

## Porous rubber cryogels: effect of the gel preparation temperature

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**Abstract** This paper examines the effect of the gel preparation temperature ( $T_{\text{prep}}$ ) on the physical properties of the rubber-based macroporous organogels prepared by solution crosslinking in benzene at subzero temperatures. Cis-polybutadiene (CBR) and styrene-butadiene rubber (SBR) were used as the rubber components, while sulfur monochloride ( $\text{S}_2\text{Cl}_2$ ) was the crosslinker in the gel preparation. It was shown that  $T_{\text{prep}}$  is an extremely important parameter to adjust the porous structure and thus, the cryogel properties. The networks formed by CBR and SBR showed an aligned porous structure with an exception of honey-comb structured porous SBR cryogels prepared at  $-2\text{ }^\circ\text{C}$ .  $10^1$ - to  $10^2$ - $\mu\text{m}$  sized regular pores of the networks caused by the benzene crystals act as a template during gelation, separated by 10–20  $\mu\text{m}$  pore walls in thickness. They exhibit fast swelling and deswelling properties as well as reversible swelling–deswelling cycles in toluene and methanol, respectively. The ability of the organogels for the removal of petroleum products from aqueous solutions was also demonstrated using diesel and crude oil as model pollutants. In addition, the reusability of the organogels and their continuous sorption capacities were checked by repeated sorption–squeezing cycles. All the tests showed that the aligned porous organogels are suitable materials for the oil spill cleanup procedures.

**Keywords** Macroporous · Aligned pore · Swelling · Gelation temperature · Cryogelation

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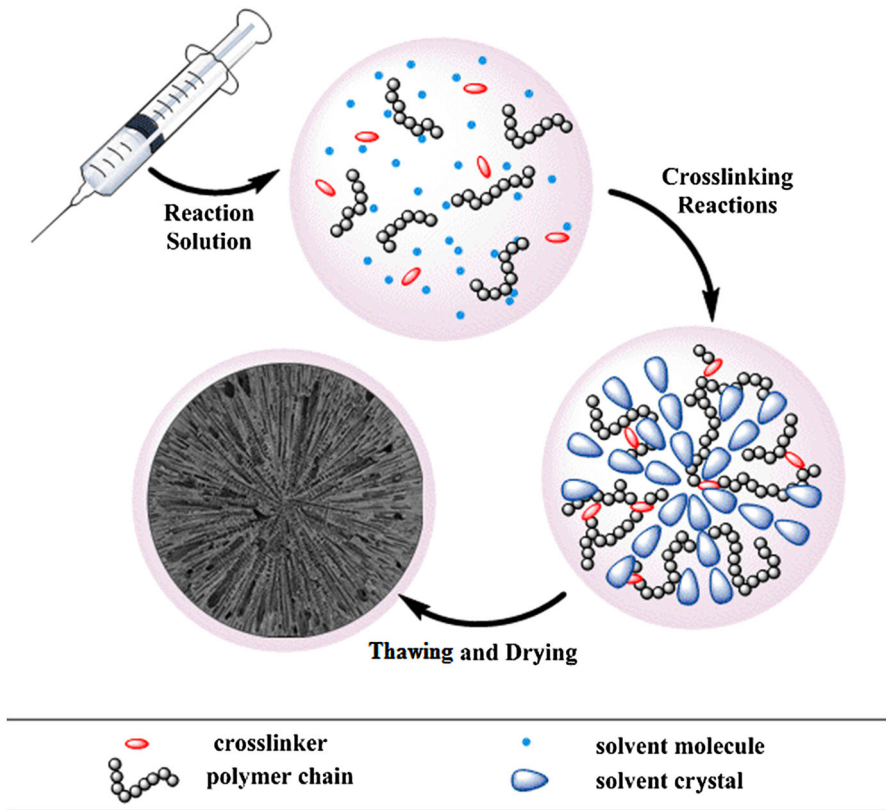
## Introduction

Oil is one of the most important energy resources in the modern era. However, as long as it is explored, transported and used there will be the risk of a spillage with the potential to cause significant environmental damage. As a result of the huge economic and environmental destruction from oil spills, several cleanup techniques have been developed, such as the use of booms, skimmers, agricultural products, dispersants and sorbents [1–5]. Among all the existing techniques, the use of sorbents is of great interest because it is cheap, simple and effective. In addition, it allows the collection and complete removal of oil. The efficiency of an oil sorbent material is determined by properties, such as hydrophobicity, high uptake capacity, retention over time, oil recovery, reusability or biodegradability.

In the previous reports, we have shown that frozen solutions of various types of rubber including cis-polybutadiene (CBR), styrene-butadiene (SBR) and butyl rubber (BR) can easily be crosslinked in organic solvents using sulfur monochloride ( $S_2Cl_2$ ) to produce tough and superfast responsive materials [6–9]. The rubber gels thus obtained were macroporous and able to absorb large volumes of organic solvents in a short period of time. It was also shown that porous rubber gels are suitable sorbent materials for oil spill cleanup from surface waters due to their high hydrophobicity, fast responsivity and reusability [6, 8].

Low-temperature gelation technique, known as cryogelation, was used to prepare the organogel sorbents by crosslinking of rubber in organic solvents. 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 [10–19]. Similar with the nature, during the freezing of a rubber solution in benzene or in cyclohexane, the solutes, i.e., the polymer chains and crosslinker molecules are expelled from the solvent crystals and concentrates within the channels between the crystals. Thus, the crosslinking reactions only take place in these unfrozen regions acting as “microreactors”. As demonstrated in Fig. 1, after the crosslinking reactions and after thawing of the solvent crystals, a macroporous material is produced whose microstructure is a negative replica of the crystals that formed. The macropores are separated from each other by thick rubber network due to the increased rubber concentration in the unfrozen part of the semi-frozen reaction system. It is known that the size of the solvent crystals and thus the pores are dependent on the freezing temperature which is not investigated before for the SBR- and CBR-based cryogel systems.

