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Graphite/Isobutylene-isoprene Rubber Highly Porous Cryogels as New Sorbents for Oil Spills and Organic Liquids

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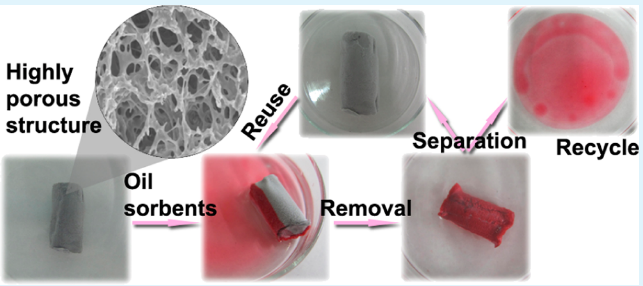

ABSTRACT: The preparation, by a freeze−thaw method, of new graphite/isobutylene-isoprene rubber (IIR) sorbents for oil and organic liquid is described. Graphite was expected to improve the adsorption properties. The cryogels were prepared by solution crosslinking IIR rubber in the presence of graphite in benzene at various temperatures, using sulfur monochloride as the crosslinker, and characterized by SEM and contact angle measurements. The dried cryogels, with interconnected macropores were sponge-like soft materials, with excellent buoyancy and hydrophobicity. They also showed excellent sorption characteristics, with the best sample exhibiting maximum sorption capacities of 17.8 g g^{-1} for crude oil, 21.6 g g^{-1} for diesel oil, and 23.4 g g^{-1} for lubricating oil, respectively. The samples also showed excellent sorption capability for organic liquids, absorbing up to around twenty times their own mass. After rapid and effective desorption, taking just 3−5 h, the cryogels were recovered. They could also be reused more than 30 times by simply centrifuging to remove the sorbed liquid. These characteristics mean that the cryogels prepared in this study are promising materials for removal of large-scale oil or toxic organic spills.

KEYWORDS: *cryogelation, graphite, oil adsorption, macroporous, isobutylene-isoprene rubber, porous polymer*

■ INTRODUCTION

There has been rapidly growing worldwide concern about the urgent need to control accidental and deliberate releases of oil and other organic liquids during transportation and storage.[1] The adverse impacts on ecosystems and the long-term effects of environmental pollution caused by oil and other organic liquids have excited more public concern.[2,3] A lot of approaches for the removal of oil using various materials have been reported in the literature. An ideal oil sorbent material should have high hydrophobicity, buoyancy, high uptake capacity, and be either reusable or biodegradable.

Cryogels are interconnected macroporous gels prepared at sub-zero temperatures, which have applications in various research fields.[4,5] The process of cryogelation is inspired by the natural process which occurs when seawater freezes.[5] Cryogel formation involves phase separation via ice-crystal formation, cross-linking, polymerization, and then thawing of ice crystals to form pores.[4] Cryogels are widely used especially in all kinds of sorption materials.[6−10] Isobutylene-isoprene rubber (IIR) is a linear polyisobutylene containing small amounts of internal unsaturated groups. Earlier studies have shown that IIR gels can take up large volumes of oil in some earlier studies.[11,12]

Carbon materials are widely used sorbents, which exhibit excellent properties for removal of oil spills;[13,14] graphite is particularly effective.[15−19] Exfoliated graphite with high sorption capacity was either directly used as a sorbent or combined with other materials to form composite sorbents in these period reports. Thus we expected that adding graphite to give a composite cryogel could improve the sorption capacity of the pure IIR cryogel. Large pieces of the graphite-containing IIR composite cryogel were formed, in an effort to avoid the awkwardness and inconvenience of reusing the sorbant if it was prepared as a powder In addition, by choosing a nano graphite powder, we expect to not only improve the oil sorption capacity of IIR cryogel, but also reinforce it to give a more rigid composite. Here we report the preparation of cryogels based on IIR 1751 modified with graphite and the sorption properties of these composites for a selection of oil and toxic liquids.

