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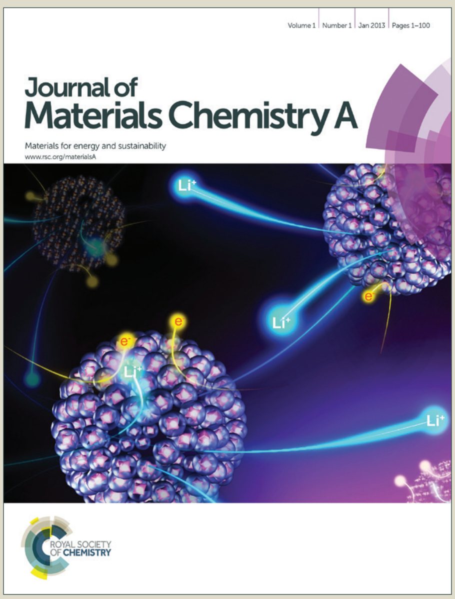

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# High internal phase emulsion (HIPE) xerogels for enhanced oil spill recovery

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**Oil spills cause serious damage to the aquatic ecosystem and require quick cleanup. Herein we report high internal phase emulsion (HIPE) xerogels for the first time as oil absorbents for enhanced oil spills recovery. The HIPE xerogels absorb diesel from water-oil mixture in 20-30 seconds. The absorption capacity of the HIPE xerogels ranges from 20-32 times to different kinds of oils, and the oils can be recovered simply by being squeezed out, with a recovery rate aroud 80%. They can be reused at least 40 times without obvious deterioration in oil separation properties from 0 to 45 °C. These novel xerogels are suitable for practical use in oil spill reclamation and wastewater treatment.**

Oil spills have become one of the major environmental issues.[1] Oil spills cause serious or irrecoverable damage to the marine environment and the ecosystem, and finally affect the human health. Therefore, these petroleum-based pollutants must be removed from water surfaces speedily and efficiently.[2] Common methods to clean the oil spills include combustion, mechanical treatment using oil sorbents materials, chemical treatment by dispersants, and bioremediation with microorganisms.[3] Among these methods, the use of sorbents is one of the most desirable options for the treatment of oil spills owing to the economy and efficiency.

Many kinds of sorbent materials have been developed for oil spill cleanup.[4-6] However, currently used sorbents have some drawbacks: slow oil absorption, low absorption capacity, production of toxic wastes, high cost and low recovery efficiency.[7] In recent years, phase-selective organogels have been used as sorbents to selectively remove oil from water due to their unique efficiency for large scale oil cleanup.[8, 9] Phase-selective organogels based on sugar-derivatives,[9] mannitol,[10] aromatic amino[11] or carbohydrates[12] have been prepared and investigated for oil spill recovery. However, these organogels still have limitations: for practical applications, a heating-cooling cycle is usually applied to initiate gelation[13] or a water-miscible carrier solvent (ethanol, tetrahydrofuran and dioxane) is needed for introduction of gelators into oil spills.[11] The heating-cooling approach is costly and complicated while the water-miscible solvent route consumes huge amount of solvent and leaves toxic chemicals in the sea which has deleterious effects on marine life.[10] Lee et al. prepared xerogels from phase-selective organogels to absorb spilled oil from water.[14] Though these xerogels are low-cost and effective, their absorption capacity is very low (c.a. 4g/g). High internal phase emulsions (HIPE) xerogels are another important series xerogels nowadays are developed for treatment of oil spill. Porous polystyrene[15] and poly(tertiary-butylmethacrylate) xerogels[16] were prepared by using HIPE gel as template and these polymer xerogels exhibited oil absorbed properties. However, low-molecular mass gelators (cholesteryl derivatives) which are costly are necessary in these procedures.

