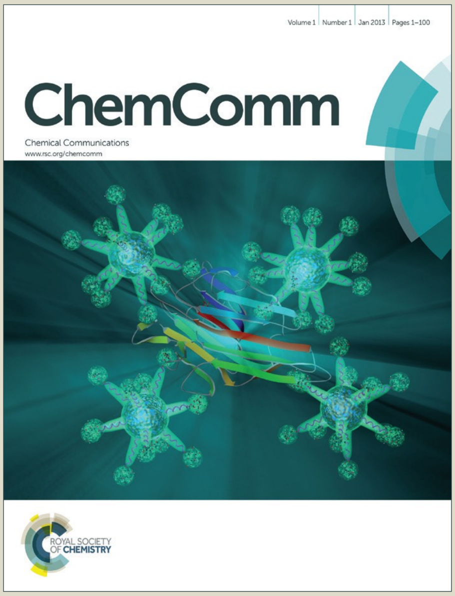
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Porous inverse vulcanised polymers for mercury capture

T. Hasell,*[a] D. J. Parker,[a] H. Jones,[a] T McAllister,[b] and S. M. Howdle[b]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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.[1] Sulfur is known as one of the most active sites for Hg adsorption.[2] 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.[3] 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,[4] first reported by Pyun *et al* in 2013,[5] 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.[6] 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 in a waxy substance that is not shape persistent (Fig. S1), 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 ($scCO_2$), an environmentally friendly foaming agent.[7] Above its critical points of 31.06 °C and 7.38 MPa, $scCO_2$ has zero surface tension, tuneable density, and high diffusivity.[8] CO_2 is non-combustible and non-toxic as well as being relatively environmentally benign,[9] and as it is a gas at ambient temperatures and pressures it can be easily removed after reaction, leaving no solvent residues in the processed material.[7] Supercritical CO_2 is typically a poor solvent for high molecular weight polymers, but conversely, the solubility of $scCO_2$ in polymers is usually substantial.[10] The permeation of $scCO_2$ into a polymer causes it to plasticise and swell in volume.[11] On release of pressure the dissolved CO_2 expands rapidly, foaming the polymer and creating pores.[12]

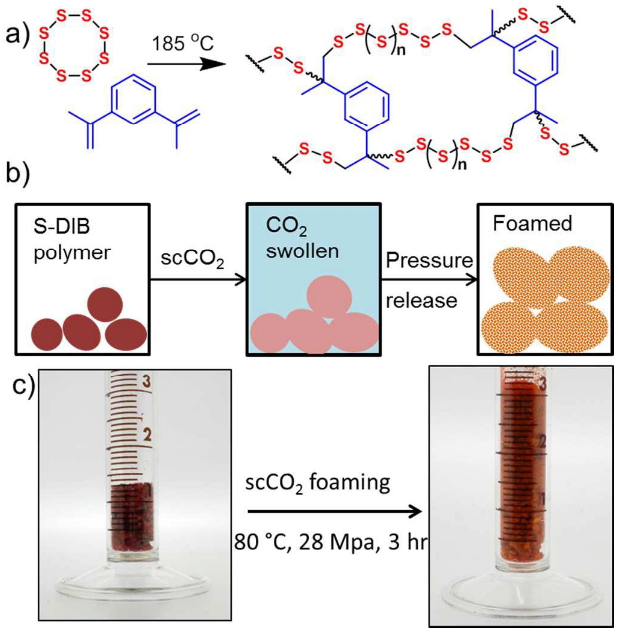


Figure 1. a) Reaction of elemental sulfur and 1,3-diisopropenyl benzene (DIB) produces a stable high sulfur polymer b) $scCO_2$ processing method to foam the polymer, c) photographs of S-DIB (50 % DIB) polymer powder (1 g) before and after $scCO_2$ foaming.

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.[6, 13] 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.

