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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.

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.

2.3. Procedure for oil removal tests

Oil removal tests were conducted using organogel samples prepared in the form of cylindrical tissues of 14 cm in diameter and 2 cm in thickness. Five mixtures were used to investigate contaminant removal abilities. Contaminants included gasoline, diesel fuel, crude oil, fuel oil and olive oil. The characteristics of each of these contaminants are listed below:

(a) Gasoline: BP super, 95 octane, lead-free, density = 0.720–0.775 g/mL, viscosity = 0.75 cP (38 °C).
(b) Diesel fuel: BP ultimate diesel, setan number = 55, density = 0.85 g/mL, viscosity = 5.0 cP (25 °C).
(c) Crude oil: from Ozan Sungurlu wells, Turkey, density = 0.89 g/mL, viscosity = 350 cP (25 °C).
(d) Fuel oil: No. 6 (Bunker C), density = 1.03 g/mL (15 °C), viscosity = 130 cP (25 °C).
(e) Olive oil: from Kent Boringer, density = 0.918–0.923 g/mL, viscosity = 69 cP (25 °C).

We note that the olive oil was a mixture of saturated (11.4%) and unsaturated fatty acids. All tests were performed at 20 ± 1 °C. The kinetics of the oil sorption process were determined by immersing 2 g of dry gel tissues into 500 mL of test solution and then monitoring the mass of the gel as a function of time. For this testing method, the gel was removed from the test solution at selected time intervals (30 s – 5 min) and weighed. The uptake capacity at time *t*, i.e., grams of pollutants absorbed by 1 g of dry gel, was calculated as $(m_t - m_{dry})/m_{dry}$ where m_t is the sorbent mass at time *t*.

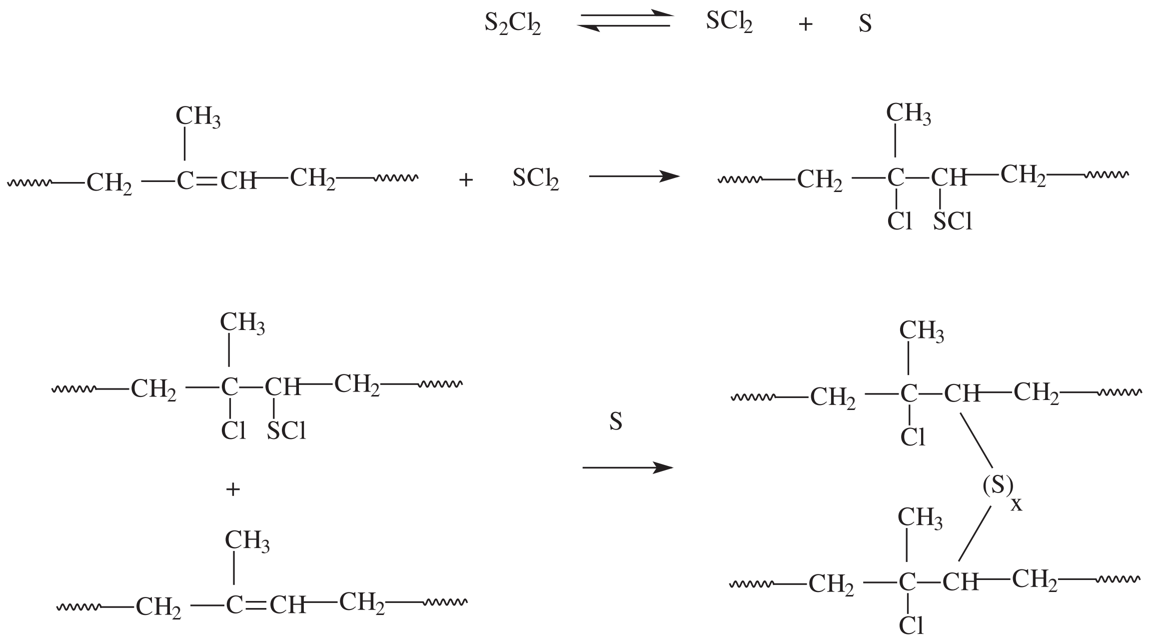
The reusability of the gels as well as their continuous extraction capacities were determined by subjecting the gels to successive sorption–squeezing cycles under identical conditions. Dry gel samples were first immersed in 500 mL of the test solution for 1 min followed by a 30-s period of drip-drying. The saturated gel was weighed and then squeezed by hand. The gel sample was weighed again to calculate the amount of pollutant sorbed by 1 g of dry gel. This sorption–squeezing cycle was repeated 20 times to obtain the recycling efficiencies and continuous extraction capacities of the rubber gels.

3. Results and discussion

3.1. Formation of the rubber gels

The solution crosslinking of PIB1, PIB2, CBR and SBR in benzene using the crosslinker S_2Cl_2 was carried out at a temperature of −18 °C, which is 23 °C below the bulk freezing temperature of benzene. We first investigated the crosslinking efficiency of S_2Cl_2 in a range of concentrations between 6% and 12%. At a rubber concentration of 5%, the gel fraction W_g, i.e., the amount of the crosslinked (insoluble) polymer obtained from one gram of rubber, was always close to unity ($W_g > 0.98$), which indicates that sulfur monochloride has a high crosslinking efficiency even at low reaction temperatures. This high efficiency is due to the high local concentrations of rubber and crosslinker in the frozen reaction system. As reported previously [5], when a 5% PIB solution was frozen at −18 °C, 14% of the benzene remained unfrozen in the frozen system. This means that, although the initial concentration of polymer was 5%, its concentration in the unfrozen liquid phase was approximately 36%. Thus, the reduced rate constant of the crosslinking reaction between sulfur monochloride and the vinyl groups at low temperatures is compensated for by the increased polymer concentration in the reaction zones. The reason why benzene does not freeze completely at the reaction temperature that was below the bulk freezing temperature is likely due to a freezing point depression caused by the polymer. As benzene freezes, the polymer concentration in the liquid phase rises continuously so that successively greater osmotic pressure is required to keep the liquid phase in equilibrium with the pure frozen benzene phase.

The crosslinking reactions between the internal unsaturated groups of the rubbers via sulfur monochloride are believed to proceed in similar steps as in the reaction between ethylene and sulfur monochloride (Scheme 1) [19–21]. According to this scheme, attack of sulfur dichloride by the internal vinyl group of the polymer leads to the formation of pendant sulfur chloride groups on the chains, which act as potential crosslinking points. Reaction of these groups with the internal vinyl groups on other chains is responsible for the formation of effective crosslinks. Assuming that the crosslinking reactions are complete, one may calculate the theoretical crosslink density, ν_{theo}, of the rubbers. In Table 1, the



Scheme 1. Crosslinking reactions between the internal unsaturated groups of the rubbers via sulfur monochloride.