■ EXPERIMENTAL SECTION

Materials. IIR 1751, containing small amounts of isoprene units (to give 1.7 ± 0.2% unsaturation) and with a Mooney viscosity of 51 ± 5, was supplied by Sinopec Beijing Yanshan Co. Ltd., China. The nano graphite powder (99%), with thickness of 40 nm, was purchased from Aladdin Chemistry Co. Ltd., Shanghai, China. The surface area of graphite powder is 28.97 m^2/g and the XRD spectrum of graphite is the same as the standard spectrum. The sulfur monochloride (S_2Cl_2, 98%) used as a cross-linking agent was purchased from Ziyi Reagent Co. (Shanghai, China). All AR reagents were supplied by Sinopharm Chemical Reagent Co, Shanghai, China.

Cryogel Preparation. The cryogels were prepared by a freeze-thaw method: IIR (5 g) was dissolved in benzene (100 mL) at room temperature for 24 h. Graphite (0, 0.5, 1, or 2 w/w %) was dispersed in 10 mL of benzene and then added into the IIR solution. Once graphite was added, stirring was continued for a further 30 min to produce a uniform mixture. Cross-linking agent S_2Cl_2 (0.3 mL, 6 v/w

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%) was added dropwise to the mixture under rigorous stirring. Then the mixture was immediately transferred to glass tubes and left to freeze in a cryostat at a preset temperatures for 24 h. After the reaction, the resulting samples were thawed at room temperature until they became transparent, and then squeezed to remove benzene. The gels were immersed and washed several times with toluene and methanol alternately (toluene first), then natural dried at room temperature (30 °C) in a chemical hood until constant weight.

Method for Oil and Organic Liquid Removal Tests. Oil sorption of the cryogel was recorded by measuring the weight of the samples before and after sorption (1×10^{-4} g accuracy). The oil sorption capacity was then calculated as

$$S_{\text{oil}} = (m_{\text{oil}} - m_{\text{dry}})/m_{\text{dry}} \quad (1)$$

where m_{oil} means the mass of the gel which had been immersed in oil and then allowed to sit on a wire mesh to remove excess oil from its surface. Sorption and desorption tests were performed in a similar way. Briefly, the cryogel samples were kept in an organic solvent for 30 min in a chemical hood. Samples were accurately weighed before sorption, immediately after sorption and at various time intervals until all the liquid evaporated from the samples.

Characterization. The pore volume V_{pore} of the dry cryogels was estimated by the method described previously for aerogels, using methanol uptake.[20] Methanol is a nonsolvent for IIR, and can only fill the pores within the gels. Thus V_{pore} could be calculated as

$$V_{\text{pore}} = (m_{\text{M}} - m_{\text{dry}})/(\rho_{\text{M}} m_{\text{dry}}) \quad (2)$$

where m_{M} is the weight of the gel saturated with methanol and ρ_{M} is the density of methanol (0.792 g/mL).

The Morphology of the cryogel (dried at room temperature (30 °C) until constant weight) was investigated by scanning electron microscopy (SEM, SU-1500, Hitachi, Japan) at an accelerating voltage of 20 kV after sputter coating samples with gold for 3 min. The hydrophobicity of the cryogel sample was quantified by measuring the contact angle (θ) of a sessile drop of water on the surface of a block of cryogel (OCA15EC, Dataphysics, Germany).

■ RESULTS AND DISCUSSION

Properties of Cryogels. The sample preparation conditions and properties of the cryogel sorbents prepared at different temperatures and graphite concentrations are summarized in Table 1. The reaction temperatures were 0, −5, −10, and −15 °C. The graphite concentration was also varied from 0 to 2 w/w% (with respect to IIR). For convenience, in the following paragraphs, these sample ID will be used: the first letter refers to the reaction temperature, and the number refers to the graphite concentration.