In the present study, a series of CBR and SBR organogels were prepared at various temperatures  $T_{\text{prep}}$ , which is the temperature of the thermostated bath in which the reactions were carried out. The solution crosslinking reactions were performed in benzene at a rubber concentration of 5 w/v%. The cryogels were characterized by swelling tests as well as by scanning electron microscopy (SEM) measurements on dry state. As will be shown below, the gel preparation temperature  $T_{\text{prep}}$  is an important parameter to regulate the properties of cryogels such as swelling behavior, porosity, sorption kinetics and morphology, and thus to obtain aligned porous materials which have particular importance for application areas of tissue engineering, microfluidics and organic electronics [20, 21].



**Fig. 1** Schematic representation of cryogel formation starting from reaction solution to a macroporous polymer

## Experimental

### Materials

Cis-polybutadiene (CBR, Nizhnekamskneftekhim Inc.) and styrene-butadiene rubber (SBR, Petroflex) were used as the rubber components. SBR is a copolymer with 86 % internal unsaturated groups whereas 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 a constant mass. Weight average 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 18 simultaneously detected scattering angles. The molecular weights,  $M_w$ , were 210 and 371 kg/mol for SBR and CBR, respectively. The characteristics of SBR and CBR are shown in Table 1. The crosslinking agent sulfur monochloride,  $S_2Cl_2$ , was purchased from Aldrich Co.

**Table 1** Characteristics of styrene-butadiene and CBR rubbers

| Rubber                              | Code | Molecular weight (g/mol) | Density (g/ml) | Molecular formula                                                                                            |
|-------------------------------------|------|--------------------------|----------------|--------------------------------------------------------------------------------------------------------------|
| Styrene-butadiene rubber (SBR-1502) | SBR  | $2.1 \times 10^5$        | 0.94           | $\text{---}(\text{CH}_2\text{---CH}(\text{C}_6\text{H}_5))_n(\text{CH}_2\text{---CH=CH---CH}_2)_m\text{---}$ |
| Cis-polybutadiene rubber (CBR-1203) | CBR  | $3.7 \times 10^5$        | 0.93           | $\text{---}(\text{CH}_2\text{---CH=CH---CH}_2)_n\text{---}$                                                  |

Benzene, toluene and methanol (all Merck reagents) were used as the solvents for the solution crosslinking reactions, swelling and deswelling experiments, respectively. Crude oil ( $d = 0.89$  g/ml, viscosity = 350 cP at 25 °C) and diesel (setan number 55,  $d = 0.85$  g/ml, viscosity = 5.0 cP at 25 °C) used in the sorption experiments were provided from Ozan Sungurlu wells of Turkey and BP ultimate diesel, respectively.

### Gelation reactions

The organogels were prepared by the solution crosslinking technique at a rubber concentration,  $C_0$ , of 5 % w/v according to the following scheme: rubber (5 g) was first dissolved in 100 mL of benzene at  $20 \pm 1$  °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 and glass Petri dishes of 140 mm in diameter and 20 mm in height. The crosslinking reactions were carried out in a cryostat at predetermined temperatures for 1 day. The crosslinker concentration in the reaction solution was expressed as  $S_2Cl_2$  v/w%, which is the volume of  $S_2Cl_2$  added per 100 g of rubber. Our previous works conducted in benzene at  $-18$  °C show that the reactions between  $S_2Cl_2$  and the internal unsaturated groups of CBR or SBR are complete, if  $S_2Cl_2$  concentration is 6 v/w% [8]. In the present study, we fixed the crosslinker content at 6 v/w%  $S_2Cl_2$  as well as at half of this amount while the gelation temperature was varied over a wide range. After the crosslinking, the reaction system was thawed at room temperature for 1 h, and the formed gel was squeezed to remove benzene. The gel was then washed several times first with toluene, then with methanol, and finally, was dried under vacuum at room temperature.

### 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 week 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. To dry the equilibrium swollen gel samples, the gels were first immersed in methanol overnight and then dried under vacuum. The gel fraction,  $W_g$ , defined as the amount of crosslinked (insoluble) polymer obtained from one gram of rubber was calculated as follows:

$$W_g = \frac{m_{\text{dry}}}{10^{-2} m_o C_0}, \quad (1)$$

where  $m_{\text{dry}}$  and  $m_o$  are the weights of the gel samples after drying and just after preparation, respectively, and  $C_0$  is the rubber concentration used in the gel

preparation in w/v%. The equilibrium volume and weight swelling ratios of the gels ( $q_v$  and  $q_w$ , respectively) were calculated as:

$$q_v = \frac{V}{V_{\text{dry}}} = \left( \frac{D}{D_{\text{dry}}} \right)^3 \quad (2)$$

$$q_w = \frac{m_{\text{swollen}}}{m_{\text{dry}}}, \quad (3)$$

where  $D$  and  $D_{\text{dry}}$  are the diameters of the equilibrium swollen and dry gels, respectively, and  $m_{\text{swollen}}$  is the weight of the equilibrium swollen gel. The swelling measurements were conducted 6 times with an experimental error of 10–20 %.

For the texture determinations of the dried gels, scanning electron microscopy (SEM) studies were carried out at various magnifications between 10 and 300 times (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.