Table 1
Crosslink densities and sulfur contents of the cryogels formed at 5% rubber concentration and in the presence of 6% and 12 % S_2Cl_2. The degree of unsaturation of the rubbers is indicated. X = the crosslinker ratio, i.e., molar ratio S_2Cl_2/unsaturated group. ν_{theo} = theoretical crosslink density calculated from the amounts of S_2Cl_2 and internal unsaturated groups of the rubbers. ν_{chem} = chemical crosslink density calculated from the sulfur content (S%) of dry cryogels. The numbers in the parenthesis are standard deviations.

Rubber	X		10^{-3} ν_{theo}/mol m^{-3}		S%		10^{-3} ν_{chem}/mol m^{-3}	
	6%	2%	6%	12%	6%	12%	6%	12%
CBR (100 mol%)	0.040	0.080	1.4	2.8	3.0 (0.3)	3.3 (0.3)	1.8 (0.2)	2.0 (0.2)
SBR (86 mol%)	0.053	0.106	1.4	2.8	2.8 (0.3)	2.7 (0.2)	1.7 (0.2)	1.6 (0.1)
PIB2 (2.3 mol%)	1.8	3.6	0.38	0.38	<1		<0.6	
PIB1 (1.1 mol%)	3.8	7.6	0.18	0.18				

crosslinker ratio X (the molar ratio S_2Cl_2/unsaturated group) and the corresponding ν_{theo} are shown for 6% and 12% S_2Cl_2. For both PIB1 and PIB2, the crosslinker S_2Cl_2 is in excess so that ν_{theo} is determined by the number of unsaturated groups of the rubbers and, thus, ν_{theo} is independent of the crosslinker concentration. However, for the rubbers with higher degrees of unsaturation, namely for SBR and CBR, the unsaturated groups are in excess and, therefore, ν_{theo} increases with increasing concentrations of S_2Cl_2. To estimate the chemical crosslink density ν_{chem} of the rubbers, the dried cryogel samples were subjected to sulfur analysis after extraction. The results are shown in the fourth column of Table 1, where the sulfur contents S% (based on the dry mass) of the cryogels prepared at 5% rubber concentration are given. We see that the S% increases in the order PIB < SBR < CBR, i.e., in the order of the increasing unsaturation degree of the rubbers. From these sulfur content measurements, the chemical crosslink density ν_{chem} was calculated as

$$\nu_{chem} = \frac{2Sd_2}{32x(100 - S)} \qquad (4)$$

where S and d_2 are the sulfur content (S%) and the bulk density of dry rubber, respectively, and x is the number of sulfur atoms in each crosslink (Scheme 1). Assuming $x = 1$ and $d_2 = 0.92$, 0.94, and 0.93 g/mL for PIB, SBR, and CBR, respectively, the calculated results of ν_{chem} are shown in the last column of Table 1 for 6 and 12% S_2Cl_2. It is seen that at 6% S_2Cl_2, ν_{chem} is close to ν_{theo}, indicating that the reactions between the internal unsaturated group and the crosslinker S_2Cl_2 are complete after cryogelation. However, for both SBR and CBR, ν_{chem} does not show a substantial increase with increasing S_2Cl_2 concentration, which suggests that there was a reduced reactivity of the internal unsaturated groups available to the crosslinker molecule.

3.2. Properties of the rubber gels

The swelling capacities of the rubber gels in toluene in terms of their equilibrium weights (q_w) and volume swelling ratios (q_v) are shown in Fig. 1A and B for 6 and 12% S_2Cl_2, respectively. The gels were prepared starting from a 5% rubber solution. At 6% S_2Cl_2 (Fig. 1A), the weight swelling ratios q_w of both CBR and SBR gels

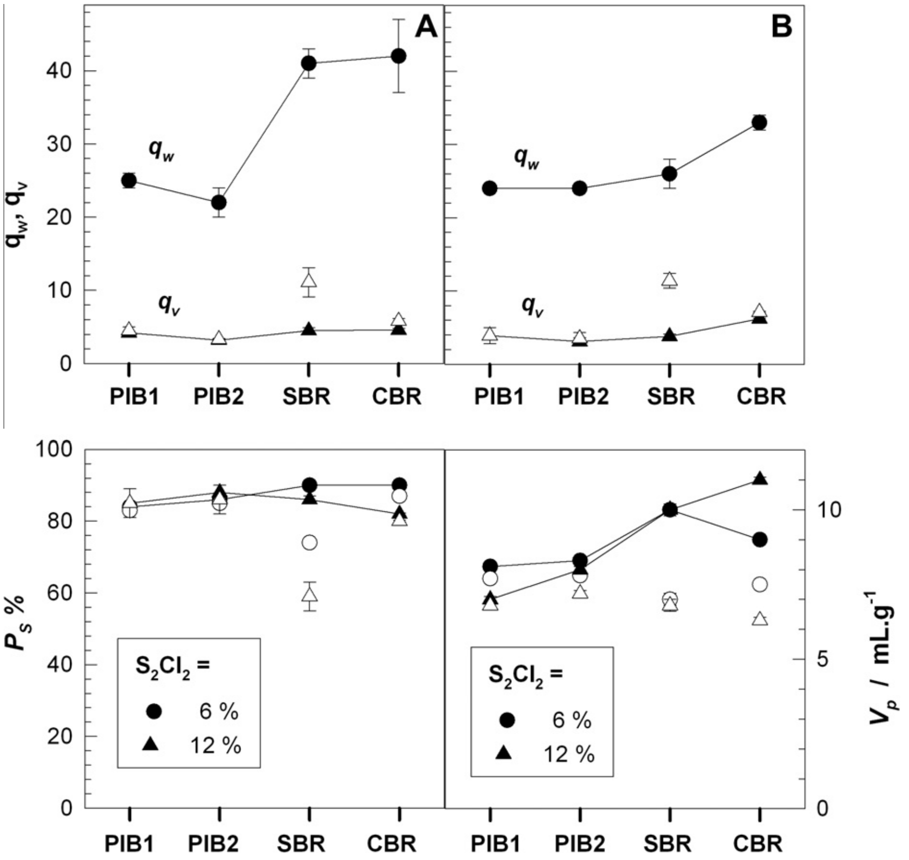


Fig. 1. A and B: the equilibrium weight (q_w, circles) and volume swelling ratios (q_v, triangles) of cryogels formed at 6 (A) and 12% S_2Cl_2 (B). C and D: the calculated porosities P_s (C) and the total volume of the pores V_p (D) of cryogels formed at 6 (circles) and 12% S_2Cl_2 (triangles). C_p = 5%. The values of q_v, P_s and V_p measured before and after drying the cryogels are represented by the filled and open symbols, respectively.

were both approximately 40, which is about twice the swelling ratio q_w of PIB gels. Increasing S_2Cl_2 content decreases the swelling capacity of the organogels, especially those obtained from SBR and CBR. Further, the volume swelling ratios q_v of all gels were much smaller than their weight swelling ratios. As mentioned in Section 2, the porous structure of gels are known to collapse upon drying, which would lead to lower porosities and higher volume swelling ratios. To check for this potential outcome, q_v values of cryogels were determined both before and after drying (as indicated in Fig. 1A and 1B by the filled and open triangles, respectively). An increase in q_v was observed for SBR cryogels after drying, suggesting a partial collapse of their porous structures.

