

Sustainable Polysulfides for Oil Spill Remediation: Repurposing Industrial Waste for Environmental Benefit

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Crude oil and hydrocarbon fuel spills are a perennial threat to aquatic environments. Inexpensive and sustainable sorbents are needed to mitigate the ecological harm of this pollution. To address this need, this study features a low-density polysulfide polymer that is prepared by the direct reaction of sulfur and used cooking oils. Because both sulfur and cooking oils are hydrophobic, the polymer has an affinity for hydrocarbons such as crude oil and diesel fuel and can rapidly remove them from seawater. Through simple mechanical compression, the oil can be recovered and the polymer can be reused in oil spill remediation. The polysulfide is unique because it is prepared entirely from repurposed waste: sulfur is a by-product of the petroleum industry and used cooking oil can be used as a comonomer. In this way, sulfur waste from the oil industry is used to make an effective sorbent for combatting pollution from that same sector.

Oil and hydrocarbon fuel spills continue to threaten both terrestrial and aquatic ecosystems, with adverse effects on the environment,^[1] economy,^[1d] and human health.^[2] The explosion on the *Deepwater Horizon* offshore drilling rig in 2010 and subsequent release of ≈4.9 million barrels of crude oil into the Gulf of Mexico is a reminder of the catastrophic scale on which these events can occur.^[3] In addition to such large-scale oil releases, there are hundreds of smaller spills each year in which diesel fuel is a common form of hydrocarbon pollution.^[4] Oil pollution is also a serious concern in developing regions where limited resources hamper the response to spills that threaten ground water, drinking water, and food staples such as fish and other aquatic organisms. The

extensive oil pollution in the Niger Delta^[5] and the Amazon basin of Ecuador^[6] are prominent examples in this regard.

Because of these ongoing challenges with oil and fuel spills, there have been calls for research into cost-effective technologies that can facilitate the response to this pollution.^[3a,7] Accordingly, there is wide interest in skimming technology and sorbents that can be produced and deployed on an immense and economically viable scale.^[7,8] Regarding sorbents, these materials are typically most effective in oil capture if they are hydrophobic and have high surface area, low specific gravity and high buoyancy in water.^[7,8] Mechanical recovery of the oil and sorbent reuse are also desirable features,^[7,8] and low cost is critical for uptake in the field.^[9] Impressive advances have been made for both sorbents and membranes, with highly effective materials reported for oil separation and recovery from water.^[7,8] Nevertheless, the majority of these high-performance materials are not economically viable on the scale required for many remediation needs and most commercial sorbents are made from nonrenewable polypropylene fibers^[10] or polyurethane foams.^[8d] Additionally, while natural biomass and fibrous vegetation have been investigated as low-cost and sustainable sorbents,^[11] these typically suffer from low buoyancy, high water sorption, or limited means by which to recover the oil.

In this report we introduce a new class of oil sorbents that is low-cost, scalable, and enable the efficient removal and recovery of oil from water. The key material is an elastic and porous copolymer made from the direct reaction of sulfur and unsaturated seed

