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Highly porous polymeric sponges for oil sorption

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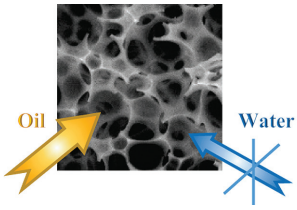
Highly porous poly(styrene-*co*-divinylbenzene) sponges with highly hydrophobic internal surface, 95 vol% porosity and controllable pore sizes were obtained by polymerization in a continuous phase of highly concentrated emulsions. Critical pore sizes for oils with different viscosity were determined; the initial rate of oil sorption exceeded the initial rate of water sorption in pores smaller than the critical size. As a result, more efficient and more effective cleaning up of oil spills can be achieved.



Oil spills lead to serious problems in marine ecosystems and for human habitation in nearshore regions. Oil spill remediation can be performed with the use of microorganisms to break down oil; controlled burning, dispersants that dissipate oil slicks; skimmer for mechanical recovery of oil from the sea surface.[1] Absorbents with hydrophobic surfaces and interconnected macroporous structures based on different materials such as polyurethane sponge coated with graphene oxide[2] or graphene,[3] polydimethylsiloxane sponge,[4] polymethylsilsesquioxane gel,[5] and electrospun polystyrene fibers[6] have been tested for oil recovery.

Porous materials based on highly concentrated emulsions (HIPE), which can be used as templates for the preparation of highly porous polymers (polyHIPEs), are of special interest. The subsequent polymerization of monomers in a continuous phase of HIPE leads to the formation of an interconnected macroporous polymer with the structure determined by the emulsion template.[7–9] During polymerization, thin films at the areas of contacts between the droplets often rupture to create interconnections known as pore throats or windows,[10,11] which make polymer foams highly permeable.

In this study, we obtained poly(styrene-*co*-divinylbenzene) [poly(St-DVB)] sponges by polymerization in a continuous phase of highly concentrated water-in-oil emulsions.† The volume-averaged porosity of the polymers was 0.95.

The pore sizes were determined by SEM image analysis‡ and varied from 5.7 to 23.0 μm by changing NaCl concentration in the aqueous phase of the initial HIPEs. Pore sizes in sponges obtained from emulsions with twice distilled water as the internal phase were ~23 μm. An increase in NaCl concentration in water droplets to 0.17 M decreased pore sizes to 5.7 μm. The main reason was that water-in-oil emulsions with twice distilled water as an aqueous phase were unstable toward Ostwald ripening. The Laplace pressure, arising due to the curvature of the droplet surface, led to diminishing smaller droplets and increasing larger ones in emulsions before polymerization. As a result, the average pore diameter in the emulsion increased. The presence of NaCl created osmotic pressure in water droplets. Water diffusion from smaller droplets towards larger ones took place in these emulsions until the Laplace pressure was compensated by the osmotic pressure.[12] Therefore, water droplets increased in sizes but to a less extent (Figure 1).

The sponges possessed open and interconnected pores, and they could be used as oil sorption materials.[13–17] In the removal of oil from a water surface, the sorption of oil and water can occur simultaneously and that reduces the oil capacity of the sorbent. The rates of oil and water sorption depend on the hydrophobicity of the internal surface of polymer sponges.

We studied the adsorption strength of oil and water. Gear oil (SAE 90), kerosene and their mixtures with various volume ratios and, consequently, different viscosities were the test oils.

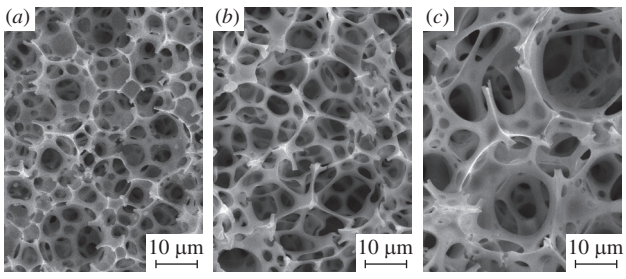


Figure 1 SEM images of poly(St-DVB) sponges obtained from emulsions with (*a*) 0.170 and (*b*) 0.017 M NaCl or (*c*) without NaCl in the aqueous phase.

† *Preparation of highly concentrated emulsions*. The highly concentrated water-in-oil emulsions were prepared by stage homogenization of the aqueous solution in a styrene/divinylbenzene/Span 80 mixture in a volume ratio of 9 : 1 : 1. Mechanical stirring was carried out using an IKA EUROSTAR power control-visc P1 overhead homogenizer at 1200 rpm and 20 °C.

Preparation of polyHIPE sponges. Poly(St-DVB) sponges were prepared by polymerization in the continuous phase of highly concentrated water-in-oil emulsions. Benzoyl peroxide (3 wt% on a monomer basis) was used as a polymerization initiator. Polymerization and drying of samples were performed at 60 °C for 6 h.

‡ *Scanning electron microscopy*. A JEOL JSM 6510LV scanning electron microscope at an acceleration voltage of 15 kV was used to characterize the structure and pore sizes in polymeric sponges. Platinum layer of 8 nm was sprayed onto the surface of the samples.