According to the Flory–Rehner theory of swelling equilibrium, the effective crosslink density of gels is related to their volume swelling ratios [22]; the higher the effective crosslink density, the lower the volume swelling ratio of the gels. However, Fig. 1A and B show that q_v slightly increases in the order PIB < SBR < CBR, which is in contrast to their chemical crosslink densities (Table 1). Due to the low unsaturation degree of PIB rubbers, it is reasonable to neglect cyclization reactions during gelation, i.e., the formation of sulfur bridges between the unsaturated groups belonging to the same primary molecule. Increasing unsaturation degrees of PIB from 1.1% to 2.3% increased the effective crosslink density such that the cryogel formed from PIB2 swells less than that the cryogel from PIB1 ($q_v = 3.2$ versus 4.2 and 3.1 versus 3.9 for 6% and 12% S_2Cl_2, respectively). In contrast, CBR and SBR had higher degrees of unsaturation and promoted cyclization reactions due to their local high concentration of internal vinyl groups in the gelation system, thus leading to increased numbers of elastically ineffective crosslinks and to higher swelling ratios. This explanation was also supported by the rubber elasticity of the cryogels (see below). The cryogels derived from both SBR and CBR exhibit lower moduli of elasticity as compared to the PIB cryogels, demonstrating lower effective crosslink densities within the former gels.

The relative values of q_w and q_v provide information about the internal structure of macroporous gels because the weight swelling ratio includes the solvent located in both the pores and in the polymer region of the gel, while (assuming isotropic swelling) the volume swelling only includes the solvent in the polymer region. From the weight and volume swelling ratios of gels, porosities P_s can be estimated using the following equation [16]:

$$P_s\% = \left(1 - \frac{q_v}{1 + (q_w - 1)d_2/d_1}\right) \times 10^2 \tag{5}$$

where d_1 is the density of the swelling agent (toluene). Using the densities of the rubbers together with $d_1 = 0.876$ g/mL, the calculated porosities P_s are shown in Fig. 1C. Calculations use the q_v values that were determined prior to and after drying the cryogels; the before and after data are represented by the filled and open symbols in Fig. 1C, respectively. We see that all gels exhibit significant porosities; the average P_s is 86 ± 3% before drying, whereas it decreases in SBR cryogels after their drying.

Fig. 1D shows the total volumes of the pores, V_p, in the cryogels, which were estimated from the methanol uptake of the gel samples. The results are given for cryogels before (filled symbols) and after their drying (open symbols). In dry cryogels, V_p does not change depending on the type of the rubber and the crosslinker concentration; the total pore volume in one gram of dry rubber is approximately 7 ± 0.5 mL, which enables the immediate penetration of the poor solvent, methanol, into the network structure. Moreover, the pore volumes of the cryogels derived from SBR and CBR are smaller after drying, which suggests that the pores partially collapse and/or the pore size decreases during the drying period of these gels. As will be seen later, the moduli of elasticity of SBR and CBR gels are much smaller than those of PIB cryogels. One may expect that, due to the weak network structure, the porous structure partially collapses during drying leading to smaller pore volumes.

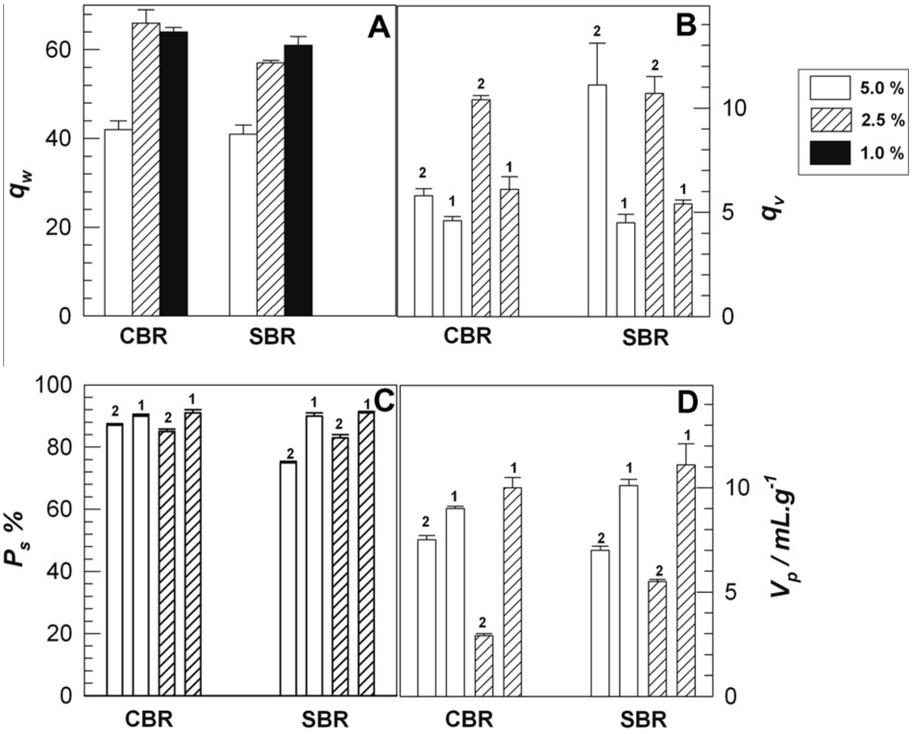


Fig. 2. q_w (A), q_v (B), P_s% (C) and V_p (D) of cryogels formed at the indicated rubber concentrations, C_p. Crosslinker (S_2Cl_2) concentration = 6%. The numbers 1 and 2 on the bars in B–D denote the data measured before and after drying the cryogels, respectively.