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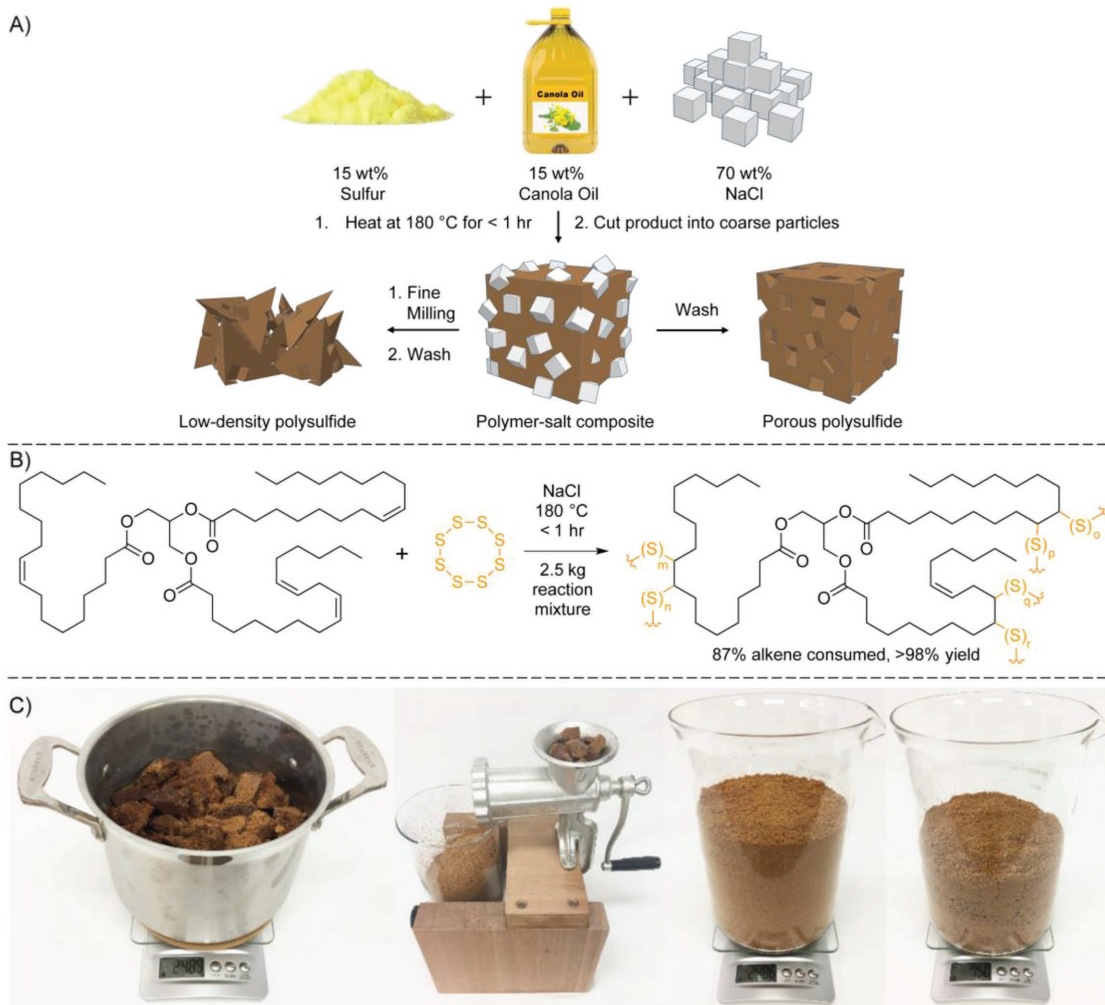


Figure 1. A) Elemental sulfur and canola oil (or used cooking oil) react directly to form a polysulfide copolymer. The polymer, equal mass in sulfur and canola oil, is a friable rubber. The inclusion of sodium chloride in the reaction mixture results in a polymer–salt composite. The sodium chloride can be removed with a water wash to introduce pores into the polymer. If the polymer is ground finely (0.5–3.0 mm particle size) and then washed with water, the void spaces formed after sodium chloride removal no longer appear as pores. In this case, the polymer tears at the salt interface where a pore would otherwise form. This finely milled polymer is referred to as a “low-density polysulfide” rather than a “porous polysulfide.” B) The polysulfide copolymer is formed by ring-opening polymerization of elemental sulfur and reaction of the resulting thiol-radical end groups with the Z-alkene of the unsaturated cooking oil triglyceride (primarily oleate and linoleate in the oils used in this study) 87% of the alkenes are consumed in the polymerization, as determined by ^1H NMR spectroscopy. C) Left to right: The polymer–salt composite was prepared on a 2.5 kg scale and ground finely before washing with water. After washing with water and drying, 750 g of the low-density polysulfide was obtained (far right image).