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. All tests were performed at  $20 \pm 1$  °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. The uptake capacity at selected time intervals and the reusability as well as their continuous extraction capacities of the sorbents for pollutants were determined by the methods described previously [6]. This sorption–squeezing cycle was repeated 10 times to obtain the recycling efficiencies and continuous extraction capacities of the rubber gels.

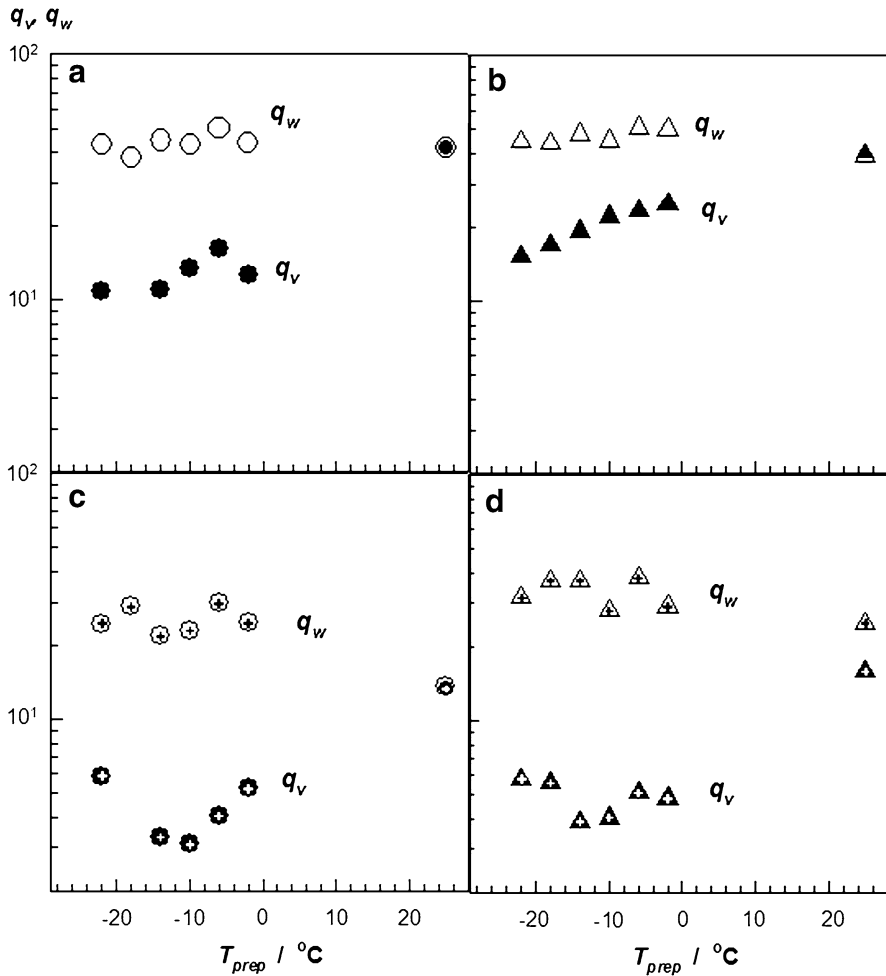
## Results and discussion

SBR and CBR gels were prepared both at low temperatures, that is, below the freezing point of benzene, and 25 °C, which were designated as cryogels and conventional gels, respectively. Before characterization of the organogels, the variation of the crosslinking efficiency of  $\text{S}_2\text{Cl}_2$  depending on the gel preparation temperature was investigated by the gel fraction measurements. It was found that gel fraction of all rubber gels reported in this study was close to unity indicating high crosslinking efficiency of  $\text{S}_2\text{Cl}_2$  at temperatures down to  $-22$  °C.

### Effect of $T_{\text{prep}}$ on swelling behavior

In Fig. 2, the swelling capacities of the rubber gels in toluene in terms of the equilibrium weight ( $q_w$ ) and volume swelling ratios ( $q_v$ ) are plotted against the gel preparation temperature  $T_{\text{prep}}$ . The gels were prepared starting from a 5 % solution of SBR and CBR in benzene in the presence of 3 and 6 v/w%  $\text{S}_2\text{Cl}_2$  crosslinker.

At 3 %  $\text{S}_2\text{Cl}_2$  (Fig. 2a, b), the weight swelling ratios  $q_w$  of both SBR and CBR gels formed at subzero temperatures are  $45 \pm 4$ , independent on the temperature



**Fig. 2** The equilibrium weight  $q_w$  (open symbols) and volume swelling ratios  $q_v$  (filled symbols) of SBR (a, c) and CBR (b, d) gels in toluene shown as a function of the gel preparation temperature  $T_{\text{prep}}$ .  $C_0 = 5$  w/v%,  $S_2Cl_2 = 3$  (a, b) and 6 v/w% (c, d)

$T_{\text{prep}}$  between  $-22$  and  $-2$  °C. As expected, increasing  $S_2Cl_2$  content from 3 to 6 %, decreases the swelling capacity of the organogels (Fig. 2c, d). Moreover, for both CBR and SBR gels prepared below the freezing point of benzene, the equilibrium weight swelling ratios  $q_w$  are much larger than the equilibrium volume swelling ratios  $q_v$ . In contrast, the gels formed at  $25$  °C exhibit similar  $q_w$  and  $q_v$  values. We should note that the weight swelling ratio  $q_w$  includes the solvent located in both pores and in the polymer region of the gel, while, assuming isotropic swelling, the volume swelling  $q_v$  only includes the solvent in the polymer region. Therefore, the difference between values of  $q_w$  and  $q_v$  provide information about the internal structure of gels such as their porosities in the swollen state [22]. The larger

the difference between  $q_w$  and  $q_v$ , the larger is the amount of solvent locating in the pores, i.e., the larger is the total volume of pores.