The polymer concentration C_p during the gel preparation is known to be an important parameter affecting the swelling properties of gels [23,24]. Experiments conducted using PIB1 and PIB2 showed no gel formation at or below 2.5% rubber concentration. This is probably due to the low degree of unsaturation (1–2%) of the PIB chains. However, organogels with complete conversion ($W_g \cong 1$) were obtained starting from the CBR and SBR polymers with unsaturation degrees of 100% and 86%, respectively. The sulfur contents of the CBR and SBR cryogels were found to be independent of C_p, indicating that the chemical crosslink density does not depend on the polymer concentration. Fig. 2 shows the swelling ratios q_w and q_v, the porosities P_s and the pore volumes V_p of CBR and SBR gels formed at various polymer concentrations C_p. The numbers 1 and 2 on the bars in Fig. 2B–D denote q_v, P_s and V_p data measured before and after drying of the cryogels, respectively. Highly swollen CBR and SBR gels with q_w values around 60 and porosities above 80% were obtained at $C_p \leqslant 2.5\%$. The total volume of the pores in these cryogels was approximately 10 mL/g, which decreased significantly after drying due to the collapse of the weak pore structure that formed. The decrease in the pore volume of the cryogels formed at $C_p = 2.5\%$ was also evident from the collapse of the gel samples upon drying, which led to an increase in the volume swelling ratio q_v from 5 to 10. Moreover, the gels formed at 1% rubber concentration were too weak to carry their own weight so that their diameters, and thus their volume swelling ratios, could not be measured.

To visualize the pores in the organogels, the morphologies of dried gel samples were observed by scanning electron microscopy (SEM). Fig. 3 shows SEM images of the gel networks formed at $C_p = 5\%$ w/v. The crosslinker concentrations are 6% and 12% in the upper and bottom panels, respectively. The gel networks formed from CBR and SBR exhibit an aligned porous structure consisting of regular pores with sizes 10^1–10^2 μm, separated by polymer domains (pore walls) of 10–20 μm in thickness. Fig. 4 shows SEM images of CBR and SBR networks formed at $C_p = 2.5\%$, which reveal that by decreasing rubber concentration C_p, an increase in the regularity of the porous structure occurs. Previous works indicates that the regularity of the pore structure formed by cryogelation increases with decreasing freezing rates of the reaction solution [6] or that pore structure regularity can be increased by conducting the cryogelation reactions under isothermal conditions [25]. Isothermal conditions facilitate homogeneous nucleation of solvent crystals such that the polymer network that forms exhibits monodisperse pores [26]. In the present case, gelation occurs non-isothermally during the initial cooling period of the reaction solution from 20 °C to −18 °C, which takes place 5 min. Because decreasing polymer concentrations also decreases the rate of the crosslinking reactions [5], the gel point is shifted toward longer reaction times as C_p decreases, such that gelation occurs isothermally in the frozen system. This leads to the formation of more regular pores. In contrast, gel networks formed from either PIB1 or PIB2 exhibit broad size distributions of irregular pores of μm to mm sizes. Thus, the use of PIB1 or PIB2 in the gel preparation destroys the regularity of the porous structures in the organogels.

To explain the differences in the morphologies of the organogel networks, homogeneous gels were prepared at room temperature, and they were subjected to swelling measurements in benzene at various temperatures extending down to the freezing temperature of benzene. The results are collected in Fig. 5 where the normalized weight swelling ratios m_{rel} of PIB2, CBR and SBR gels in benzene are plotted against the swelling temperature. Both CBR and SBR gels exhibit temperature-independent swelling behavior, and, thus, benzene is a good solvent for these polymers over the whole range of temperatures investigated. This indicates that CBR and SBR remain in solution during the initial cooling period of the gelation reactions such that only the cryogelation mechanism is responsible for the formation of the pores in these networks. Thus, in these gelation systems, although there is no phase separation during the network formation process, the frozen zones of the reaction system act as inert diluents during gelation; the frozen solvent can easily be removed from the gel by thawing, and the process leads to the formation of a macroporous structure [9,27–29]. The aligned porous structure of these networks is, therefore, a result of the directional freezing of the benzene crystals in the direction from the surface to the interior of the reactor, i.e., in the direction of the temperature gradient. In contrast, the swelling capacity of the PIB2 gel strongly depends on the temperature (Fig. 5); the gel continuously deswells as the temperature is decreased and as

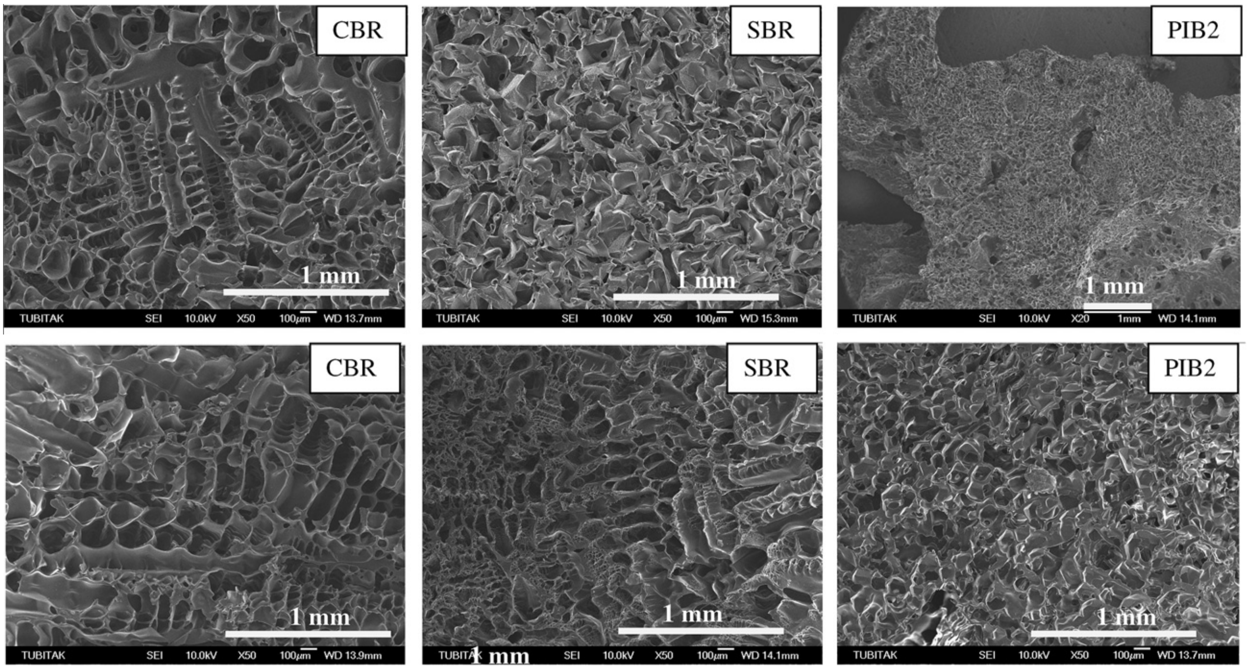


Fig. 3. SEM of the gel networks formed from the indicated rubbers. Rubber concentration = 5%. Crosslinker (S_2Cl_2) concentration = 6% (upper panel) and 12% (bottom panel).