oils such as canola oil, with inexpensive sodium chloride crystals serving as a porogen to impart higher surface area to the polymer (Figure 1). Because sulfur is a by-product of the petroleum industry^[12] and used cooking oils are suitable starting materials, this oil sorbent can be made entirely from industrial waste that is inherently low in cost. Furthermore, because both sulfur^[12,13] and canola oil^[14] are produced in millions of tonnes each year, the starting materials are sustainable and available on the scale required for addressing the oil spill problem.^[15] Additionally, this advance would constitute a valuable use for sulfur polymers^[16] that is distinct from recent applications of high-sulfur materials in battery technology,^[16a,c] optics equipment,^[16c,17] and heavy-metal remediation.^[18] Importantly, a polysulfide made from sulfur and canola might also be effective in oil spill remediation because both

comonomers are hydrophobic. Furthermore, a porous and flexible version of this material might enable recovery of bound oil by simple mechanical compression. We therefore set out to test the hypothesis that hydrophobic, porous, and compressible sulfur polymers will enable the separation and recovery of oil from water.

The porous canola oil polysulfide was first prepared using either pristine, food-grade canola oil, or used unsaturated cooking oils obtained directly from a restaurant (Figures S1–S9, Supporting Information). We aimed for kilogram-scale batch processes at the outset to demonstrate scalability—an important consideration for use in oil spill remediation. Accordingly, the optimized polymerization was carried out in 4 L reactors using an overhead stirrer with torque control to account for changes in viscosity (Figure S3, Supporting Information). The unsaturated

cooking oil (375 g) was first added to the reactor and heated to 170 °C, with the internal reaction temperature monitored directly throughout the synthesis. Elemental sulfur (375 g) was then added over 10 min, with the slow addition ensuring the reaction temperature did not fall below 155 °C. The reaction mixture appears as two transparent liquid phases at this stage: the sulfur appears orange or red on the bottom phase, while the yellow cooking oil resides in the top phase. Thermal homolysis of S–S bonds in elemental sulfur under these conditions generates thiyl radicals that initiate ring-opening polymerization of sulfur. The thiyl radical end groups contained in the resulting polysulfide intermediates also react with the alkenes of the cooking oil to form a crosslinked polysulfide (Figure 1).^[16e,18b] As this copolymerization occurs, the reaction mixture gradually becomes opaque and appears as one phase. At this stage, the reaction temperature was increased to 180 °C and the sodium chloride porogen (1.75 kg) was added over 15–20 min. As the copolymerization continues, the reaction mixture gradually forms a paste. Approximately 10–15 min after the addition of sodium chloride was complete, the viscosity increased such that the torque of the overhead stirrer registered 40 N cm. At this point, the synthesis was complete so the stirring was stopped and the reactor was removed from the heating source. After cooling the reaction to room temperature, the solid polymer–salt composite was broken into smaller pieces (Figure 1) and then washed with water to remove the sodium chloride porogen.

After removing the porogen from coarse particles (e.g., >2.5 mm diameter) of the salt–polysulfide composite, the resulting polymer contains pores measuring $119 \pm 53 \mu\text{m}$ diameter (Figure 1 and Figure 2A). We refer to material prepared in this way as a “porous polysulfide.” The salt–polymer composite can also be cut into a desired shape such as a cube and then converted into the porous polysulfide through a simple water wash as shown in Figure 2A. If the polymer is ground more finely (<2.5 mm particle diameter, Figure 1C), the friable polysulfide tears at the salt interface where a pore would otherwise form. After removing the salt from these smaller particles, a textured surface results, instead of pores (Figures S10 and S11, Supporting Information). We refer to this material as a “low-density polysulfide” rather than a porous polysulfide. Both the porous polysulfide and low-density polysulfides were dried to a constant mass by passing warm air (<45 °C) over the polymer for several hours.