#### Effect of $T_{\text{prep}}$ on porosity

From the weight and volume swelling ratios of rubber gels, their swollen state porosities ( $P_s$ ) can be estimated using the equation [22]:

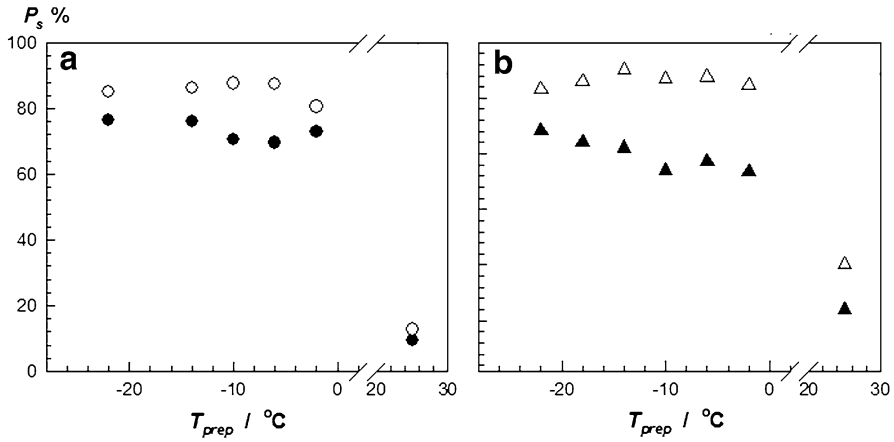
$$P_s \% = \left( 1 - \frac{q_v}{1 + (q_w - 1)\rho/d_1} \right) 10^2 \quad (4)$$

where  $\rho$  and  $d_1$  are the densities of the rubber and the swelling agent (toluene), respectively. Assuming that  $\rho = 0.94$  and  $0.93$  g/mL for CBR and SBR, respectively (Table 1), and  $d_1 = 0.876$  g/mL, the calculated swollen state porosities  $P_s$  are shown in Fig. 3a, b plotted against the  $T_{\text{prep}}$  for SBR and CBR gels, respectively. The gels formed at subzero temperatures exhibit significant porosities.  $P_s$  is close to 90 at 3 %  $\text{S}_2\text{Cl}_2$  contents while, for SBR gels, it slightly decreases to about 75 % as the crosslinker content is increased to 6 %. Further, the swollen state porosity rapidly decreases as  $T_{\text{prep}}$  is increased and becomes almost zero above the freezing point of benzene.

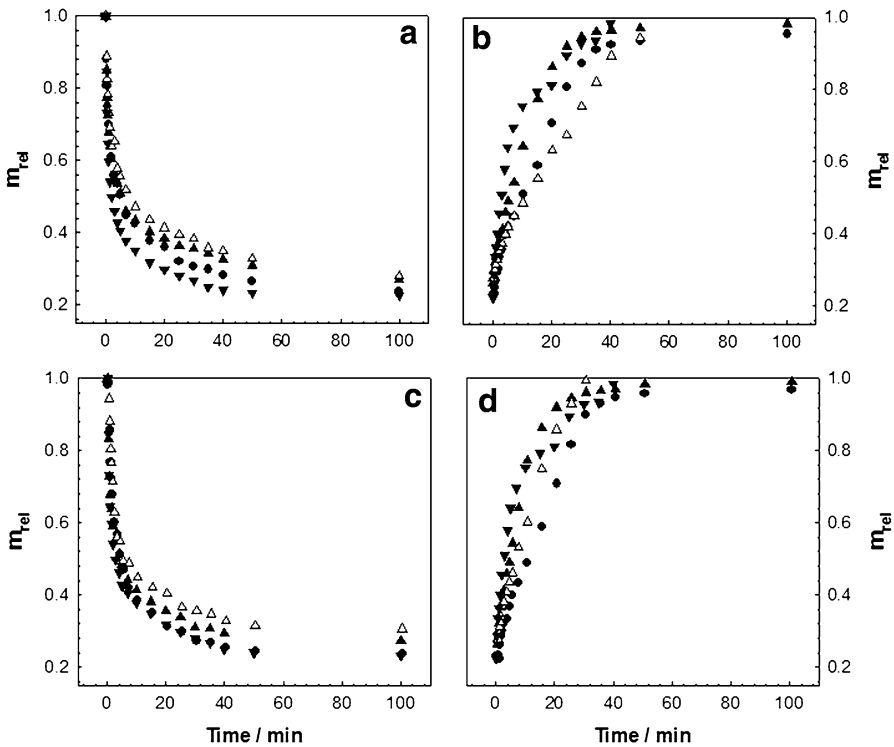
#### Effect of $T_{\text{prep}}$ on swelling–deswelling kinetics

CBR and SBR cryogels formed at various  $T_{\text{prep}}$  were subjected to swelling and deswelling processes in toluene and in methanol, which are good and poor solvents, respectively. For this purpose, the swollen gel was first immersed in methanol and the weight change of the gel was determined as a function of the deswelling time. After reaching the equilibrium state in methanol, the gel was immersed in toluene and the reswelling process was monitored by recording the weight increase with time. To check the durability of the gel sample against the volume changes, this swelling–deswelling cycle was repeated twice.