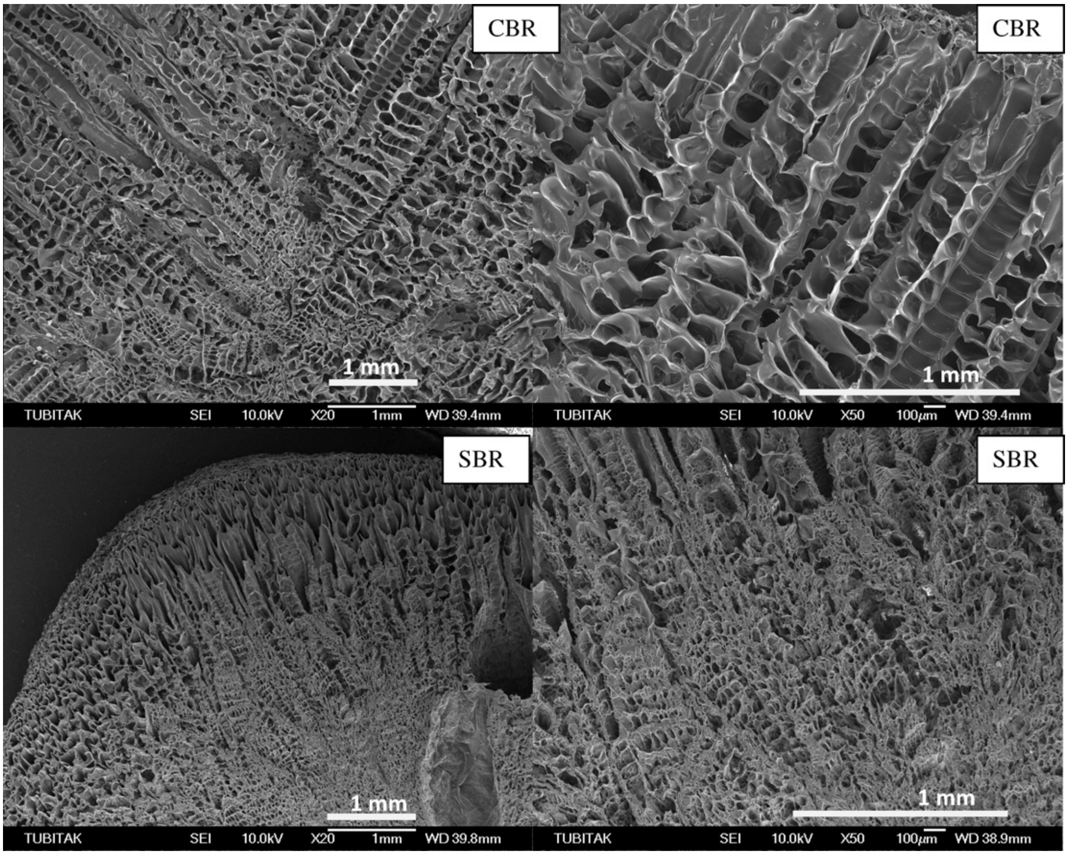


Fig. 4. SEM of CBR and SBR networks formed at a 2.5% concentration. Crosslinker (S_2Cl_2) concentration = 6%.

benzene becomes a poor solvent at low temperatures. Thus, PIB chains are not only expelled from the solution due to the freeze-induced concentrations, but they also undergo cooling-induced phase separation to form agglomerates of various sizes. Accordingly, both cryogelation and cooling-induced phase separation mechanisms govern the formation process of the pores in PIB networks. Formation of mm-sized large pores also support the hypothesis that two mechanisms are operative in the formation of the porous structures in the PIB1 and the PIB2 networks.

The mechanical properties of equilibrium swollen rubber gels in the form of rods were investigated by compression tests. Typical stress–strain data of the gels in the form of f versus $(\alpha - \alpha^{-2})$ plots are shown in Fig. 6A. PIB gels formed at a 5% rubber concentration exhibited moduli of elasticities of 1200 ± 200 Pa, which is about twice the moduli of CBR or SBR gels (540 ± 20 Pa). The lower elastic moduli of CBR and SBR gels as compared to the PIB gels is in accordance with their high volume swelling ratios in toluene (Fig. 1A). Thus, although the degrees of unsaturation in SBR and CBR are much larger than in PIB, PIB undergoes more efficient crosslinking reactions with sulfur monochloride. Further, CBR and SBR gels formed at 2.5% rubber concentration exhibited elastic moduli of approximately 110 ± 30 Pa. We have to mention that all the gels were very tough and could be compressed up to about 100% strain without any crack development. This behavior is shown in Fig. 6B where the stress–strain curves in the form of f versus $1 - \alpha$ (fractional deformation) plots are given. No rubber gels broke even at a strain of 100%. Photographs in Fig. 6C also demonstrate how the SBR gel sustains a high compression. The gel remains mechanically stable up to complete compression, and, after the release of the load and the addition of toluene, the sample immediately recovers its original shape.

3.3. Sorption of crude oil, petroleum products and olive oil

Sorption tests for the various pollutants mentioned in Section 2 were conducted using organogel samples prepared in the form of cylindrical tissues of 14 cm in diameter. Pictures given in Fig. 6D

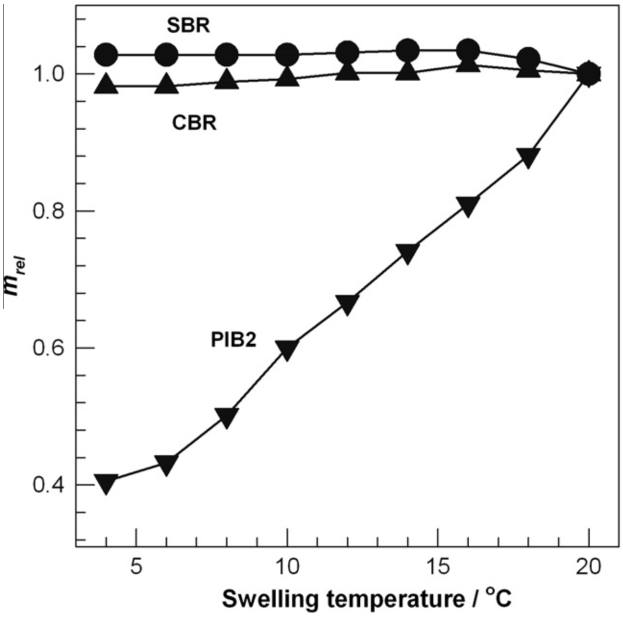


Fig. 5. Normalized weight swelling ratio m_{rel} of the organogels based on SBR, CBR and PIB2 in benzene shown as functions of the swelling temperatures. The gels were prepared at 20 °C in the presence of 12% S_2Cl_2.