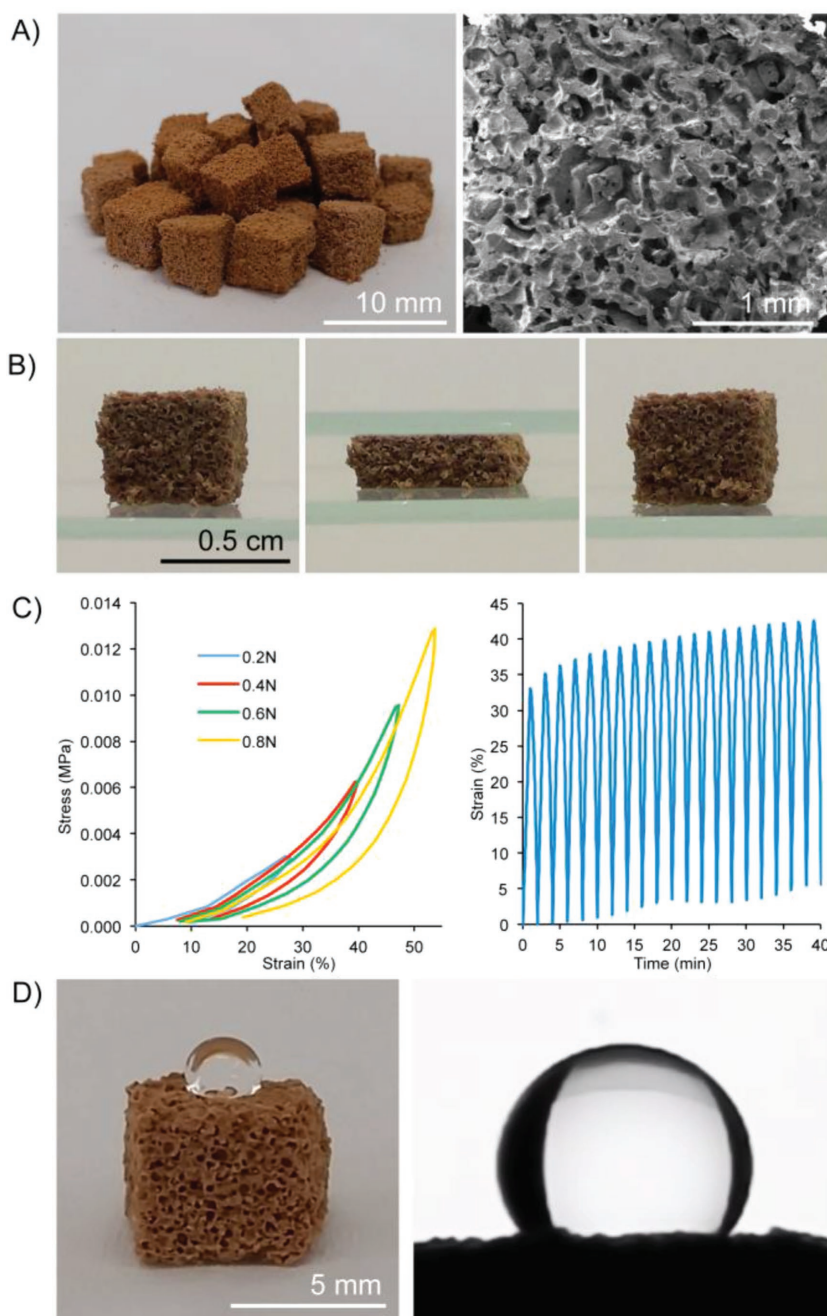


Figure 2. A) Blocks (5 mm × 5 mm × 5 mm) of the porous canola oil polysulfide and an SEM image of a polymer cross section showing the micrometer-scale pores ($119 \pm 53 \mu\text{m}$ diameter, measured for 50 randomly sampled pores in SEM images of the cross-section). B) The porous polysulfide is compressible. C) Left: Stress–strain curve of porous polysulfide when stress of 0.5 N is applied at 1 N min^{-1} up to 0.2, 0.4, 0.6, and 0.8 N force, with a relaxation of 1 N min^{-1} in between each compression step. The polymer can be compressed to increasing amounts of strain and recover, but there is an offset to a fixed strain (polymer deformation) that increased after each cycle. Right: Strain of the porous polysulfide when a stress of 0.5 N is applied at 0.5 N min^{-1} , followed by a return to zero force at 0.5 N min^{-1} , repeated over 20 cycles. This analysis shows that there is good repeatability of the compression and relaxation cycle. The polymer can be squeezed to 35% strain (0.5 N force) repeatedly. At this strain, there is only a small increase in compression set (the permanent deformation that remains after the cycle). D) The porous polysulfide is hydrophobic, with a water contact angle of $130^\circ \pm 10.5^\circ$, with a minimum observed angle of 111° and a maximum of 156° over 15 individual measurements. The photographs show a bead of water on the polymer and a representative image used to calculate water contact angles.

^1H NMR spectroscopy of the canola oil polysulfide in perdeuterated pyridine indicated 87% of the alkenes were consumed in the copolymerization for both pristine canola oil and used cooking oil (Figures S12–S15, Supporting Information). Pyridine was used in this analysis as it was the only solvent identified that could fully dissolve the canola oil polysulfide. The density of the canola oil polysulfide was 0.5 g cm^{-3} , which was anticipated to aid in buoyancy during oil spill remediation on water (Figure S16, Supporting Information). The surface area of the polymer