Table 1. Sample Preparation Conditions and Properties of Cryogel Samples

	preparation conditions		properties	
sample ID	reaction temp (°C)	graphite (w/w %)	pore volume (mL/g)	water sorption capacity (g/g)
A0	−2	0	2.66 ± 0.32	0.22 ± 0.13
A0.5	−2	0.5	2.78 ± 0.25	0.31 ± 0.17
A1	−2	1	3.72 ± 0.15	0.28 ± 0.11
A2	−2	2	2.67 ± 0.27	0.35 ± 0.12
B0	−5	0	2.67 ± 0.29	0.23 ± 0.06
B0.5	−5	0.5	3.86 ± 0.16	0.46 ± 0.08
B1	−5	1	4.00 ± 0.23	0.25 ± 0.04
B2	−5	2	3.05 ± 0.26	0.29 ± 0.10
C0	−10	0	3.79 ± 0.29	0.28 ± 0.14
C0.5	−10	0.5	3.89 ± 0.26	0.17 ± 0.06
C1	−10	1	5.50 ± 0.19	0.61 ± 0.22
C2	−10	2	5.01 ± 0.28	0.24 ± 0.09
D0	−15	0	1.69 ± 0.09	0.17 ± 0.03
D0.5	−15	0.5	1.87 ± 0.06	0.13 ± 0.02
D1	−15	1	2.22 ± 0.11	0.12 ± 0.04
D2	−15	2	2.24 ± 0.09	0.04 ± 0.01

Table 1 also shows the pore volumes and water sorption capacities of the cryogels. Pore volume was measured in the deswollen state. The pore volumes of the cryogels prepared at −5 and −10 °C were large, and the pore volumes of cryogels with added graphite were larger than those for the samples without graphite. However, there was no significant difference in water sorption capacity among the samples. This means that these cryogels are water repellent, because their hydrophobic surface effectively prevents water drops from entering the porous structure.

Surface Morphology and Hydrophobicity. SEM micrographs showing the morphologies of dried gel samples are presented in Figures 1 and 2. In Figure 1, cryogel samples prepared using various conditions exhibited interconnected porous network structure on their fracture surfaces, with the exception of the sample prepared at +2 °C, which was nonporous, showing a compact fracture surface with no pronounced microstructure. This was because the temperature of +2 °C was not low enough to freeze the benzene and thus form pores. Interconnected pores distributed throughout the gel structure formed at temperatures below zero. The macropore sizes were ranged from 20 to 30 μm, and the strut thicknesses (i.e., pore wall thicknesses) ranged from 10 to 20 μm. The gel prepared at -15 °C had more but smaller pores (about 20μm).According to nucleation theory, a higher nucleation rate decreases the size of nuclei. Therefore, the pores structure of sample prepared at -15 °C arose because of