Recently, we reported the preparation of HIPE organogels from charge-driven assembled polymer organogels,[17-19] and it is interesting to find that these HIPE organogels exhibited oil separation properties.[17-19] Herein we report HIPE xerogels as oil absorbents for the cleanup of oil spills. The HIPE xerogels with high porosity and low density were obtained by removal of solvents from HIPE organogels by freeze drying, and HIPE organogels were prepared from polypropylenimine (PPI) dendrimer and a block ionomer sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) (see ESI). The HIPE xerogels obtained were examined as sorbents for oil spills recovery, and they showed high oil absorption capacity, absorption rate and reusability. To the best of our knowledge, this is the first polymer xerogels based on charge-driven assemblied polymer HIPE organogels. And the polymer xerogels exhibit excellent oil absorption and reused properties.

The HIPE organogels were characterized by confocal microscopy. It can be seen from Fig. 1a that the disperse domains are water phase, and that the sizes of the water droplets vary from several to tens of micrometers. Because of high volume fraction of dispersed phase in the HIPE organogels,[17] it is possible to obtain porous HIPE xerogels with light density after removal of solvents. The HIPE xerogels were obtained after the water and solvents were removed by freeze drying. The morphology of the HIPE xerogels was further investigated by SEM. It can be seen from Fig. 1b that the HIPE xerogels exhibit porous structure. However, the porous network structure remained after treatment of freeze-drying as shown in Fig. 1b. With the fraction of water phase being over 74% by volume in HIPE organogels, the as-prepared HIPE xerogels are highly porous and lightweight. The density of the as-prepared HIPE xerogels is 0.108 g/cm$^3$. Due to the existence of high porosity and oleophilicity, the HIPE xerogels are expected to have high absorption capacity and absorption rate for oils.

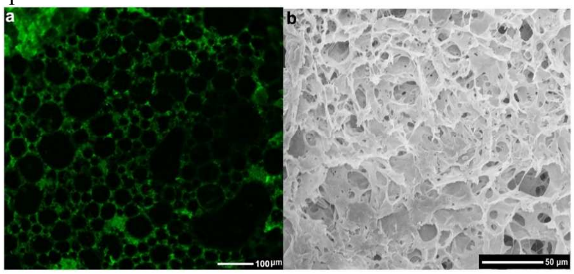


**Fig.1** (a) Confocal image of HIPE organogels; (b) SEM image of HIPE xerogels.

To examine HIPE xerogels as effective oil absorption agents, a number of oils and organic solvents, including diesel, gasoline, engine oil and a variety of organic solvents, were employed to mimic the spilled oil. It was found that the HIPE xerogels absorbed oil from water-oil mixtures quickly, and the HIPE xerogels were observed floating on the surface of water after the absorption. Fig. 2 illustrates a typical separation process of oil from water by HIPE xerogels. Diesel can be absorbed completely by the HIPE xerogels in one minute and then the resultant oil-absorbed xerogels remain floating on the water layer (Movie of ESI). The oil absorbed in the xerogels can be recovered by simply squeezing out although the recovery is about 81.6% (Fig. 4a). This process has demonstrated that the spilled oil can be successfully separated and reclaimed from water with HIPE xerogels as sorbents. The other organic liquids can also be recovered by the xerogels in the similar way as diesel. Compared with the other methods such as vaporization[20] and washing with solvents[21] or burning[22], the squeezing-out process for reusing oil sorbents is relatively simple and inexpensive. As the HIPE xerogels can absorb oil/organic solvents from the surface of water, it is expected that this process can be scaled-up, promising for practical applications.