was calculated to be in the range of $0.02\text{--}0.04\text{ m}^2\text{ g}^{-1}$, using the measured surface area of the sodium chloride porogen as a proxy for this feature (Figure S13, Supporting Information). It should be noted that no effort was made to optimize the surface area (for instance by preparing smaller porogen crystals), so that the sodium chloride could be used as received and not require laborious recrystallization. Thermogravimetric analysis indicated stability up to $200\text{ }^\circ\text{C}$. Above this temperature two major mass losses are observed at (≈ 230 and $\approx 340\text{ }^\circ\text{C}$).^[18b] The first mass loss is attributed to degradation of the more labile polysulfide domain (regions of the material containing S–S bonds) and the mass loss at higher temperature corresponds to degradation of remaining organic matter. The thermal analysis also revealed that there is typically 10–15% free sulfur in the final polymer product, as determined by integration of the endotherm detected through differential scanning calorimetry upon the melting of free sulfur. Similar thermal profiles were observed for polymer made from pristine canola oil and polymer made from used cooking oil (Figures S17 and S18, Supporting Information).

The formation of the polysulfide structure (S–S bonds) in the polymer was consistent with X-ray photoelectron spectroscopy (XPS) signals for S $2p_{3/2}$ at 163.8 eV (Figure S19, Supporting Information) as well as a signal at 463 cm^{-1} in the Raman spectrum. Angle resolved XPS also indicated residual sodium chloride (<3% fractional composition) is retained in the polymer even after extensive water washing (Figure S19, Supporting Information). Angle resolved XPS and neutral impact collision ion scattering spectroscopy were also used to profile the surface composition of the polysulfide, revealing a higher relative amount of carbon to sulfur down to 4 nm , and a constant ratio of carbon to sulfur in the bulk of the polymer at depths greater than 4 nm (Figures S19 and S20, Supporting Information).