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 SI).[5] 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 added directly to the molten sulfur and heating continued for

---

[a] *Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK E-mail: t.hasell@liv.ac.uk; Tel +44 (0)1517943502*

[b] *University of Nottingham, School of Chemistry, University Park, Nottingham, UK NG7 2RD.*

Electronic Supplementary Information (ESI) available: Synthetic and characterisation methods and additional SEM and photographic images. See DOI: 10.1039/x0xx00000x 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 SI for details). During soaking, polymer granules were placed in a stainless steel autoclave which was then filled with 5.5 MPa of CO_2. The autoclave was then heated to the desired temperature (usually 80 °C) and topped up to 28 MPa. The $scCO_2$ was maintained under these conditions (normally 3 hours) in order to allow the $scCO_2$ to infuse fully into the polymer. In the expansion step, the $scCO_2$ was then vented rapidly in less than one minute. The 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 (powder density drops from 0.8 g/cm^3 to 0.3 g/cm^3, Figs. 1c, and S2-S3).

Processing temperatures of 40, 60, and 80 °C were investigated. Pressures of 10, 20, and 28 MPa were investigated. Higher pressure equates to a higher concentration of CO_2 in the sample, which should lead to increased foaming. For a given pressure, lower temperature should give a higher density of CO_2 – and hence potentially higher foaming. E.g. at 40 °C, and 28 MPa, the CO_2 density is 0.90 g/cm^3, whereas by 80 °C, at the same pressure, the density drops to 0.72 g/cm^3. However, at lower pressures the rate of infusion of CO_2 into the polymer was limited, <1 mm/hour (as demonstrated by zones of foamed material around a solid core, see image S4). At 80 °C the rate of infusion was ~4 mm/hour, a result of higher rate of diffusion at increased temperature. We therefore chose 80 °C as the soak temperature, and 3 hours as 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 between 5 and 100 µm in some areas (fig. S5). Presumably 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 reduced degree (fig. S6), 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.[5] However, the increase in organic content is also likely to increase the solubility of CO_2 in the polymer, aiding partitioning of CO_2 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). This effect is caused by increased homonucleation at higher pressures, as a result of the enhanced level of CO_2 dissolved in the swollen polymer.[14] This increase in void concentration, and reduction in volume, with pressure allows a degree of control over the structures produced.