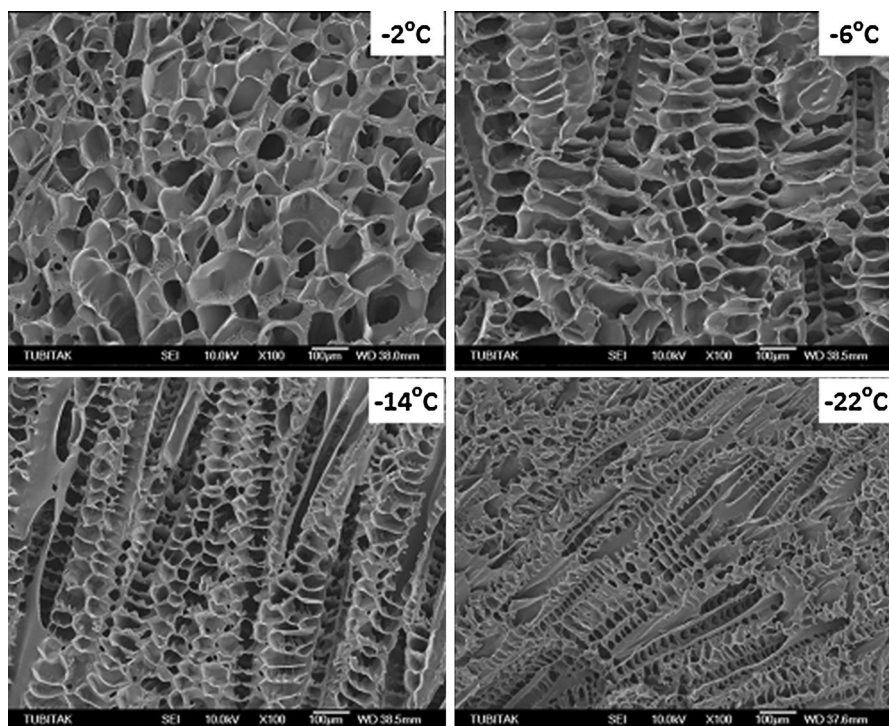
Typical results for CBR gels are shown in Fig. 4 where the normalized gel mass  $m_{\text{rel}}$  (mass of gel at time  $t$ /equilibrium swollen mass in toluene) is plotted against the time of deswelling in methanol (a, c) and reswelling in toluene (b, d). Completely reversible swelling–deswelling cycles were obtained using gel samples prepared at various temperatures. Independent of the  $T_{\text{prep}}$ , all the CBR gels attain their equilibrium collapsed and equilibrium swollen states within 1 h. As will be seen in the next section, all the gels formed at subzero temperatures have an interconnected pore structure. This microstructure is responsible for their fast swelling and deswelling rates. Thus, solvent molecules can enter or leave the cryogel through interconnected pores by convection instead of the diffusion process that dominates the conventional gels. They also exhibit completely reversible swelling–deswelling cycles, i.e., the gels return to their original shape and mass after a short reswelling period. Similar results were also obtained for organogel samples formed from frozen SBR solutions.



**Fig. 3** Swollen state porosities  $P_s$  of SBR (a) and CBR (b) gels shown as a function of the gel preparation temperature  $T_{\text{prep}}$ .  $C_0 = 5$  w/v%,  $S_2Cl_2 = 3$  (open symbols) and 6 w/v% (filled symbols)



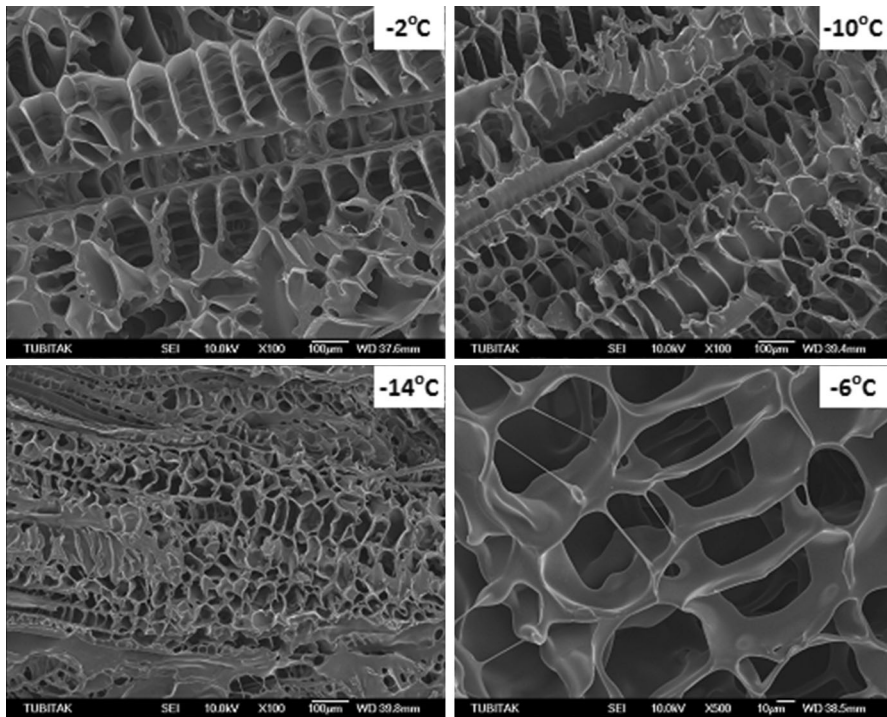
**Fig. 4** Deswelling and reswelling cycles of CBR gels in methanol (a, c) and in toluene (b, d), respectively, shown as the variation of the relative gel mass  $m_{\text{rel}}$  with the contact time.  $C_0 = 5$  w/v%,  $S_2Cl_2 = 6$  v/v%.  $T_{\text{prep}} = -2$  (filled circle),  $-6$  (filled triangle),  $-10$  (open triangle) and  $-22$  °C (filled inverted triangle)