Mechanical properties of the porous polysulfide were investigated through dynamic mechanical analysis (Figure 2C and Figures S21–S24, Supporting Information). Stress–strain curves indicate that polymer can be compressed repeatedly to 30% strain and can return to its original shape. Above 40% strain, polymer deformation is substantial (Figure S24, Supporting Information). The flexibility of the polysulfide gives it a sponge-like consistency

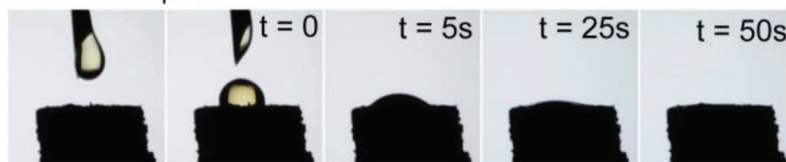
(Figure 2B) anticipated to be important in recovering bound oil through mechanical compression. The polymer was also hydrophobic, with a water contact angle of $130^\circ \pm 10^\circ$ (Figure 2D and Figure S25, Supporting Information). This property was expected for a material comprised of a hydrophobic triglyceride crosslinked with low-polarity polysulfide groups. The uptake of water is also relatively low, with only 56 mg of water sorbed per gram of polymer after 5 min of complete immersion in water.

Next, the porous polysulfide was tested in oil sorption experiments. The uptake of diesel fuel, motor oil (10W-30), and crude oil were all evaluated (Figure 3 and Figures S26–S30, Supporting Information). Diesel fuel uptake into the porous polysulfide was rapid, with complete sorption of a $5\text{ }\mu\text{L}$ drop within 3 s (Figure 3A). The more viscous motor oil was somewhat slower to permeate the polymer, but complete sorption was observed within 50 s (Figure 3B). Similar rates of uptake were observed for crude oil obtained directly from wellheads at multiple locations (Figures S28 and S29, Supporting Information). The sorption capacity for each of these oils was determined by partially immersing a $5.0\text{ mm} \times 5.0\text{ mm} \times 5.0\text{ mm}$ cube of the porous polysulfide into each respective oil. After the oil was visible at the top of the cube (transported through capillary action), the cube was removed and weighed after removing unbound oil. One gram of porous polymer typically absorbed 0.9 mL motor oil, 1 mL crude oil, and 1.4 mL of diesel fuel in this experiment (Figure S31, Supporting Information). The polymer was also effective at removing oil from water (Figure 3C). When the polymer particles ($2.5\text{--}5.0\text{ mm}$) were added to the oil–water mixture, the oil

A) Diesel fuel sorption



B) Motor oil sorption



C) Motor oil removal from water and recovery by compression



Figure 3. A) Sorption of $5\text{ }\mu\text{L}$ of diesel fuel into the porous polysulfide occurs within 3 s. B) Sorption of viscous motor oil (10-W30) into the porous polysulfide occurs over 50 s. C) 1.00 g of the porous polysulfide ($2.5\text{--}5.0\text{ mm}$ diameter particles) was added to a mixture of motor oil (1.00 mL) and water (5.00 mL). The polymer rapidly absorbs the oil and forms an oil–polymer aggregate, which can be easily removed from the water. The oil–polymer aggregate can be mechanically compressed to recover the oil (compression between two glass slides is shown). The polymer can be reused in oil–water separation.

was bound to the polymer within seconds. Additionally, the polymer particles aggregated upon oil sorption thereby facilitating recovery of the polymer-bound oil. Gratifyingly, both the oil and the polysulfide could be recovered by simply compressing the sorbent (Figure 3D). Imaging the surface of the bound oil by scanning electron microscopy (SEM) revealed that the pores were filled with oil (Figure S32, Supporting Information). After recovering the oil by compression, a film of oil remains on the surface of the polymer, as indicated by SEM analysis and infrared and Raman spectroscopy (Figures S33–S38, Supporting Information). Fortunately, this retained oil had minimal impact on the reuse of the polymer and the same oil sorption performance was observed for five sorption and oil recovery cycles (Figure S39, Supporting Information).