were taken from SBR gel tissues before the sorption tests. The sorption properties were first analyzed by immersing dry gel samples in oil media until attaining swelling equilibria. The results of the sorption kinetics of the organogels in contact with various pollutants are shown in Fig. 7, in which the sorbed amount of pollutants is plotted against the contact time. The crosslinker content of the organogels was 6%, while the rubber concentrations during the gel preparation were 5% (filled symbols) and 2.5% (open symbols). The sorption rates of all gels were very rapid and absorption of the pollutants occurred in less than 10–20 min. The fast sorption rate is due to the interconnected pore structure of these materials (Figs. 3 and 4); the pollutants are sorbed through the micrometer-sized pores by convection, which is much faster than the diffusion process that dominates nonporous gels. Fig. 7 also shows that CBR and SBR gels prepared at $C_p = 2.5\%$ exhibit the highest sorption capacities. Moreover, PIB gels exhibit the fastest uptake rate for the pollutants, probably due to their large pores that were formed by phase separation.

Fig. 7 demonstrates that the sorption capacity of cryogels greatly varies depending on the type of rubber used. Among the cryogels prepared at $C_p = 5\%$, the uptake of crude oil and its derivatives is much higher for cryogels derived from PIB than the uptake seen in CBR- or SBR-based cryogels. Furthermore, a reverse situation is observed for the uptake of olive oil; in this case, CBR and SBR cryogels exhibit higher uptake capacities compared to the PIB cryogels. These results can be explained by examining the solubility parameters of the liquid components and the rubbers. According to the Hildebrand theory [30], the solvating (swelling) power of a polymer–solvent medium can be estimated from $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. The solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized, i.e., when the solubility parameters of the two components are most closely matched. δ_1 of vegetable oil is 18–19 MPa$^{1/2}$ [31,32], which is close to δ_2 of CBR and SBR (18.0 and 18.1 MPa$^{1/2}$, respectively [33]). As a consequence, vegetable oils are good solvents for both rubbers and, therefore, cryogels derived from these rubbers exhibit large uptake capacities. Thus, favorable interactions between the olive oil and CBR or SBR increase the adherence of oil onto the surface of the polymer such that more oil is retained within these cryogels. However, δ_2 of PIB is much lower (16.5–16.8 MPa$^{1/2}$ [21,31]), but is close to the δ_1 of aliphatic and some aromatic hydrocarbons such

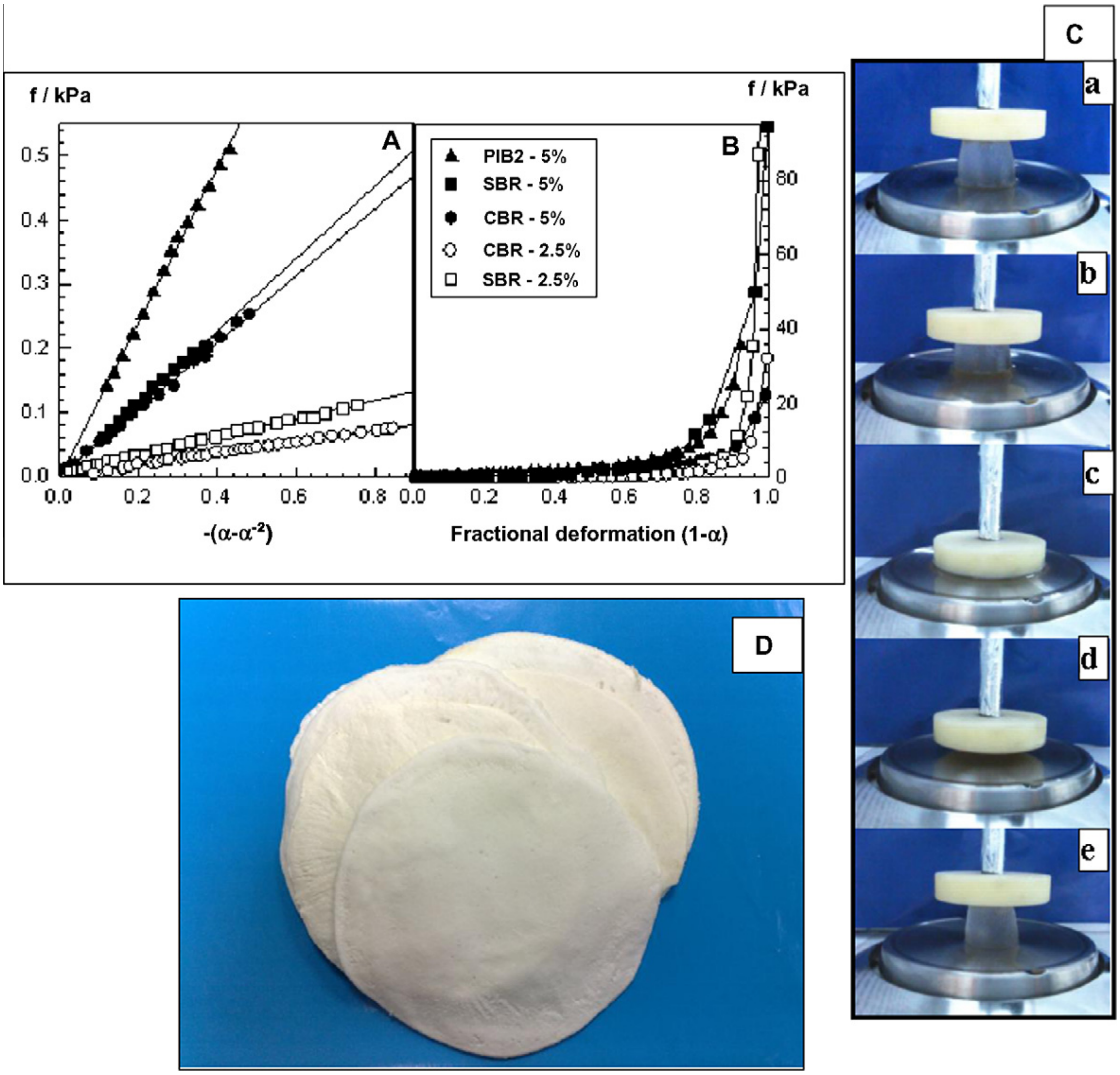


Fig. 6. Typical stress–strain data of rubber gels as the dependence of f on $\alpha - \alpha^{-2}$) (A) and $1 - \alpha$ (B). S_2Cl_2 = 6%. Types of rubber and the rubber concentrations used during gel preparation are indicated. (C) Photographs of the SBR gel formed at 5% rubber concentration during the compression test. After compression of the gel, addition of toluene converted the gel back to its initial state. S_2Cl_2 = 6%. (D) Photographs of the SBR gel formed at 5% rubber concentration in the form of tissues. S_2Cl_2 = 6%.

