Macroporous rubber gels as reusable sorbents for the removal of oil from surface waters

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ABSTRACT

Macroporous organogels were prepared by solution crosslinking various rubbers in benzene at −18 °C. Butyl rubber (PIB), cis-polybutadiene (CBR) and styrene–butadiene rubber (SBR) were used as the rubber components, while sulfur monochloride was the crosslinker in the gel preparation. The organogel networks consist of large pores of 10^1–10^2 μm in size caused by the benzene crystals acting as a template during gelation. The networks formed by CBR and SBR showed an aligned porous structure consisting of regular pores, whereas those derived from PIB had irregular pores with a broad pore size distribution due to the phase separation of PIB chains at low temperatures. All organogels were very tough and could be completely compressed without any crack development. Sorption tests showed that the organogels were efficient at removing crude oil, gasoline, diesel, fuel oil and olive oil. The organogels are reusable once they are squeezed, leading to continuous sorption capacities of CBR or SBR gels for crude oil and olive oil of 33–38 g/g and 24–27 g/g, respectively. These sorption capacities are two to three times the capacity of the gels derived from PIB.

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1. Introduction

Accidents involving oil tankers can result in the release of large volumes of crude oil, and this risk significantly increases along narrow seaways with heavy maritime traffic. Therefore, removal of crude oil and petroleum products that are spilled at sea is a serious problem [1]. Among existing techniques for the removal of oil, the use of sorbents is generally considered to be one of the most efficient techniques [2–4]. Properties of an ideal sorbent material for oil spill cleanup include high hydrophobicity, high uptake capacity, high rate of uptake, buoyancy, reusability or biodegradability and recoverability of the sorbed oil.

Recently, we have reported the preparation of macroporous organogels based on butyl rubber (PIB), which is a linear polyisobutylene containing small amounts of internal unsaturated groups (isoprene units) [5–7]. It was shown that macroporous PIB gels are able to absorb large volumes of organic solvents in a short period of time. The organogels were prepared by solution crosslinking PIB by the cryogelation technique using sulfur monochloride (S_2Cl_2) as a crosslinker. This technique is based on the natural principle that sea ice is less salty than sea water, i.e., crystallization results in the exclusion of solutes from growing crystals [8–13]. As in nature, during the freezing of a PIB solution in benzene or in cyclohexane

with normal freezing temperatures of 5.5 and 6 °C, respectively, the solutes expelled from the solvent crystals concentrate within the channels between the crystals so that the reactions only take place in these unfrozen liquid channels. After polymerization and thawing of the solvent crystals, a macroporous material is produced whose microstructure is a negative replica of the crystal that formed. It was shown that the frozen solutions of PIB in benzene or in cyclohexane can easily be crosslinked using S_2Cl_2 to produce responsive and durable materials with macroporous structures [5,6]. Due to their high hydrophobicities, fast responsivities, and reusabilities, macroporous PIB gels are suitable sorbent materials for a variety of applications including oil spill cleanup from surface waters [14].

Because the degree of unsaturation in PIB is low (1–3%), one may expect that other rubbers with a higher degree of unsaturation will undergo crosslinking reactions at lower rubber concentrations, which would lead to the formation of organogels with higher sorption capacities. Here, we describe the preparation of macroporous organogels starting from various types of rubbers and compare their potentials as reusable sorbents for the removal of oil. In addition to PIB (which has two different degrees of unsaturation), cis-polybutadiene (CBR) and styrene–butadiene rubber (SBR) were used as the rubber components for gel preparation. The crosslinking reactions were conducted in benzene using S_2Cl_2 as a crosslinker at −18 °C. As will be shown below, organogels derived from CBR and SBR exhibit different microstructures and

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much higher sorption capacities as compared to those based on PIB.

2. Experimental

2.1. Materials

Butyl rubber (PIB, Exxon Chem. Co.), cis-polybutadiene (CBR, Nizhnekamskneftekhim Inc.) and styrene–butadiene rubber (SBR, Petroflex) were used as the rubber components. PIB is a linear polyisobutylene containing small amounts of isoprene units. The PIB-065 and PIB-365 used in this work contained 1.1% and 2.3% unsaturation and are denoted by PIB1 and PIB2, respectively. SBR is a copolymer with 86% internal unsaturated groups. Each repeat unit of CBR has one unsaturated group. The rubbers were dissolved in toluene followed by precipitation in methanol and drying at room temperature under vacuum to obtain constant masses. Weight-averaged molecular weights $\bar{M}_w$ of the rubbers were determined in cyclohexane using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically-polarized 30-mW Gallium-arsenide laser operating at $\lambda = 690$ nm and the ability to detect 18 scattering angles simultaneously. The molecular weights for PIB1, PIB2, SBR and CBR were $\bar{M}_w = 310$, 360, 210 and 371 kg/mol, respectively. The crosslinking agent sulfur monochloride, S_2Cl_2, was purchased from Aldrich Co. Benzene, toluene and methanol (all Merck reagents) were used as the solvents for the solution crosslinking reactions, swelling and deswelling experiments, respectively.