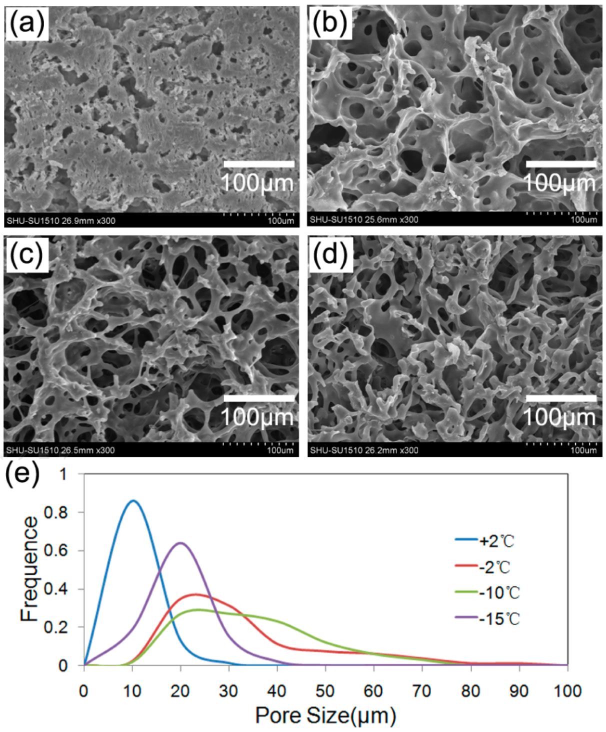

Figure 1. SEM images of cryogels. Reaction temperature: (a) +2, (b) −2, (c) −10, and (d) −15 °C. Graphite% = 1 w/w %. The scale bars were 100 μm. (e) Pore size distributions with ImageTool.

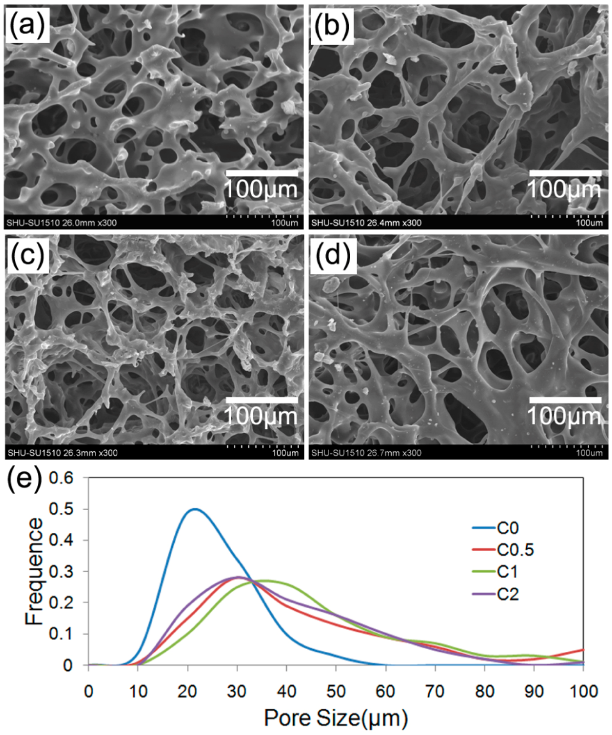

Figure 2. SEM images of cryogels prepared at −10 °C: (a) C0 graphite% = 0 w/w %; (b) C0.5 graphite% = 0.5 w/w %; (c) C1 graphite%= 1w/w %; (d) C2 graphite% = 2 w/w %. The scale bars were 100 μm. (e) Pore size distributions with ImageTool.

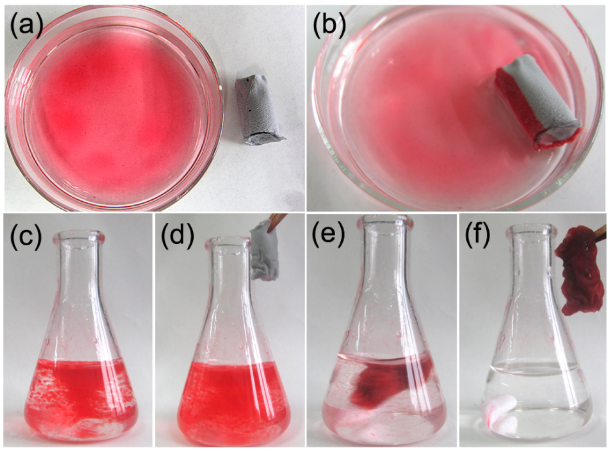

Figure 3. Optical images for the removal of diesel oil (dyed with oil red) from water by the C1 cryogel. (a) The dry cryogel. (b) The excellent buoyancy of the cryogel. (c) Appearance of diesel oil suspension with magnetic stirring. (d) Cryogel was added. (e) Diesel oil being taken up by the cryogel. (f) The swollen oil-filled cryogel.

the faster nucleation of benzene crystals at this low temperature, which meant that smaller benzene crystals formed.[21,22]