**Fig. 5** SEM of SBR networks prepared at  $T_{\text{prep}} = -2, -6, -14$ , and  $-22$  °C.  $C_0 = 5$  w/v%,  $S_2Cl_2 = 6$  v/w%. The scaling bars and magnifications are 100  $\mu\text{m}$  and  $\times 100$ , respectively

### Effect of $T_{\text{prep}}$ on morphology

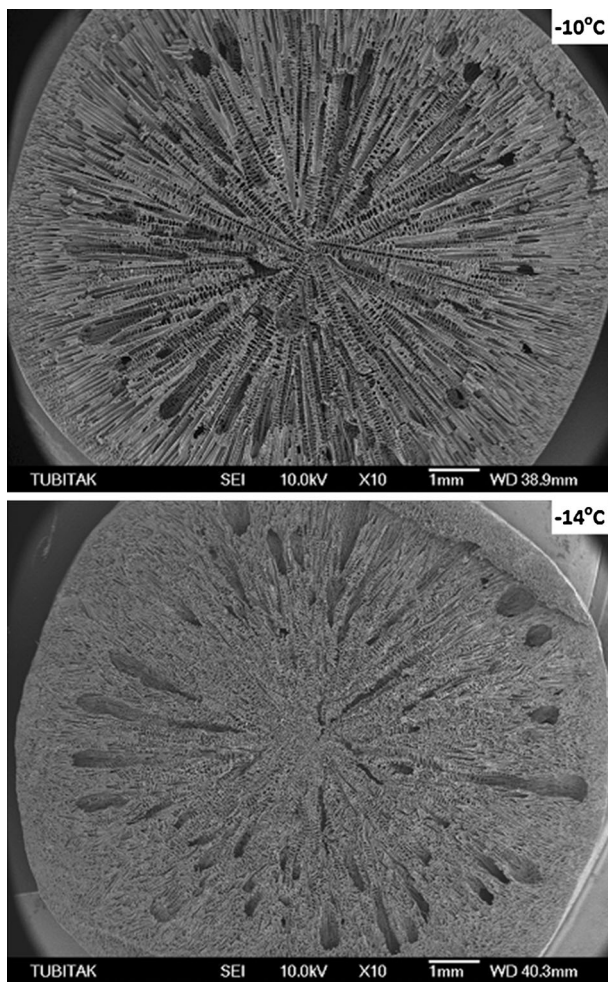
Macroporous morphology of rubber organogels was investigated after drying of the gel samples under vacuum. Visual observations showed that all the cryogels retain their original shape without any distortion in their cylindrical form during the drying process, indicating the mechanical stability of their network structure. To visualize the morphological texture and to explore the effect of the gel preparation temperature on the size and especially the regularity of the pores, dried organogel samples were examined by SEM. Figure 5 shows SEM images of SBR networks formed at various  $T_{\text{prep}}$  between  $-22$  and  $-2$  °C. Initial rubber and the crosslinker concentrations used in the gel preparation were 5 and 6 %, respectively. All the gel samples formed below the freezing point of benzene ( $5.5$  °C) have a regular porous structure with pore sizes of  $10^1$ – $10^2$   $\mu\text{m}$ . We can explain the formation of regular pores with the fact that benzene used as a solvent during the cryogelation reactions is a good solvent for both CBR and SBR polymers over the whole range of  $T_{\text{prep}}$  [8]. Thus, due to the absence of a phase separation during the initial cooling period, only cryogelation mechanism is responsible for the formation of the porous structures in both SBR and CBR cryogels. After cryogelation, removing the frozen solvent that acts as a porogen leads to a regular pore structure [14, 23, 24].



**Fig. 6** SEM of CBR networks prepared at  $T_{\text{prep}} = -2, -10, -14$  and  $-6$  °C.  $C_0 = 5$  w/v%,  $S_2Cl_2 = 6$  v/w%. The scaling bars are 100  $\mu\text{m}$  ( $-2, -10$  and  $-14$  °C) and 10  $\mu\text{m}$  ( $-6$  °C)

Figure 5 also shows that, as  $T_{\text{prep}}$  is decreased, the pore size decreases from  $10^2$ – $10^1$   $\mu\text{m}$ . Decreasing the gelation temperature means faster freezing of the reaction solution which necessarily reduces the time available for solvent crystals to grow. This would prevent the formation of large crystals. Since solvent crystals in the cryogelation systems act as a template for the formation of pores, the same relationship also exists between the pore size and  $T_{\text{prep}}$  of the cryogels. Under fast freezing conditions, formation of small solvent crystals leads to the small porous networks after thawing the reaction system. In addition, increasing freezing rate shortens the duration of the initial nonisothermal period of the reactions so that the crosslinking mainly occurs in the unfrozen microzones of the apparently frozen reaction system which may also decrease the size of the pores [16]. Freezing point depression may also be responsible for large pores of cryogels prepared at relatively higher temperatures.