Further investigation of the low-density polysulfide (prepared as finer particles varying in size from 0.5 to 2.5 mm in diameter) revealed a similar behavior of binding to crude oil and forming an oil–polymer aggregate (Figure S40, Supporting Information). These particles could typically bind twice their mass in crude oil. In a control experiment in which the polysulfide was prepared without using the sodium chloride porogen, crude oil sorption was still observed but the oil capacity was 2.4 times lower than the low-density polysulfide (Figure S40, Supporting Information). Additionally, preparing the polysulfide without the porogen leads to a denser polymer that is less buoyant in water after binding to oil. Similarly, elemental sulfur can bind to crude oil and aggregate, but its binding sorption capacity is ≈ 2.5 times lower than the low-density polysulfide and the sulfur–crude oil aggregate sinks in water (Figure S40, Supporting Information). Buoyancy of the polymer-bound oil is a critical feature of a sorbent because it facilitates removal from the surface of contaminated water by skimming.

With these encouraging oil sorption and recovery results, we were motivated to assess the low-density polysulfide's ability to remove crude oil from seawater (Figure 4). For this experiment, the low-density polysulfide was first prepared from unsaturated waste cooking oil obtained from a restaurant (Figures S5–S9, Supporting Information). Next, 100 mL of crude oil was added to a glass dish containing 1.5 L of seawater. The low-density polysulfide (100 g) was added to the oil–water mixture and rapid uptake of oil was observed over a few seconds with simultaneous aggregation of the oil-soaked polymer particles. After 1 min of total treatment time, the oil–polysulfide aggregate was removed from the water using a net (Figure 4A) and the crude oil

could be recovered by compressing the oil–polymer aggregate (Figure 4B). A video of the oil sorption and removal from water is provided in Movie S1 in the Supporting Information. The protocol is fast, technically simple, and fully compatible with seawater (Figures S41 and S42, Supporting Information). Similar results were also observed in a similar experiment with motor oil (Figure S41, Supporting Information).

Due to the rapid sorption of the oil, the oil water separation could also be completed in a continuous process (Figure 4C and Movie S2, Supporting Information). In this experiment,