By altering graphite concentrations, cryogels C0−C2, containing 0 w/w % to 2 w/w % graphite, were successfully created. Figure 2 shows the differences between these samples. The pores of C0.5, C1 and C2 ranged from 30 to 50 μm, which were larger than C0 (Figure 2a). It was surmised that the graphite powder was embedded in to the IIR cryogel during ice-crystal formation, cross-linking and polymerization. In the C2 sample, the strut thickness was increased. Larger pores are conducive to sorption of long-chain oil molecules, and thinner struts are likely to be more conducive to swelling. Hence, adding the appropriate dosage of graphite is very important.

Contact angle tests revealed that the cryogels were hydrophobic. The CA of the pure IIR gel sample C0 was 104.1°. As expected, the hydrophobic graphite powder dispersed through the gel improved the hydrophobicity. Consequently, the CAs of modified samples, C0.5, C1, and C2 were 125.2, 139.9, and 127.1°, respectively. Although the CAs increased with addition of graphite, C2 didn't show the largest angle. This is probably because the larger amount of graphite powder in this sample increased the strut thickness and decreased the surface roughness of the cryogel.

Oil Adsorption Capacities of the Cryogels. The dried cryogels were sponge-like soft materials. The pure IIR cryogel was white, while the graphite-modified ones were different shades of gray. In images a and b in Figure 3, sample C1 was placed into a stratified oil−water mixture. Oil Red dye was used to stain the diesel oil and give a brilliant contrast. The excellent buoyancy of the cryogel can help to increase the contact area between sorbent and oil. When sample C1 was placed into the diesel oil suspension, the small oil drops dispersed in the emulsion were taken up within a few seconds (Figure 3c−f). Even if the system is stirred for a few minutes more, the diesel is not desorbed into the water again. The remarkable swelling shown in Figure 3f emphasizes the fact that the linear polyisobutylene of IIR is swollen in nonpolar solvents. The swelling rate of the materials can be controlled by appropriate cross-linking, thus giving more space for oil sorption and retention. Centrifuging was used to remove the sorbed oil from the swollen cryogel. After centrifuging (4000 r/min) for 3 min, the volume of the cryogels remained as large when they were originally swollen. This means that a number of oil molecules still adhered to the linear polyisobutylene of the IIR and maintained the cryogel in a swollen state. To determine the amount of water taken up by the cryogels, we mixed the oil collected during centrifuging with 50 mL of n-hexane, shook it violently, and allowed it to rest in a separating funnel for half an hour. After stratification, there was almost no water phase observed at the bottom of the funnel.

Static sorption tests for crude oil, diesel, and lubricating oil were conducted using cryogel samples prepared in the form of cylindrical pieces, about 1.2 cm in diameter and 2 cm long when unswollen. The sorption properties were then measured by mass method. Figure 4 shows the sorption capacities of the various cryogel sorbents. The x-axis letters indicate the reaction temperature, whereas the shades of gray of the bars correspond to different graphite concentrations of the sorbents.

Overall, the samples of group B and C, formed at −5 and −10 °C, exhibited better sorption capacities for various oils. The poorer sorption properties, observed in groups A and D, were attributed to the smaller pores of the samples in these groups (Table 1 and Figure 1), since sorption capacity increases with increasing volume and size of pores. In addition, for samples prepared at the same temperature, sorbents containing 0.5 or 1 w/w% graphite exhibited greater sorption capacities. This implies that the appropriate amount of graphite can improve the sorption capacity of the cryogels, while, as shown by the dark grey (2 w/w %) bars; too much graphite can have a negative influence on sorption. Figure 2d showed that the strut thickness of sample C2 increased, but the sorption capacity was lower than other samples. It may be because the linear polyisobutylene of IIR in cryogels added with too much

