  
concern, and effective and inexpensive technologies are needed  
to remove it from waste streams and the environment.<sup>6,13</sup>  
Materials made from sulfur have the potential to be made in  
bulk, with low enough cost to make them viable for large scale  
use in Hg capture.

15 Inverse vulcanised S-DIB co-polymers were synthesised as  
previously described, and at a ratio of either 70 wt% sulfur to 30  
wt% DIB, or 50 wt% sulfur to 50 wt% DIB (see ESI†).<sup>5</sup> Briefly,  
sulfur powder was heated in a stirred glass vial, at 185 °C until  
the sulfur melted to become an orange/yellow liquid. DIB was  
20 added directly to the molten sulfur and heating continued for  
another 8–10 minutes, until the products vitrified as a ruby red  
solid. The process used to foam the co-polymers consists of two  
steps: soaking and expansion (Fig. 1b, and ESI† for details).  
During soaking, polymer granules were placed in a stainless  
steel autoclave which was then filled with 5.5 MPa of CO<sub>2</sub>. The  
25 autoclave was then heated to the desired temperature (usually  
80 °C) and topped up to 28 MPa. The scCO<sub>2</sub> was maintained  
under these conditions (normally 3 hours) in order to allow the  
scCO<sub>2</sub> to infuse fully into the polymer. In the expansion step,  
the scCO<sub>2</sub> was then vented rapidly in less than one minute. The  
30 heating was then stopped, and the autoclave opened to remove  
the foamed sample. The sulfur polymer itself is a ruby-red,  
transparent, glassy material but after foaming becomes  
expanded, orange, opaque, and of notably lower density (pow-  
der density drops from 0.8 g cm<sup>-3</sup> to 0.3 g cm<sup>-3</sup>, Fig. 1c and Fig.  
35 S2, S3, ESI†).

Processing temperatures of 40, 60, and 80 °C were investi-  
gated. Pressures of 10, 20, and 28 MPa were investigated.  
Higher pressure equates to a higher concentration of CO<sub>2</sub> in  
the sample, which should lead to increased foaming. For a  
40 given pressure, lower temperature should give a higher density  
of CO<sub>2</sub> – and hence potentially higher foaming. *E.g.* at 40 °C,  
and 28 MPa, the CO<sub>2</sub> density is 0.90 g cm<sup>-3</sup>, whereas by 80 °C,  
at the same pressure, the density drops to 0.72 g cm<sup>-3</sup>.  
However, at lower pressures the rate of infusion of CO<sub>2</sub> into  
45 the polymer was limited, < 1 mm per hour (as demonstrated by  
zones of foamed material around a solid core, see image S4,  
ESI†). At 80 °C the rate of infusion was ~4 mm per hour, a  
result of higher rate of diffusion at increased temperature. We  
therefore chose 80 °C as the soak temperature, and 3 hours as  
50 sufficiently excess time to allow complete infusion into a  
coarsely ground sample.

Scanning electron microscopy (SEM) of the resulting powder  
reveals successful generation of macropores in the foamed  
samples (Fig. 2). For a 50 wt% sulfur sample, the pores are  
predominantly in the ~10–20 μm range (Fig. 2) but vary  
55 between 5 and 100 μm in some areas (Fig. S5, ESI†). Presumably