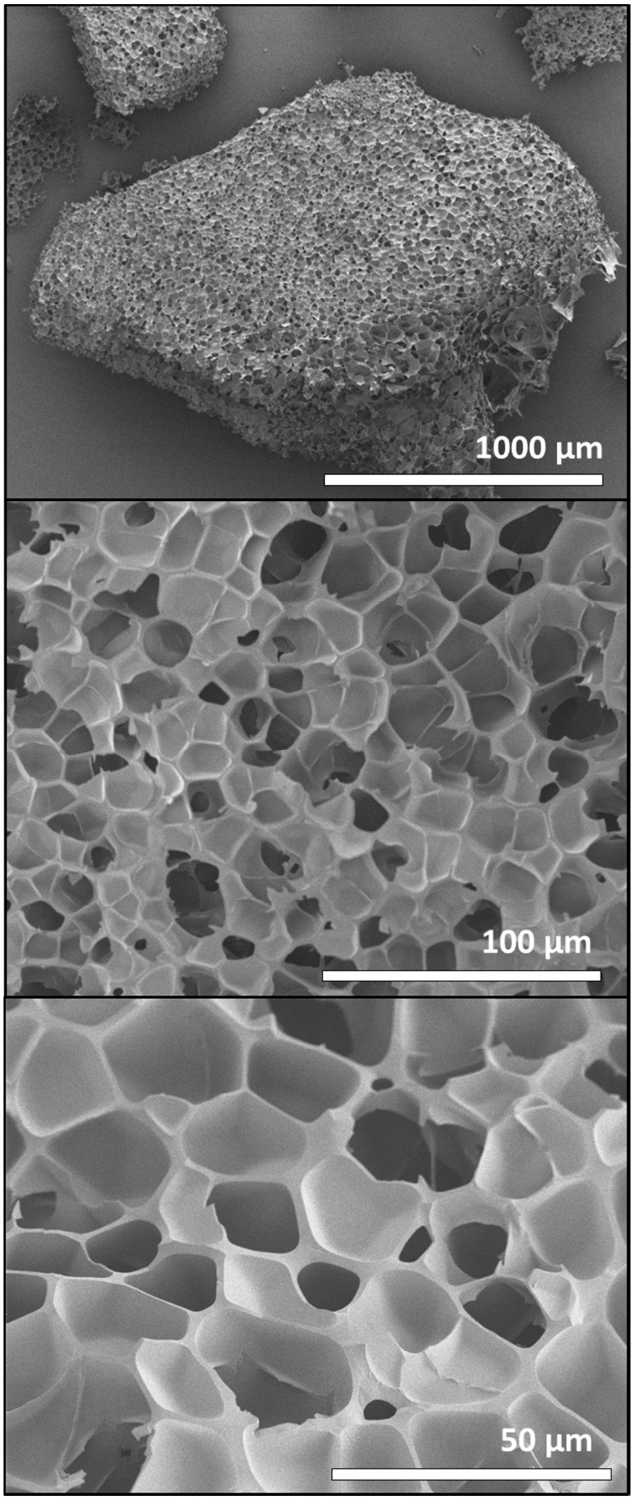


Figure 2. SEM imaging of $scCO_2$ foamed sulfur-DIB crosslinked polymer (50 wt% sulfur). The sample was exposed to CO_2 at 28 MPa and 80 °C for 3 hours. The sample shows both closed cell and connected macropores. Scale bars indicate 1000, 100, and 50 µm from top to bottom.

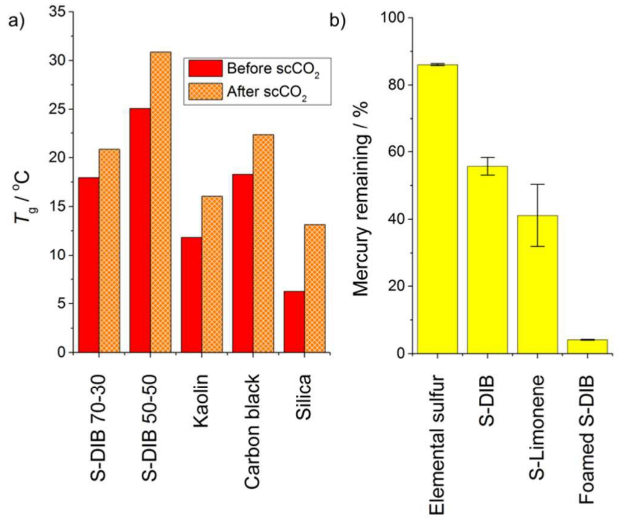


Figure 3. a) Glass transition temperatures (T_g) determined by DSC for polymer samples before and after $scCO_2$ treatment. Kaolin, carbon black, and silica refer to S-DIB samples (30 wt% DIB) with those additives. b) The percentage mercury remaining in solution after 3 hours exposure to each of the materials listed. Values are given as a mean of three repeats with standard deviation shown as error bars.

Three additional samples were produced with industrially relevant additives: carbon black, fumed silica, and kaolin (Fig. S8). 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 (Figs. S9-S10) 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, S12).

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.[5] Previously published results give values of 16.5 °C for 30 wt% DIB, and 28.4 °C for 50 wt% DIB.[5] 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 (Figs. 3a, S13).[‡] Not only is there no adverse effect, but $scCO_2$ 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 $scCO_2$, 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).