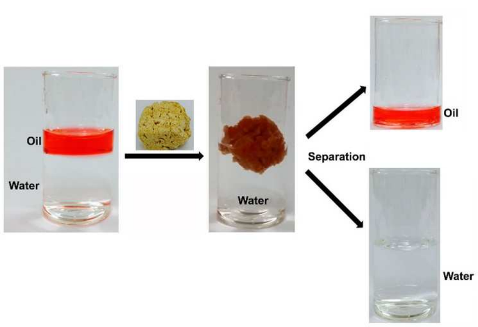


**Fig. 2** Separation of diesel from water by HIPE xerogels. The diesel was dyed with Oil red O.

The absorption of different oils and organic solvents with the HIPE xerogels was investigated. When the xerogels were immersed into the oils or organic solvents for overnight, saturated absorption was reached. The absorption capacity of the xerogels is calculated from the weight of oils or organic solvents in the HIPE xerogels relative to the dry weight of the xerogels, and the results are shown in Fig. 3a. These xerogels exhibit high mass absorption capacities for a variety of solvents: 19.8 g/g (hexane), 22.3 g/g (toluene), 24.9 g/g (xylene), 22.6 g/g (dichloroethane), 32.2g/g (chloroform), 24.2 g/g (vegetable oil), 21.2 g/g (gasoline), 23.8 g/g (diesel), 31.5 g/g (engine oil) and 15.1 g/g (crude oil). The results show that the absorption capacities of the HIPE xerogels are larger than these of many xerogels[14, 23] and are close to or higher than these of oil absorbents or organogels reported in literatures (Table S1).[24, 25] Such high absorption performance can be attributed to their porous nature and oleophilic properties of the alkyl and aromatic moieties in the xerogels, which lead to large capillary action for wetting by oil or organic solvent.[26] Two other HIPE xerogels prepared from the SEBS samples with 28 and 68 mol % polystyrene blocks also exhibit high oil absorption capacities (Fig. S1 and S2).

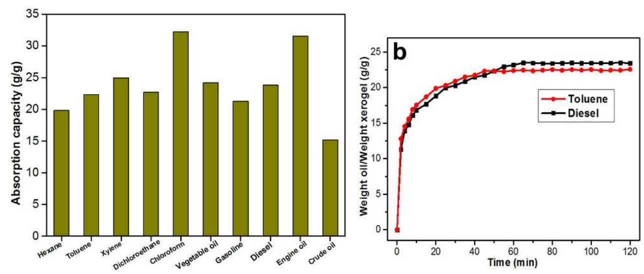


**Fig. 3** (a) Absorption capacities of the HIPE xerogels for various organic solvents and oils; (b) Weight gain by the HIPE xerogels in the toluene and diesel versus time.

The oil absorption rate of HIPE xerogels was tested using toluene and diesel as model organic solvents and oils; the results are presented in Fig. 3b. It is noted that toluene and diesel were absorbed into the xerogels quickly in the first few minutes, and the absorption equilibrium was reached within 50 minutes for toluene and within 60 minutes for diesel. The absorption rate is much higher than that of xerogels prepared from phase-selective organogels,[14] oleophilic polyelectrolyte gels[27] and PAN/DMSO gels[28] which may need a few days to reach saturated absorption.

The reusability of HIPE xerogels for oil absorption/recovery was studied, as one of the key factors to recover the oil spill effectively is to reduce the cost and reuse the oil sorbents is an effective method.[29] The HIPE xerogels can be reused for oil spill recovery through a repeatable absorbing – squeezing out – separation process. Fig. S3 demonstrates such absorption-recovery process of oil from water-oil mixture with HIPE xerogels, and that the xerogels can be used repeatedly. The reusability of HIPE xerogels for absorption and recovery of diesel was examined for 40 cycles. It can be seen from Fig. 4 that the absorption and recovery capacity of the HIPE xerogels do not change obviously even after 40 cycles. The diesel absorbed by the HIPE xerogels can be recovered with a recovery rate of 75-82 %.