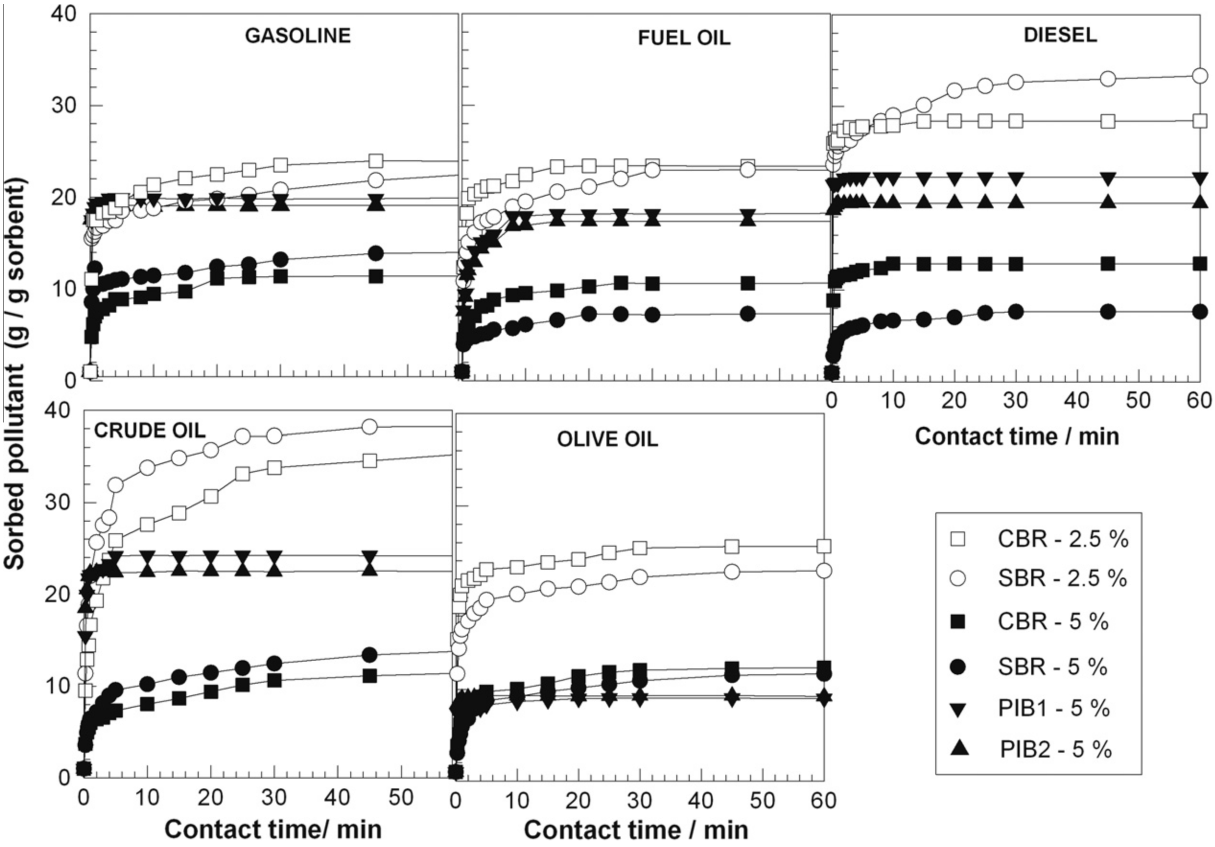


Fig. 7. Sorption capacities of the organogels versus contact time with various pollutants. Crosslinker concentration = 6%. C_p = 5%: PIB1 (▼), PIB2 (▲), CBR (■), SBR (●). C_p = 2.5%: CBR (□), and SBR (○).

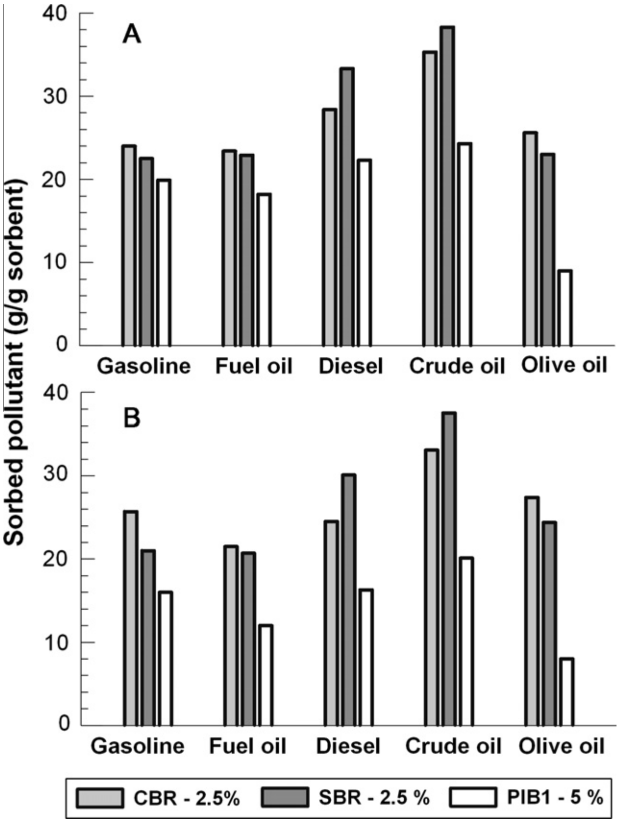


Fig. 8. Maximum (A) and continuous sorption capacities (B) of the organogels for various pollutants. Crosslinker concentration = 6%. Amounts of sorbed pollutants are shown on the bars.

that the uptake of crude oil and its derivatives is much higher for PIB cryogels.