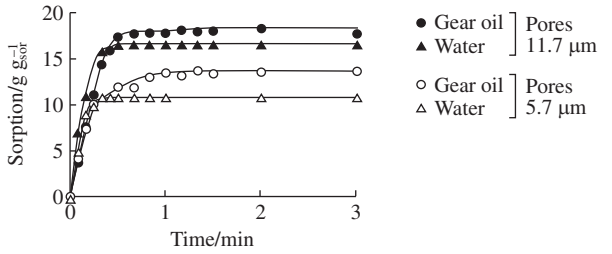


Figure 2 Sorption kinetic curves of gear oil and water in sponges with different pore sizes.

Figure 2 illustrates the gear oil and water uptake by sponges with different pore sizes. Oil sorption was very fast during the first 1.0 and ~0.5 min in sponges with 5.7 and 11.7 μm pores, respectively. The values of the oil sorption in these sponges were 13.8 and 18.4 g g^{-1}_{sor}, respectively. After that point, the oil sorption increased very slowly and reached a limiting capacity of 29.3 g g^{-1}_{sor} after a day in both sponges.

The sorption of water was faster in sponges with larger pores, and it increased with pore sizes: 13.7 g g^{-1}_{sor} for 5.7 μm pores and 16.6 g g^{-1}_{sor} for 11.7 μm pores in 10 s. The water limiting capacity was the same as that of oil and was also reached in a day.

The main reason for the different rates of oil and water sorption is different mechanisms of oil and water penetration into the sponge pores. The internal surface of the sponge was highly hydrophobic because it was prepared from emulsions stabilized with the surfactant Span 80, which has a low value of the hydrophilic–lipophilic balance and did not take part in the polymerization of a continuous phase of emulsion. After polymerization, Span 80 located at the internal surface of poly(St-DVB) sponges giving them hydrophobic properties. Therefore, oil penetrated into the interior of pores flowing along the walls and gradually filled the whole pore volume. A similar behavior was observed for crude oils confined in the pores of sand.[18]

To penetrate into the internal space of pores, water had to overcome capillary pressure. On the outside of the samples, the pores were sufficiently large (5.7–23.0 μm), and water was able to fill them. The further way inside the sample was through the throats that were much smaller and had a hydrophobic surface. Water penetrated much more slowly through throats. Whereas the sizes of throats decreased with decreasing pore size, the water sorption rate was slower in sponges with smaller pores.

The initial sorption rates of gear oil, the mixture of gear oil/kerosene and water were determined as the initial slopes of the sorption kinetic curves. As an example, Figure 3 shows the sorption rates of gear oil, the mixture of gear oil/kerosene and water as functions of pore sizes in sponges. The results indicated that relationships between the sorption rates and pore sizes were linear with varying slopes. The greatest slope in the plot had the line of water sorption, which intersected the sorption lines of oil/kerosene mixture. The initial rate of the oil sorption was higher than the initial rate of water sorption in pores smaller than

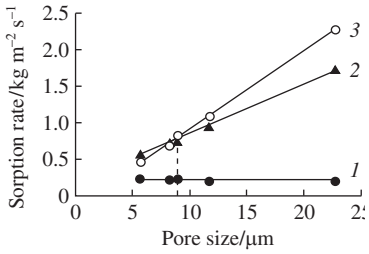


Figure 3 Sorption rates of (*1*) gear oil, (*2*) a mixture of gear oil and kerosene (1 : 1, v/v), and (*3*) water at the initial time. Dashed line corresponds to the critical pore size for the mixture of gear oil and kerosene (1 : 1).

Table 1 Oil characteristics and critical pore sizes for sorption.

Oil (volume ratio)	Viscosity at 20 °C/mPa s	Critical pore size/μm
Gear oil–kerosene (3 : 1)	60	5.7 ± 0.5
Gear oil–kerosene (1 : 1)	12	8.8 ± 0.7
Kerosene	1.5	16.0 ± 1.0

critical ones, and *vice versa*, water was sorbed faster than oil at the initial time in pores with sizes bigger than the critical size.

The critical pore sizes depended on the viscosities of oils (Table 1), which were measured using Ostwald viscometers. The critical pore size decreased with raising the viscosity of oil. Kerosene was sorbed faster in pores smaller than 16 μm. Pores smaller than 5.7 μm are required for the preferable sorption of gear oil.

Aquatic ecotoxicity tests were carried out with poly(St-DVB) sponges. Algal growth inhibition test on *Scenedesmus quadricauda* and cute *Daphnia magna* immobilization test were conducted.[§] The tests revealed the absence of toxic effects of the samples of highly porous polymers.

Therefore, it is possible to control sorbent filling with oil and water. The use of sorbents with required pore sizes provides the conditions when the highly porous polymer can sorb oil at a rate much higher than the rates at which water diffuses into the pores. This allows one to achieve the more efficient and more effective cleaning up of oil spills. The preliminary evaluation indicates that the poly(St-DVB) samples both possess good sorption properties and are nontoxic. Therefore, they are promising for practical applications.

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[§] *Aquatic ecotoxicity tests*. The water extract was prepared after placing sponge samples in pure water at volume ratio of 1 : 3 for 2 h. The test vials with *Scenedesmus quadricauda* or *Daphnia magna* were kept under conditions with a photoperiod of 16 : 8 h (light : dark), 21±1 °C. Algal growth was determined after 72 h by cell counting. The immobilization of the daphnids was determined after a 96-h exposure period.