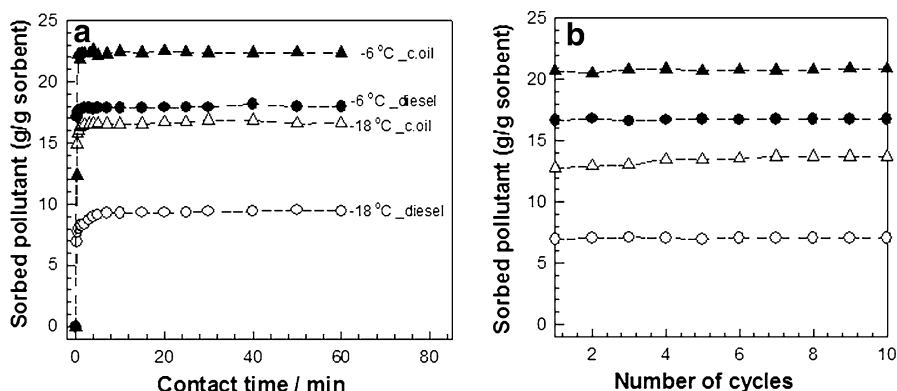
SEM images of the macroporous CBR networks formed at various  $T_{\text{prep}}$  are shown in Fig. 6. Similar to the SBR networks, decreasing  $T_{\text{prep}}$  also decreases the size of the pores and destroys their regularity due to the poor thermal conductivity of the reaction solution. Thus, the pore size of SBR and CBR networks can be reduced by decreasing the temperature of the cryogelation system. Note that



**Fig. 7** SEM of CBR networks prepared at  $T_{\text{prep}} = -10$  and  $-14$  °C.  $C_0 = 5$  w/v%,  $S_2Cl_2 = 6$  v/w%. The scaling bars and magnifications are 1 mm and  $\times 10$ , respectively

experiments carried out at smaller reactors with a diameter of 3.7 mm partially destroyed the regularity of the pore structures due to the increasing rate of the freezing of the reaction solution. Figure 6 (right-bottom) is also presenting the SEM image of an organogel at a larger magnification indicating that the rubber cryogels consist of an interconnected pore structure.

According to the theoretical results, the transition from gelation to cryogelation regime occurs at temperatures close to the freezing point of the pure solvent [17]. For the CBR and SBR rubber system the transition occurs at around  $-2$  °C, i.e., about 8 °C below the freezing point of benzene. When a polymer solution or an aqueous suspension of solid particles is frozen very rapidly, the polymer or particles are typically encapsulated into the freezing front. If the freezing rate is below a



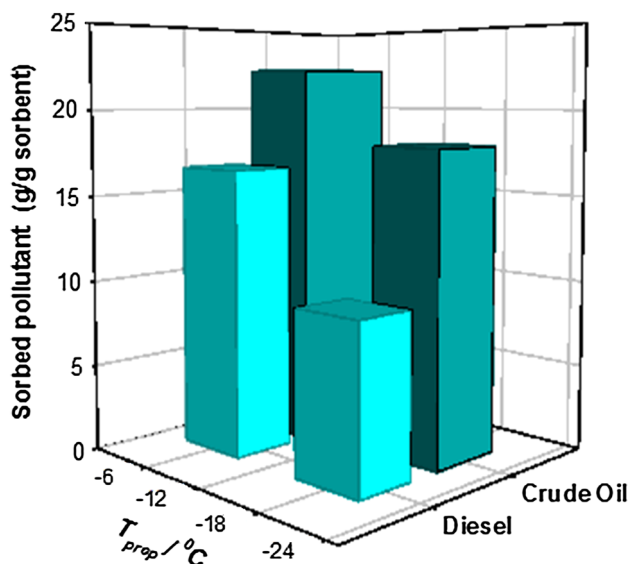
**Fig. 8** Crude oil (triangles) and diesel (circle) sorption capacities of CBR gels prepared at  $T_{\text{prep}} = -18$  (open symbols) and  $-6^{\circ}\text{C}$  (filled symbols) shown as functions of the contact time (a) and the number of cycles (b).  $C_0 = 5$  w/v%,  $S_2\text{Cl}_2 = 6$  v/w%

critical velocity, the polymer or solid particles are rejected from the freezing front and concentrated between the orientated ice crystals [25]. As shown in Fig. 5, SBR network has honey-comb morphology instead of aligned porous structures prepared only at  $-2^{\circ}\text{C}$  which is the transition temperature of these systems. However, CBR network has an aligned morphology at the same temperature (Fig. 6). The difference between SBR and CBR cryogels related with the different molecular structure of these polymers, i.e., bulky styrene groups on the main chain of SBR rubber that affect critical velocity of the freezing system.

Freezing of the benzene starts from the surface of the cylindrical reactor which is in contact with the cooling liquid and both the polymer chains and  $S_2\text{Cl}_2$  are encapsulated into the freezing front. By the time, across the moving freezing front temperature and polymer concentration gradient establish. This leads to the macroscopic instabilities due to which moving freezing front collapses, leaving behind pockets of unfrozen concentrated polymer solution [9, 21]. After the crosslinking reactions, the polymer phase becomes insoluble and, after thawing, preserves this aligned structure. The micrographs in Fig. 7 evidence the alignment of the pores in the CBR networks formed at  $-10$  and  $-14^{\circ}\text{C}$ , respectively. The images clearly indicate directional freezing of the solvent crystals in the direction from the surface to the interior. In contrast to the regular and aligned morphology of CBR and SBR networks prepared in benzene, the networks formed from butyl rubber (BR) exhibited a broad size distribution of pores from micrometer to millimeter size due to the poor solvent characteristic of benzene for BR leading to the thermally induced phase separation mechanism [9].