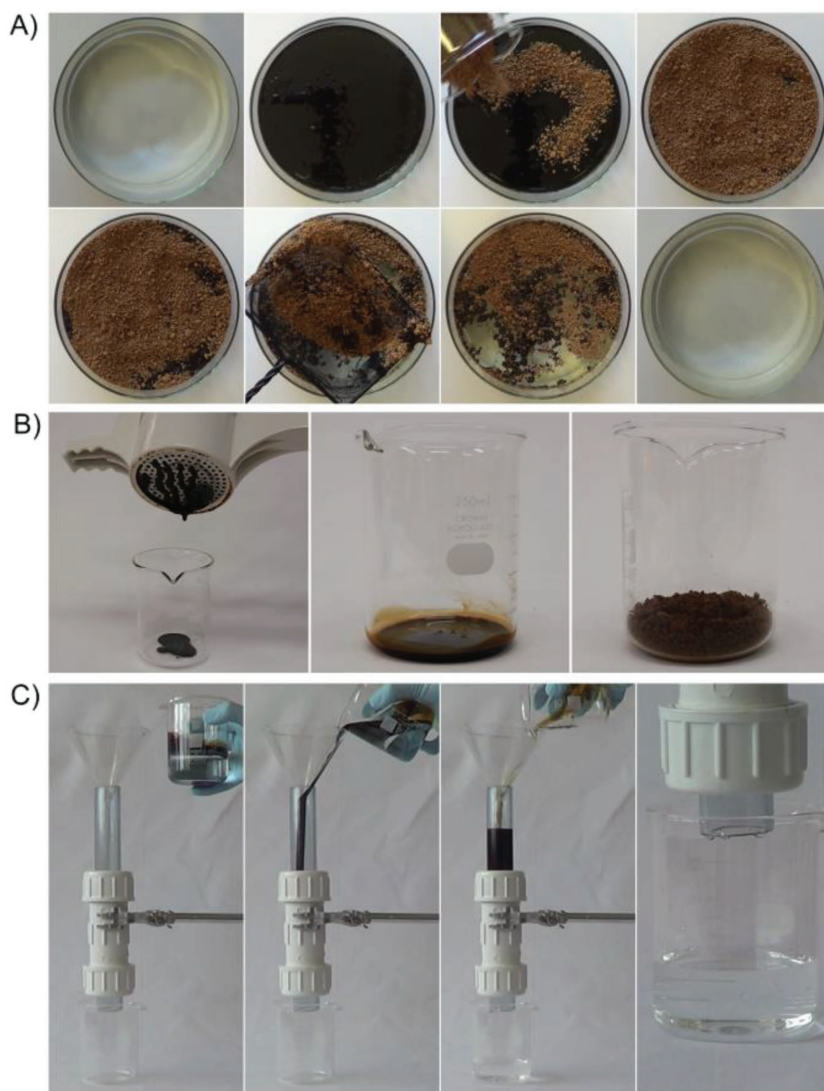


Figure 4. A) Crude oil (100 mL) was added to 1.50 L of seawater. The low-density polysulfide (100 g) was then added to the oil–water mixture. In less than 1 min, the oil and polymer form an aggregate that can be removed from the water by skimming with a net. A video of this process is provided in Movie S1 in the Supporting Information. B) The crude oil can be recovered from the low-density polysulfide by mechanical compression and the recovered polymer can be reused in oil sorption. C) A filter was constructed in which 30 g of the low-density polysulfide was packed into polyvinyl chloride (PVC) pipe. The polymer was immobilized using PVC mesh on the inflow end and cotton fabric on the outflow end (Figure S39, Supporting Information). A mixture of crude oil (10 g) and seawater (100 g) was poured through the filter. The oil remained bound to the polymer while the purified seawater passed through the filter. A video of this process is provided in Movie S2 in the Supporting Information.

the low-density polysulfide (30 g) was used as filtration media (Figures S43 and S44, Supporting Information). Pouring a mixture of seawater (100 g) and crude oil (10 g) through the filter resulted in efficient capture of the oil and purification of the seawater. We anticipate that the continuous process will be useful in cases where it is more convenient to pump oil and water mixtures through a filter, rather than depositing the sorbent directly on the oil spill.

In summary, a polysulfide was prepared by the copolymerization of sulfur and unsaturated cooking oils. This material binds oil and aggregates upon contact, allowing straightforward separation from water. Because of the unique material properties of the featured sulfur polymer, the bound oil can be recovered by mechanical compression and the polymer can be reused in oil sorption. The material can also serve as filtration media for the separation of oil and water in a continuous process. All starting materials are available in megaton quantities at low cost, so the prospect for using this material in large-scale oil spill remediation is promising. The sorbent was also prepared from sulfur and used cooking oil, meaning that every atom of the sorbent, in principle, can be derived from industrial waste. In the case of sulfur, it is a by-product of the petroleum sector—an industry closely tied to oil spills. Therefore, this study represents an intriguing way to extend industrial chemical life-cycles: a by-product from the petroleum industry was used to make a polymer that could remediate oil pollution directly associated with that same industry. We also note that the use of canola oil aligns with a growing interest in identifying low-cost and sustainable crosslinkers for sulfur polymers.^[16e,18a,d,19] The use of such polysulfides in oil spill remediation is an entirely new and environmentally beneficial application for polymers made from sulfur. This application consumes excess waste sulfur that is stockpiled around the globe and may help mitigate the perennial problem of oil spills in aquatic environments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

Two authors (M.J.H.W. and J.M.C.) are inventors on a patent associated with the synthesis and applications of the canola oil polysulfide material (Patent No. WO 2017181217).

Keywords

inverse vulcanization, oil spills, polysulfides, sulfur, waste valorization

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