The organogels were prepared by the solution crosslinking technique at various rubber concentrations (C_p) between 1% and 5% w/v according to the following scheme: Rubber (1–5 g) was first dissolved in 100 mL of benzene at 20 ± 1 °C overnight. Then, 25-mL portions of this solution were transferred to volumetric flasks, and different amounts of sulfur monochloride were added under rigorous stirring. The homogeneous reaction solutions were transferred into plastic syringes of 16.4-mm internal diameters. The crosslinking reactions were carried out in a cryostat at −18 °C for 1 day. The crosslinker concentration in the reaction solution was expressed as the volume of S_2Cl_2 added per 100 g of butyl rubber.

The organogels in the form of cylindrical tissues of 14 cm in diameter were also prepared as described above, except that the gelation reactions were carried out in several glass Petri dishes of 140 mm in diameter and 20 mm in height. The dishes were sealed with glass plates, and the reaction was conducted in a cryostat at −18 °C for 1 day. After the reaction, the reaction system was thawed at room temperature for 1 h, and the gel that was formed was squeezed to remove benzene. The gel was then washed several times first with toluene and, then, with methanol, and they were finally dried under vacuum at room temperature.

2.2. Characterization

The gels were taken out of the syringes, and they were cut into specimens of approximately 10 mm in length. Each gel sample was placed in an excess of toluene at 20 °C, and the toluene was replaced every other day over a period of at least 1 month to wash out the soluble polymer and the unreacted crosslinker. The swelling equilibrium was tested by measuring the diameter of the gel samples through the use of an image analyzing system consisting of a microscope (XSZ single zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. The swelling equilibrium was also tested by weighing the gel samples. In order to dry the equilibrium swollen gel samples, the gels were first immersed in methanol overnight and then dried under vacuum. The gel fraction W_g was defined as the amount of

crosslinked (insoluble) polymer obtained from one gram of butyl rubber and was calculated as follows:

$$W_g = \frac{m_{dry}}{10^{-2}C_P m_o / d_B} \tag{1}$$

where m_{dry} and m_o are the weights of the gel samples after drying and just after preparation, respectively. C_p is the rubber concentration used in the gel preparation in w/v%, and d_B is the density of benzene at 20 °C (0.877 g/mL). The equilibrium volume and the equilibrium weight swelling ratios of the gels (q_v and q_w, respectively) were calculated as

$$q_v = (D/D_{dry})^3 \tag{2a}$$
$$q_w = (m/m_{dry}) \tag{2b}$$

where D and D_{dry} are the diameters of the equilibrium swollen and dry gels, respectively, and m is the weight of the equilibrium swollen gel. The temperature-dependent swelling measurements were conducted by following the mass of the gel samples immersed in benzene as a function of temperature. The weight changes of gels were measured gravimetrically after blotting the excess surface solvent. The results were interpreted in terms of the normalized gel mass m_{rel} with respect to its value at 20 °C, i.e., $m_{rel} = m(t\,°C)/m$.

Uniaxial compression measurements were performed on equilibrium swollen gels in toluene. All mechanical measurements were conducted in a thermostatted room kept at a temperature of 20 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus that was previously described [15]. The elastic modulus G was determined from the slope of linear dependence, $f = G(\alpha - \alpha^{-2})$, where f is the force acting per unit cross-sectional area of the undeformed gel specimen, and α is the deformation ratio (deformed length/initial length).

The pore volume V_p of the networks was estimated through methanol uptake of dry gels. Because methanol is a nonsolvent for the rubbers, it only enters into the pores of the polymer networks. Thus, V_p (expressed as mL in the pores of one gram of the polymer network) was calculated as

$$V_p = (m_M - m_{dry})/(d_M m_{dry}) \tag{3}$$

where m_M is the weight of the network immersed in methanol after 2 h, and d_M is the density of methanol (0.792 g/mL).

For the texture determinations of the dry gels, scanning electron microscopy (SEM) studies were carried out at various magnifications between 20× and 300× (Jeol JSM 6335F Field Emission SEM). Prior to the measurements, network samples were sputter-coated with gold for 3 min using a Sputter-coater S150 B Edwards instrument. The sulfur contents of the dried cryogels were determined using a Thermo Finigan, Flash EA 112 CHNS analyzer.

We note that all structural characterizations of the cryogels described above were performed on samples in their dry states. Previous research indicates the possibility of the collapse of the pore structure in macroporous gels during the drying process [6,16]. The collapse of the porous structure in these previous studies was attributed to the buildup of cohesional forces when the polymer chains approach each other caused by the loss of solvent [17,18]. To estimate the porosity of swollen cryogels, part of each gel sample was subjected to V_p measurements before drying. Thus, cryogels swollen in toluene were immersed in methanol that was refreshed several times over a 1-week period. After weighing (m_M), the samples were dried to calculate m_{dry} and V_p according to Eq. (3). Moreover, because the collapse of the gel samples results in a decrease in the gel diameter, the volume swelling ratios q_v were also calculated using the gel diameters in methanol instead of the diameters of the dry gels.