#### Effect of $T_{\text{prep}}$ on oil sorption capacity

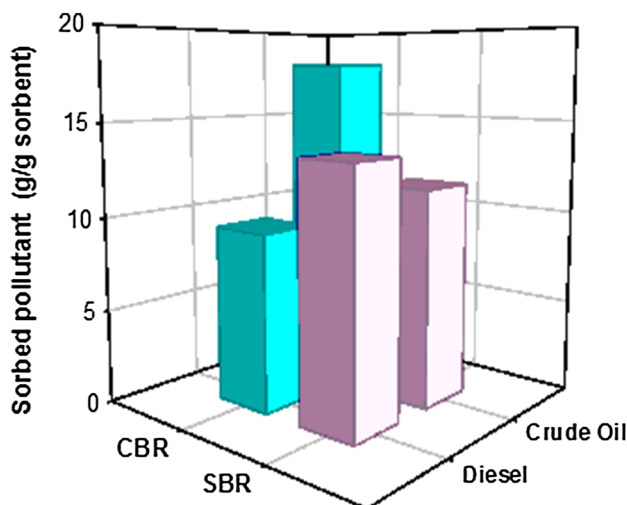
Sorption properties of organogels were analyzed by immersing dry gel samples in oil media until attaining swelling equilibria. Figure 8a shows the sorption kinetics



**Fig. 9** Sorption capacities of CBR gels prepared at  $T_{\text{prep}} = -18$  and  $-6$  °C shown as functions of the type of pollutants and  $T_{\text{prep}}$ .  $C_0 = 5$  w/v%,  $S_2Cl_2 = 6$  v/w%

of the cryogels prepared at two different temperatures  $T_{\text{prep}}$ , namely at  $-6$  and  $-18$  °C. Our previous work demonstrates that butyl rubber sorbent prepared at  $-18$  °C ( $-18\text{BR}$ ) is an efficient material for oil spill cleanup [6]. Therefore, in the present study, we selected  $-18$  °C as well as  $-6$  °C arbitrarily to compare and demonstrate the effect of the temperature on the oil sorption capacities of the rubber cryogels. Here, the sorbed amount of the model pollutants, diesel and crude oil, is plotted against the contact time. It is seen that CBR cryogels absorb the pollutants in  $<1$  min to attain the thermodynamic equilibrium. The fast sorption rate is due to the convection of the pollutants through the micrometer-sized and interconnected pore structure (Fig. 6, right-bottom).

Figure 9 was derived from Fig. 8a to compare the maximum sorption capacities of CBR gels for crude oil and diesel as pollutants. The gels prepared both at  $-18$  and  $-6$  °C have a higher sorption capacity for crude oil than the diesel. This is due to the higher viscosity of crude oil that increases the adherence of oil onto the surface of the rubber by favorable hydrophobic interactions between the crude oil and the hydrophobic polymer. Figure 9 also shows that, decreasing the preparation temperature from  $-6$  to  $-18$  °C, leads to a lower sorption capacity for the model pollutants. For example, diesel sorption capacity of cryogels prepared at  $-6$  °C is  $17 \text{ g g}^{-1}$ , which is about 2 times of the cryogels formed at  $-18$  °C. The same tendency is observed for crude oil sorption capacities that are 18 and  $22 \text{ g g}^{-1}$  for the gels prepared at  $-6$  and  $-18$  °C. We have to mention that widely used oil sorbents based on polypropylene (PP) have sorption capacities 15 and  $11 \text{ g g}^{-1}$  for crude and diesel, respectively. Thus, considering the gel preparation temperature CBR cryogels has higher sorption capacities than commercial oil sorbent PP.



**Fig. 10** Sorption capacities of CBR (cyan) and SBR (pink) gels prepared at  $-18\text{ }^{\circ}\text{C}$  shown as functions of the type of pollutants and  $T_{\text{prep}}$ .  $C_0 = 5\text{ w/v}\%$ ,  $\text{S}_2\text{Cl}_2 = 6\text{ v/w}\%$  (color figure online)

Although the reusability of the sorbents is an important aspect of the oil spill cleanup, commercial oil sorbents are not reusable and thus, they form a solid waste after the cleanup procedure [3]. Therefore, the reusability of the present organogels and their continuous sorption capacities were checked by repeated sorption–squeezing cycles. The results of the sorption–squeezing cycles are shown in Fig. 8b, where the sorption capacity of the cryogels in each cycle is plotted against the number of cycles. Comparison of Fig. 8a, b shows that the amount of the sorbed pollutant in each cycle is almost constant and is close to the maximum sorption capacity, indicating the high reusability of the rubber cryogels.

Figure 10 compares the pollutant sorption capacities of CBR and SBR cryogels prepared at  $-18\text{ }^{\circ}\text{C}$ . CBR cryogels have a higher crude oil sorption capacity as compared to SBR cryogels. In contrast, the sorption capacity of SBR cryogels for diesel is larger than CBR cryogels. Therefore, there is no correlation between the type of the rubber and their sorption capacities.

Mechanical properties of CBR and SBR rubber gels were also investigated by the compression tests. The general trend is that all the gels prepared at subzero temperatures between  $-2$  and  $-22\text{ }^{\circ}\text{C}$  exhibited moduli of elasticity around 2 kPa. No substantial variation of the elastic modulus was observed depending on  $T_{\text{prep}}$ . Moreover, all the low-temperature gels were very tough and can be compressed up to about 100 % strain without any crack development.

## Conclusions

Aligned porous rubber cryogels were prepared from frozen solutions of CBR and SBR in benzene at various  $T_{\text{prep}}$  with an exception of honey-comb porous structured

SBR cryogels prepared at  $-2^{\circ}\text{C}$ . The networks formed from CBR and SBR showed  $10^1$ - to  $10^2$ - $\mu\text{m}$  sized regular pores caused by the benzene crystals acting as a template during gelation. The pore size of the rubber networks can be reduced by decreasing the gel preparation temperature of the cryogelation system. Cryogels exhibited fast swelling and deswelling properties as well as reversible swelling–deswelling cycles in toluene and methanol, respectively. The sorption tests showed that CBR and SBR cryogels are efficient reusable sorbent materials for oil spill cleanup due to their high sorption capacities for diesel and crude oil as well as their reusability after simple squeezing.

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