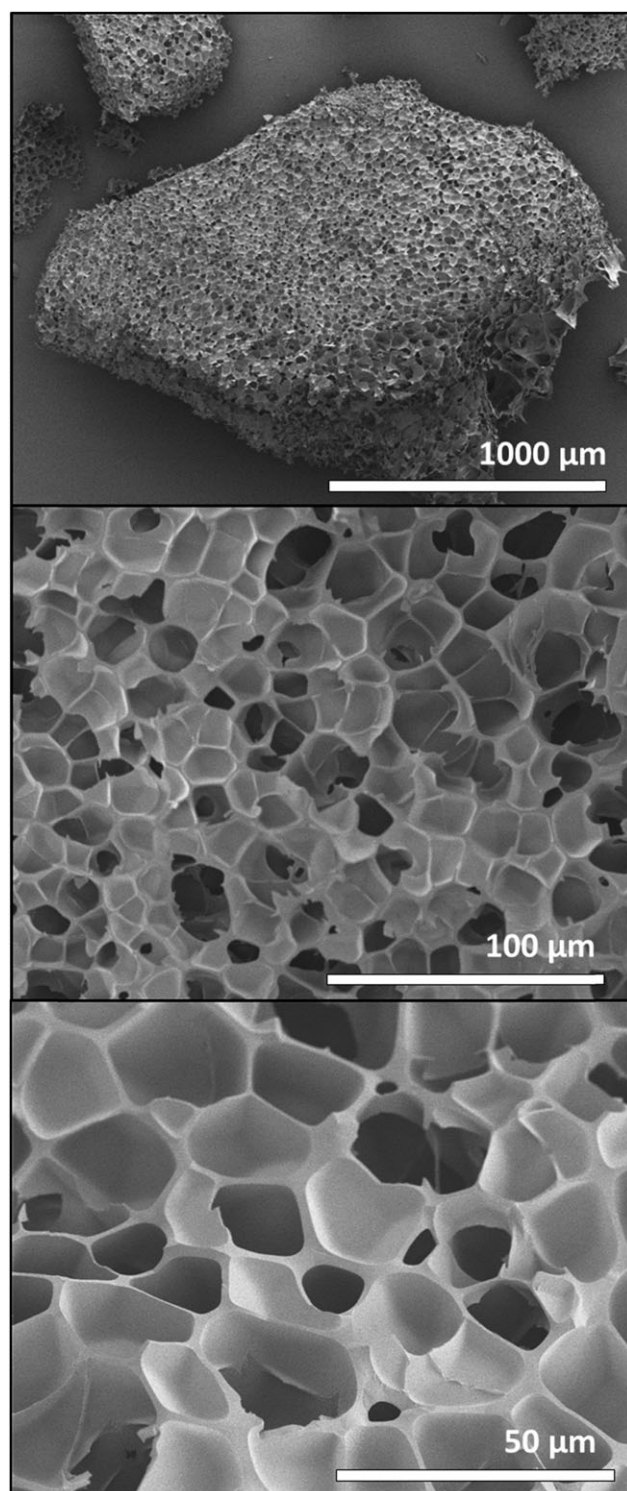


Fig. 2 SEM imaging of scCO<sub>2</sub> foamed sulfur-DIB crosslinked polymer (50 wt% sulfur). The sample was exposed to CO<sub>2</sub> at 28 MPa and 80 °C for 3 hours. The sample shows both closed cell and connected macropores. Scale bars indicate 1000, 100, and 50 μm from top to bottom.

this is a result of inhomogeneous conditions during venting at  
different depths within the sample. If the sulfur content is  
increased to 70 wt%, the samples still foam, but to a slightly  
55 reduced degree (Fig. S6, ESI†), resulting in smaller pores (5–10 μm)



with an increased wall thickness. It seems counterintuitive that the higher % DIB polymer should foam more extensively, as it should have a higher degree of crosslinking, and hence a higher glass transition temperature.<sup>5</sup> However, the increase in organic content is also likely to increase the solubility of CO<sub>2</sub> in the polymer, aiding partitioning of CO<sub>2</sub> into the polymer, and therefore enhanced foaming on release of pressure. Higher pressures were found to produce more, though smaller, voids, whereas lower pressure produced fewer, but larger voids (Fig. S7, ESI†). This effect is caused by increased homonucleation at higher pressures, as a result of the enhanced level of CO<sub>2</sub> dissolved in the swollen polymer.<sup>14</sup> This increase in void concentration, and reduction in volume, with pressure allows a degree of control over the structures produced.

Three additional samples were produced with industrially relevant additives: carbon black, fumed silica, and kaolin (Fig. S8, ESI†). Fillers such as these are often used to reduce material costs and improve the physical properties of industrial polymers. It was therefore desirable to determine if their presence in the co-polymer feedstock would affect the foaming process. No significant difference in foaming was observed in the presence of activated carbon or fumed silica, both of which are small and roughly spherical particles (Fig. S9 and S10, ESI†) at a loading of 5 wt%. However, the kaolin caused a reduction in foaming and pore size, likely as a result of the exfoliated platelet structure of the additive resisting bubble formation (Fig. S11 and S12, ESI†).

The glass transition temperature ( $T_g$ ) of S-DIB polymers is known to be close to room temperature, and increases as a function of the proportion of DIB.<sup>5</sup> Previously published results give values of 16.5 °C for 30 wt% DIB, and 28.4 °C for 50 wt% DIB.<sup>5</sup> Any reduction in the  $T_g$  of the polymers, as a result of the supercritical process, could adversely affect their function. We therefore analysed the  $T_g$  of each of our polymers, before and after treatment (Fig. 3a and Fig. S13, ESI†). Not only is there no adverse effect, but scCO<sub>2</sub> treatment appears to actually increase the  $T_g$  of each sample by a few degrees. We attribute this to the extraction of trace low molecular weight material, soluble in the scCO<sub>2</sub>, which would otherwise act to plasticise the polymer. The pores remain relatively stable over time at room temperature, with little change after 1 month. However, there are signs of a reduction in porosity if the temperature is raised significantly above the  $T_g$  (e.g. 50–100 °C) for extended periods, as would be expected (Fig. S14, ESI†).