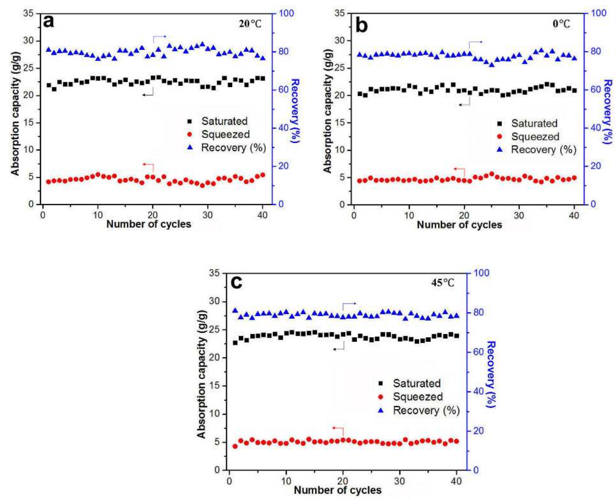


**Fig. 4** Absorption capacities of HIPE xerogels and spilled oil recovery with diesel absorption/squeezing-out cycle number at (a) 20 °C, (b) 0 °C and (c) 45 °C.

As the environment temperature, such as the temperature of sea water, changes with the climates. The effects of temperature were attended, and the oil absorption of HIPE xerogels was also examined at 0 and 45 °C. As shown in Fig. 4b and 4c, the oil recovery remains almost unchanged although the absorption capacity is only slightly affected when the temperature is down to 0 °C or increased to 45 °C. The HIPE xerogels developed in this study are the first polymer xerogels with such high reusability at a broad range of temperatures. The excellent reusability of these HIPE xerogels within a broad range of temperature can reduce the cost of the process.

The water absorption of the HIPE xerogels was examined with different aqueous media, including distilled water, 0.5M aqueous NaCl solution and sea water. The mass gained after 2 hours was 0.82 g/g in distilled water, 0.95 g/g in 0.5M NaCl aqueous solution, and 0.89 g/g in seawater (Fig. S4). The contact angles of distilled water, 0.5M NaCl aqueous solution and seawater on the surface of HIPE xerogels as shown in Fig. 5 are 144, 137 and 138°, respectively. These results suggest that the xerogels have highly selective absorption for oil in the mixture of oil and water.

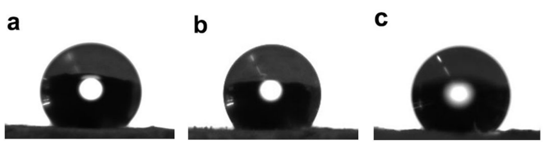


**Fig. 5** Optical images of a droplet of (a) distilled water, (b) 0.5M NaCl aqueous solution and (c) seawater on the surface of HIPE xerogels.

In conclusion, the HIPE xerogels prepared in this work exhibited high absorption capacity and easy recovery for a wide range of oils and organic solvents from oil-water mixtures. The absorption capacity of the HIPE xerogels ranges from 20-32 times to different kinds of oils, and the oils can be recovered simply by being squeezed out, with recovery rate as high as 80%. The HIPE xerogels absorb oil from water-oil mixture in 20-30 seconds. The HIPE xerogels can be reused more than 40 times without obvious deterioration in oil separation properties in a broad of temperature range from 0 to 45 °C. These HIPE xerogels are suitable for practical use in oil spill reclamation and wastewater treatment.

## Notes and references

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Electronic Supplementary Information (ESI) available: Experimental section; absorption capacities, absorption-squeeze process and water absorption capacity of HIPE xerogels; Movies. See DOI: 10.1039/c000000x/

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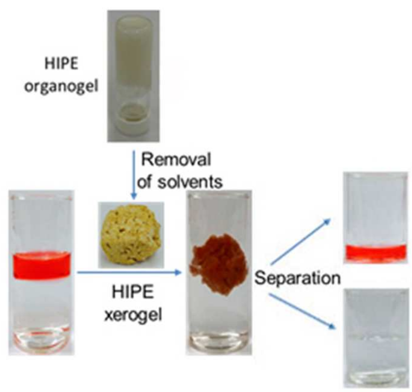
*Graphical Abstract*

# High internal phase emulsion (HIPE) xerogels for enhanced oil spill recovery

*Yuanpeng Wu, Tao Zhang, Zhiguang Xu and Qipeng Guo**




High internal phase emulsion (HIPE) xerogels based on charge-driven polymer HIPE organogels were prepared through freeze-drying and examined as oil absorbents for oil spills recovery.