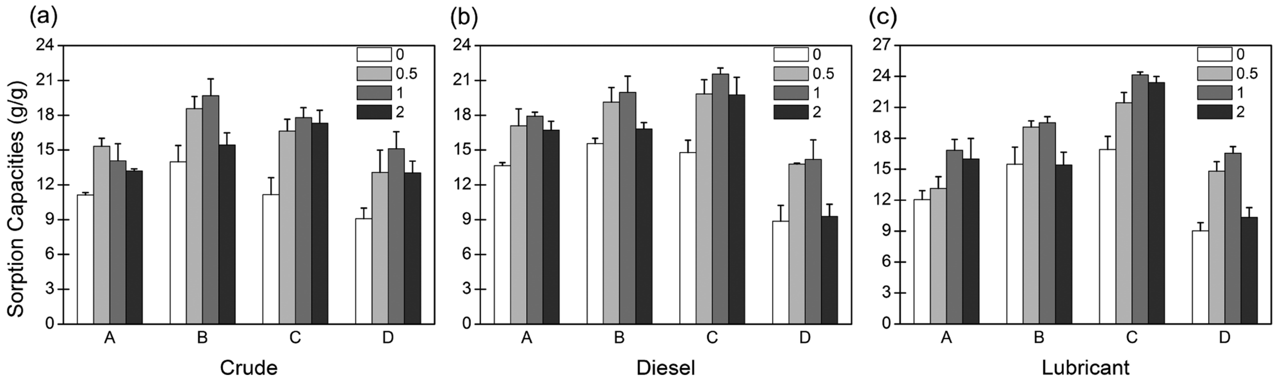

Figure 4. Sorption capacity of the cryogels for various oils: (a) crude, (b) diesel, and (c) lubricant.

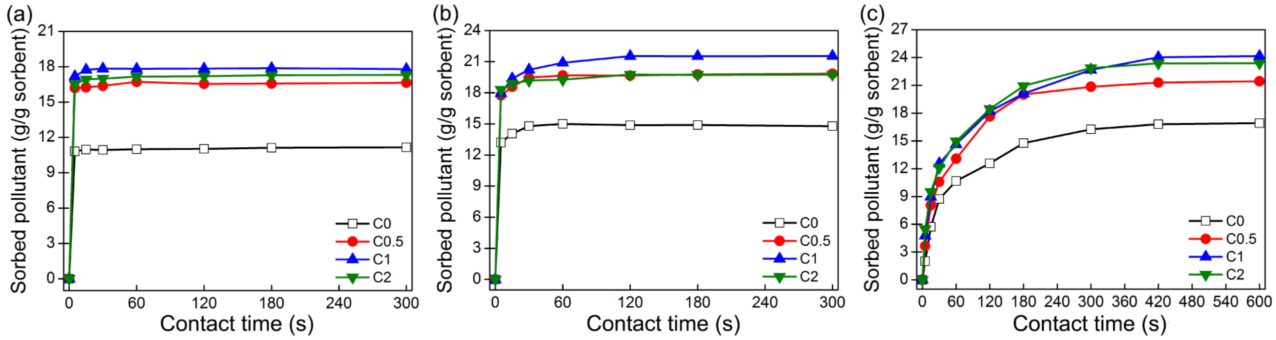

Figure 5. Sorption capacity of the cryogels versus contact time: (a) crude, (b) diesel, and (c) lubricant.

graphite would be under greater resistance when it stretched after contacting with oil. Thus cryogels could not swell fully in oils and their swollen volume and oil storage space were significantly lower. And the lower swollen volume and storage space were not conducive to oil sorption. In Figure 4, cryogel sorbent with the maximum sorption capacity was sample C1. 1g of C1 cryogel could sorb 17.8 g of crude oil, 21.6 g of diesel, or 23.4 g of lubricant, respectively.