In Fig. 8A, the maximum sorption capacities of the best rubber sorbents, namely CBR and SBR formed at C_p = 2.5%, and PIB1 are compared for various pollutants. One gram of SBR or CBR sorbs 35–38 g crude oil or 23–26 g olive oil as compared to 23 g/g and 9 g/g, respectively, obtained using the PIB1 gel. One should also compare these values with those of commercial oil sorbents. The widely-used oil sorbents based on polypropylene have sorption capacities for both crude oil and olive oil of about 15 g/g [14]. Thus, SBR and CBR gels have sorption capacities that are about twice the capacity of the commercial oil sorbents. Another result gleaned from Fig. 8A is that the sorption capacity of the organogels is the highest for crude oil, i.e., for the pollutant with the highest viscosity. This implies that, although increased viscosity of the pollutant decreases the rate of sorption, favorable hydrophobic interactions between the crude oil and the hydrophobic polymer dominate the sorption process so that more oil is retained within the rubber gels.

The reusability of the sorbents and the recoverability of the pollutants are important aspects within oil spill cleanup procedures [2]. Commercial oil sorbents are not reusable, thus they form a solid waste after the cleanup procedure [14]. However, all organogels prepared in this work can be squeezed completely to give up the pollutants without any crack developments (Fig. 6C). The reusability of the organogels and their continuous sorption capacities were checked by repeated sorption–squeezing cycles. The sorption–squeezing cycles were repeated 20 times to obtain the recycling efficiency and continuous extraction capacity of the organogels. The results are shown in Fig. 9 in which the uptake capacity of the organogels in each cycle for various pollutants is plotted against the number of sorption–squeezing cycles. It is seen that

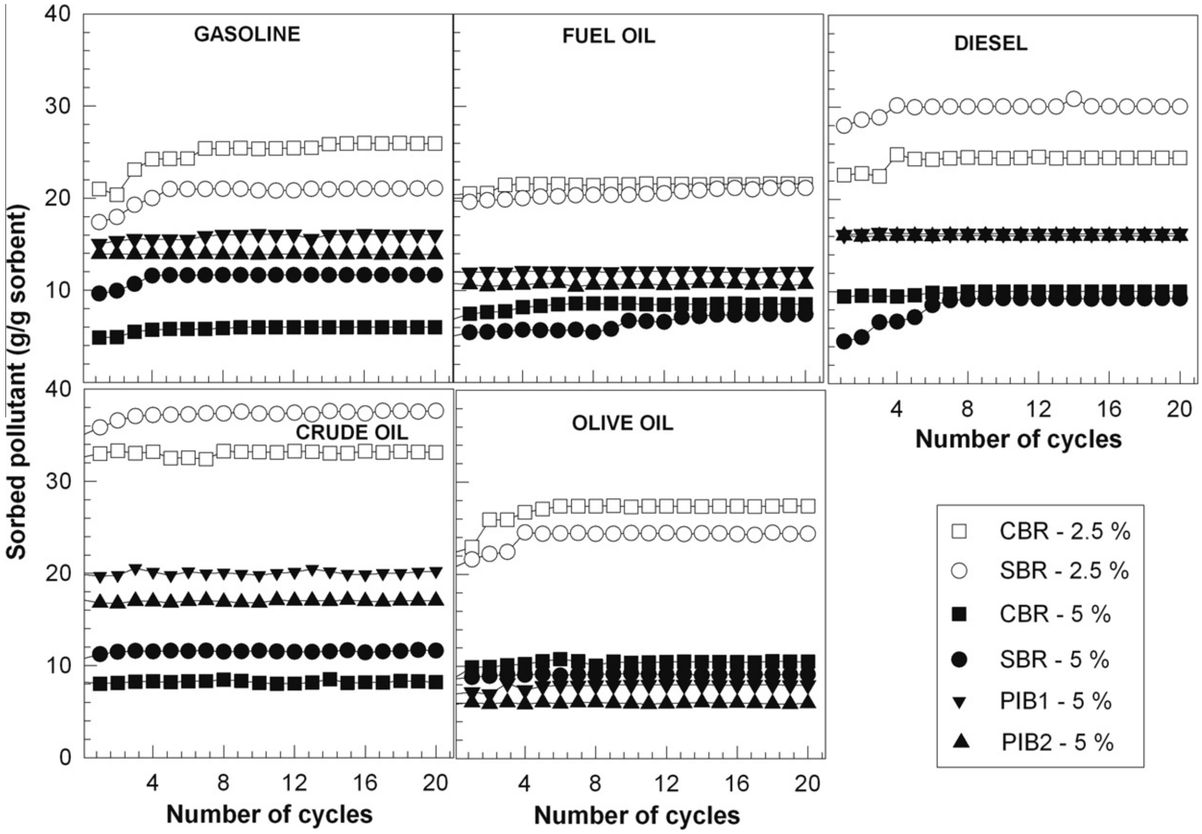


Fig. 9. Continuous extraction capacities of the organogels for various pollutants as a function of the number of cycles. Crosslinker concentration = 6%. C_p = 5%: PIB1 (▼), PIB2 (▲), CBR (■), SBR (●). C_p = 2.5%: CBR (□), and SBR (○).

the amount of pollutant sorbed in each cycle is almost constant for all cycles larger than 6. For example, the amount of pollutant sorbed is equal to 37.5 ± 0.1 g/g and 24.4 ± 0.1 g/g for SBR gels formed at C_p = 2.5% in contact with crude oil and olive oil, respectively. The average sorption capacities, i.e., the continuous extraction capacities of the best sorbents, are reported in Fig. 8B. These results demonstrate that the continuous capacity is close related to the maximum capacity of gels, indicating the high reusability of all organogels and high recoverability of the crude oil, petroleum products and olive oil. Sorption tests were also conducted using pollutants that spread in water, as described in the literature [14]. Similar results as those given in Fig. 8B were obtained. The fact that 37.5 g of crude oil could be recovered by the SBR gel in each cycle means that about one ton of crude oil could be separated from the surface waters through the use of 1 kg of SBR gel networks over 25 cycles.

4. Conclusions

Macroporous organogels were prepared from frozen solutions of PIB, CBR and SBR in benzene at −18 °C using sulfur monochloride as the crosslinker. The pores in CBR and SBR networks are regular and oriented along a common direction, whereas those in PIB networks are irregular with broad size distributions from μm to mm sizes. It was shown that the regular morphology of CBR and SBR networks is due to the fact that benzene is a good solvent for CBR and SBR chains such that pores are only generated by the cryogelation mechanism. Sorption tests conducted using the organogels demonstrate that they are efficient materials for the removal of crude oil, petroleum products and olive oil from surface waters. The most important feature of the rubber gels is their reusability after simply being squeezed; the continuous sorption capacities of CBR and SBR gels for crude oil and olive oil are 33–38 and 24–27 g/g, which are two to three times the capacity of the gels derived from PIB. The measured sorption capacities of all organogels are also much higher than those of commercial oil sorbents, suggesting that the rubber gels are a better alternative to the widely used polypropylene sorbents because of their improved efficiency for oil sorption and their reusability.

Acknowledgements

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