Mercury capture tests were performed by soaking 100 mg of sample in 5 mL of aqueous HgCl<sub>2</sub> (2 ppm), for 3 hours, before analysing the remaining mercury content in the water (Fig. 3b, and see ESI† for details). These tests showed that the scCO<sub>2</sub> foamed samples performed an order of magnitude better than either un-foamed S-DIB, or sulfur-limonene polysulfide (Fig. 3b). Remarkably, the water treated with foamed S-DIB contained < 0.1 ppm Hg in all three repeats (78, 83, and 83 ppb detected). Although sulfur is an excellent active site for Hg<sup>2+</sup>, it is also necessary for the absorbent bring the Hg into the solid state from solution. As a small molecule, it is too easy for S<sub>8</sub> to instead be pulled into the aqueous phase by the Hg – hence

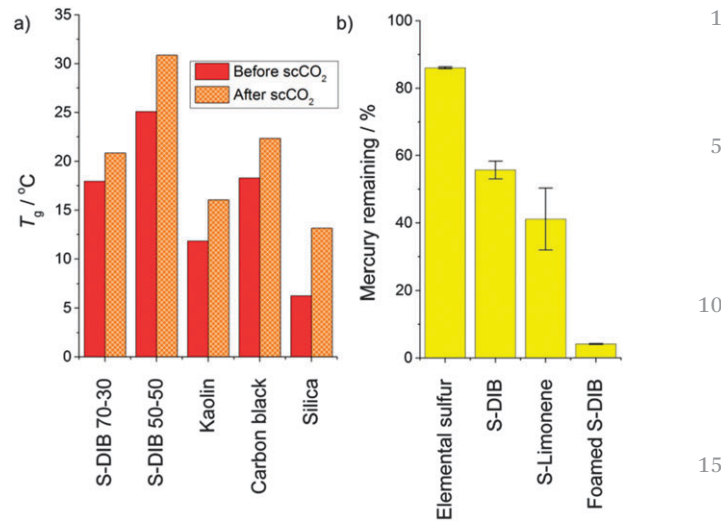


Fig. 3 (a) Glass transition temperatures ( $T_g$ ) determined by DSC for polymer samples before and after scCO<sub>2</sub> treatment. Kaolin, carbon black, and silica refer to S-DIB samples (30 wt% DIB) with those additives. (b) The percentage mercury remaining in solution after 3 hours exposure to each of the materials listed. Values are given as a mean of three repeats with standard deviation shown as error bars.

resulting in poor removal of Hg by elemental mercury (Fig. 3b). The polymeric samples are able to fair much better, as any bound Hg will be removed from solution. However, the effectiveness is therefore determined by the available surface area. This explains the dramatic increase in uptake for the foamed S-DIB over the bulk material (Fig. 3b). In the case of the S-limonene, we believe that the soft nature of the material causes some regeneration of the surface to occur by the action of stirring to expose fresh material – this gives it a slightly higher uptake than the un-foamed S-DIB under the same conditions. The effect of scCO<sub>2</sub> pressure, and resultant foaming, on Hg uptake was also investigated (Fig. S15, ESI†). The lower pressure samples retained effectiveness for Hg capture, but at a reduced efficiency. This indicates that the higher pressure, and resultant higher void concentration, is beneficial for Hg uptake by maximising the available surface adsorption sites. While these results are encouraging, it is also useful to test the effectiveness of the material in a flow situation, as would be more consistent to a filter application. 500 mg of foamed S-DIB powder was packed into a 1 cm diameter glass column (Fig. S16, ESI† for details), and 5 mL of aqueous HgCl<sub>2</sub> solution poured through. This resulted in a 41% reduction of the Hg concentration in the water.

In summary, scCO<sub>2</sub> processing of high sulfur “inverse vulcanised” polymers, and specifically S-DIB which is of high current interest, has been reported for the first time. This scCO<sub>2</sub> treatment itself is shown to raise the  $T_g$  of the materials, as well as allowing the production of the first highly macroporous inverse vulcanised sulfur-polymer foam. This foamed material has a significantly enhanced function for Hg capture in comparison to both non-foamed S-DIB, and sulfur-limonene polysulfide.

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## Notes and references

- 5 ‡ While the  $T_g$  of the as made pure S-DIB polymers is in close agreement with published values, the silica and kaolin enriched samples show a reduction in  $T_g$ . We attribute this to inferior mixing of reactants, caused by increased viscosity, leading to incomplete polymerisation.
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