The sorption capacity of a commercial polypropylene (PP) sorbent, mentioned in previous literature,[12,23,24] can be compared with that of our cryogel samples. PP sorbents have a sorption capacity of about 8−10 g g^{-1}, our cryogels show much higher values than that. This difference is most likely because PP sorbent cannot change its volume much during the sorption process, whereas the cryogels can expand upon contact with the pollutants.

The sorption kinetics of the C group cryogel sorbents are shown in Figure 5, where the uptake of pollutants is plotted against the contact time. Overall, the sorption of the cryogels was very rapid. For crude, adsorption equilibrium was reached in just a few seconds, while diesel oil took about 1 minute. The rapid sorption was because of the interconnected macro porous cryogel networks and the rapid swelling process of the IIR framework. The sorption rate for lubricant was slower than for the other pollutants, which is probably because of higher viscosity and cycloalkane content of lubricant. Adsorption equilibria occurred after 8 min. The high viscosity oil molecules slowly entered the pores, then swelled the IIR and remained in the newly enlarged pores. This implies that though increased viscosity of the pollutant decreases the rate of sorption, favorable hydrophobic interactions between the lubricating oil and hydrophobic gel increases the adherence of the oil onto the linear polyisobutylene of IIR, so that more oil is eventually retained within the cryogel sorbent. When compared to sample C0, cryogels modified with graphite have much higher sorption capacities. This significant advantage of the graphite-embedded cryogels shows that adding graphite was effective, and achieved remarkable increases in sorption.

Reusability of sorbents is becoming important for oil spill cleanup procedures. All the cryogels prepared in this work can be reused after squeezing or centrifuging completely. The reusability of the cryogels was checked by repeated sorption-centrifuging cycles, using diesel as the pollutant, and the results are shown in Figure 6. Comparing with the maximum sorption capacity reported in Figures 4 and 5, the sorption capacities during reuse were stable and close to the maximum sorption capacities. This means that the cryogel networks were still in excellent condition after 30 cycles of centrifuging and sorption. After centrifugation, some oil molecule still adhered to the linear polyisobutylene of IIR and kept cryogel swelling. There is

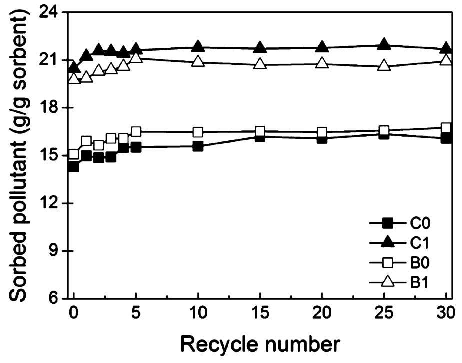

Figure 6. Sorption capacity of the cryogel samples during recycling.

no difference between the gels before and after centrifugation except the swelling state, because the gels are a kind of spongelike elastomer and can restore the original shape after the removal of outside force.

Sorption and Desorption of Organic Liquids. The dried samples, when immersed in most of the nonpolar organic liquids in this study, swelled and took up more than 10 times their own weight in organic liquid. In the experiment, three aromatic compounds (benzene, toluene, and xylene) and three alkanes (hexane, heptanes, and cyclohexane) were used. Sorption capacities of the cryogels were determined by mass change.

It was expected that the chain length and polar groups of the pollutants would influence the swelling behavior and sorption. Indeed, a distinct trend can be observed in Figure 7a. Among the three aromatic compounds, the amount taken up was smallest for benzene and highest for xylene. This suggests that the methyl groups of toluene and xylene have a high affinity for the cryogel networks. For each pollutant compound, the sorption capacities of samples modified with graphite were much higher than that for sample C0. Sample C1, which showed the best performance, took up 14.1 g of benzene, 17.6 g of toluene, or 21.4 g of xylene per gram of sorbent. In previous literature,[12,23] the sorption capacities of PP sorbent for benzene (about 8 g g^{-1}) were much lower than that found for sample C1 (11 g g^{-1}). The right-hand chart in Figure 7a compares the sorption of different alkanes – the uptake of n-heptane was the highest, and that of cyclohexane was a little higher than hexane. This may be because of the longer chain length of heptanes. One gram of C1 cryogel took up 13.7 g of hexane, 22.8 g of heptanes, and 14.4 g of cyclohexane. As found for the aromatics, the overall performance of C0.5, C1, and C2 gels was better than that of the pure IIR cryogel C0.