Mercury capture tests were performed by soaking 100 mg of sample in 5 mL of aqueous $HgCl_2$ (2 ppm), for 3 hours, before analysing the remaining mercury content in the water (Fig. 3b, and see SI for details). These tests showed that the $scCO_2$ 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[2], 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_8 to instead be pulled into the aqueous phase by the Hg – hence 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 $scCO_2$ pressure, and resultant foaming, on Hg uptake was also investigated (Fig. S15). 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, SI for details), and 5 mL of aqueous $HgCl_2$ solution poured through. This resulted in a 41 % reduction of the Hg concentration in the water.

In summary, $scCO_2$ 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 $scCO_2$ 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.

We thank G. Miller, J. Donnelly, and T. Garcia-Sorribes for ICP analysis, S. Higgins for help with DSC, and J. Bear for advice on S-DIB synthesis. TH is a Royal Society University Research Fellow.

Notes and references

‡ 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.

1. L. Jarup, *Br. Med. Bull.*, 2003, **68**, 167-182.
2. a) W. Feng, E. Borguet and R. D. Vidic, *Carbon*, 2006, **44**, 2998-3004; b) H. C. Hsi, M. J. Rood, M. Rostam-Abadi, S. G.

Chen and R. Chang, *J. Environ. Eng.-Asce*, 2002, **128**, 1080-1089.

3. J. C. Bear, W. J. Peveler, P. D. McNaughter, I. P. Parkin, P. O'Brien and C. W. Dunnill, *Chem. Commun.*, 2015, **51**, 10467-10470.
4. a) P. T. Dirlam, A. G. Simmonds, T. S. Kleine, N. A. Nguyen, L. E. Anderson, A. O. Klever, A. Florian, P. J. Costanzo, P. Theato, M. E. Mackay, R. S. Glass, K. Char and J. Pyun, *Rsc Advances*, 2015, **5**, 24718-24722; b) J. J. Griebel, G. Li, R. S. Glass, K. Char and J. Pyun, *J. Polym. Sci. Pol. Chem.*, 2015, **53**, 173-177; c) J. Lim, J. Pyun and K. Char, *Angew. Chem. Int. Ed.*, 2015, **54**, 3249-3258; d) M. Arslan, B. Kiskan and Y. Yagci, *Macromolecules*, 2016.
5. W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char and J. Pyun, *Nat. Chem.*, 2013, **5**, 518-524.
6. M. P. Crockett, A. M. Evans, M. J. H. Worthington, I. S. Albuquerque, A. D. Slattery, C. T. Gibson, J. A. Campbell, D. A. Lewis, G. J. L. Bernardes and J. M. Chalker, *Angew. Chem. Int.Ed.*, 2016, **55**, 1714-1718.
7. L. J. M. Jacobs, M. F. Kemmere and J. T. F. Keurentjes, *Green Chem.*, 2008, **10**, 731-738.
8. a) T. M. Letcher and J. L. Scott, *Materials for a sustainable future*, RSC Pub., Cambridge, UK, 2012; b) H. M. Woods, M. Silva, C. Nouvel, K. M. Shakesheff and S. M. Howdle, *J. Mater. Chem.*, 2004, **14**, 1663-1678.
9. A. I. Cooper, *J. Mater. Chem.*, 2000, **10**, 207-234.
10. J. Yang, T. Hasell, D. C. Smith and S. M. Howdle, *J. Mater. Chem.*, 2009, **19**, 8560-8570.
11. T. Hasell, in *Nanocomposites*, John Wiley & Sons, Inc, 2013, Ch 1, pp. 1-43.
12. J. J. A. Barry, M. Silva, V. K. Popov, K. M. Shakesheff and S. M. Howdle, *Philos. T. Roy. Soc. A*, 2006, **364**, 249-261.
13. J. Wang, X. Feng, C. W. N. Anderson, Y. Xing and L. Shang, *J. Hazard. Mater.*, 2012, **221–222**, 1-18.
14. a) S. K. Goel and E. J. Beckman, *Polym. Eng. Sci.*, 1994, **34**, 1137-1147; b) I. Tsivintzelis, A. G. Angelopoulou and C. Panayiotou, *Polymer*, 2007, **48**, 5928-5939.