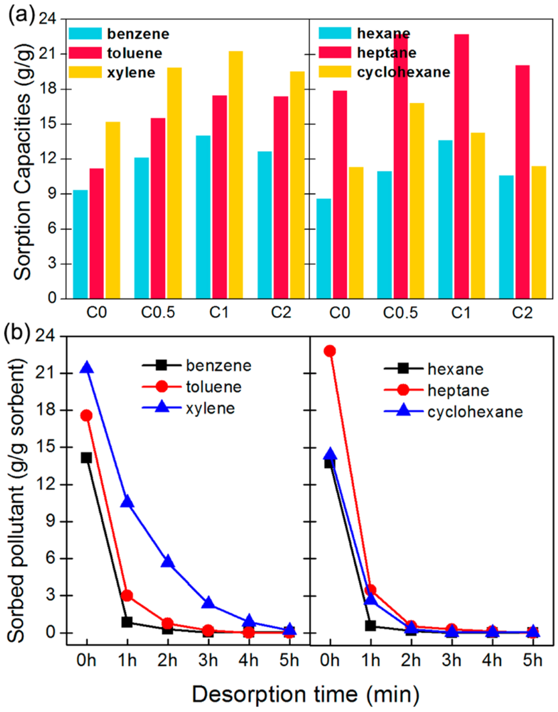

Figure 7. (a) Sorption capacities of the cryogel samples (C group) for toxic organic liquids. (b) Desorption curves for various toxic organic liquids from cryogel C1.

To study the desorption of the organic liquid from the cryogels (i.e., the time taken for the liquid to completely evaporation from the cryogel pores once sorption was completed), the cryogel samples were immersed in organic solvent for 30 min and then placed in a chemical hood for 5 h, and their masses recorded at various time intervals. Figure 7b showed the mass of the cryogel samples as a function of time during desorption at room temperature. The desorption process was rapid and effective, with the volume and mass of the cryogels returning to their original values within just 3−5 h.

CONCLUSIONS

Graphite/IIR rubber cryogels were prepared by a cryogelation method. Graphite was used to modify the cryogels and improve the sorption properties. The interconnected macropores in the cryogel ranged in size from 20 to 30 μm, and the strut thickness (or pore walls) ranged from 10 to 20 μm. The dried cryogels were spongelike soft materials, with excellent buoyancy and hydrophobicity. In dynamic sorption tests, remarkable swelling was observed. The cryogels were efficient sorbents for the removal of small oil drops dispersed in an emulsion. The excellent sorption characteristics were also demonstrated in static sorption tests. Samples of group C, formed at −10 °C, exhibited the best sorption capacity for various oils. Of the samples formed at the same temperature, sorbent containing with 1 w/w% graphite exhibited the highest sorption capacities. One gram of C1 cryogel took up 17.8 g of crude oil, 21.6 g of diesel oil, or 23.4 g of lubricating oil. The samples also showed excellent sorption capability for aromatic compounds and alkanes, with the C1 sample adsorbing 17.6 g of toluene, 21.4 g of xylene, and 22.8 g of heptanes per gram of sorbent, respectively. After a rapid and effective desorption process, taking just 3−5 h, the volume and mass of the cryogels returned to their original values. After oil uptake, simple squeezing or centrifuging allowed the cryogels to be recycled and reused at least 30 times. The high continuous sorption capacity demonstrated that the cryogels prepared in this study are promising removal materials for use in the cleanup of large-scale oil or toxic organic liquid spills.

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Notes

The authors declare no competing financial interest.

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