



Facile fabrication of hierarchical porous resins via high internal phase emulsion and polymeric porogen



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ABSTRACT

To achieve the dual features of fast oil absorption rate and high oil absorbency for the practical application in emergency treatment of spilled chemical pollutants, hierarchical porous resins were synthesized. The polymerization of high internal phase emulsion was applied to fabricate the porous structure for the purpose of high oil absorbency. Polymeric porogens were proposed to adjust the second-order or interconnected pore structure for fast oil absorption rate. SEM revealed the hierarchical porous structure. Molecular weight and dose of polymeric porogen were investigated for the effect on the formation of porous structure and absorption features. Optimized resins have 31.5 g/g or 17.1 g/g absorbency for chloroform and toluene, respectively, and only 5 min is needed to reach their saturation absorption. Besides, the porous resins demonstrated high oil retention under pressure. The absorption/desorption cycling results revealed the high repeatability of recovered resins. All these tests predicted the potential applications of porous resins of this kind particularly in the emergency treatment of oil and chemical pollution.

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1. Introduction

Massive marine oil spills have occurred frequently and resulted in a great deal of damage to the marine and coastal habitats, economical impacts on fisheries. Offshore and shoreline water was often polluted during oil drilling operations, and accidents involving the runoff of oil from offshore oil exploration and production. Inland water bodies would be polluted accidentally by the oil leaking from pipelines, refineries, storage facilities, and in some cases, process effluent from chemical plants [1–3]. In order to deal with these problems, absorption resins are commonly employed to absorb the oil spills [4–6]. The preferable absorption resins should possess such properties as fast oil absorption rate, high oil absorption capacity, high oil retention capacity, and good reusability [7,8]. Among these properties, fast oil absorption rate and high oil absorption capacity are indispensable for the emergency treatment.

Porous structure is often required for absorption resins to achieve high oil absorption capacity [7]. Polymerization of high

internal phase emulsion (PolyHIPE) as a method offers a route to prepare such porous resins with controllable pore morphology [9–11]. HIPE, an emulsion, features a high-dispersed phase volume fraction, generally over 74% [12]. A porous material would be conveniently produced by the polymerization of the HIPE continuous phase containing polymerizable monomers and a cross-linking agent, and the subsequent removal of the dispersed phase [13,14]. A highly porous material is readily attained because of the high volume fraction of dispersed phase.

The high pore volume will allow high oil absorption capacity. However, high oil absorption rate cannot be obtained on the resins with sufficiently high pore volume whose pores were not interconnected each other. In fact, there is few reported study on the resins with fast oil absorption rate. It usually took a couple of hours for current porous resins to get oil absorption saturation [15–17]. Therefore, a highly interconnected porous and permeable structure, i.e. hierarchical pore structure should be produced in absorption resins to acquire high oil absorption rate. It is known that hierarchical pore structure can be obtained by HIPE method directly in most cases. However, the realization of the highly interconnected porous and permeable structure is very difficult in some specific cases, such as the interface-initiated polymerization in HIPE polymerization process [18,19], and Pickering high internal phase emulsions [9,20,21]. Therefore, it is necessary to improve

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the classic PolyHIPE method for synthesizing such a resin with fast oil absorption rate.

In this study, we propose a strategy of improving the poor pore interconnectivity of resins synthesized in particular HIPE systems. PolyHIPE route was implemented in the generation of high pore volume fraction for the purpose of high oil absorption capacity. Polymeric porogens were utilized in the formation of the highly interconnected porous and permeable structures for the achievement of fast oil absorption rate. Morphology, structure, and specific surface area were characterized by scanning electron microscopy (SEM), nitrogen gas sorption technique. The oil absorption rate, oil retention and reusability were evaluated intensively as well.

2. Experimental

2.1. Materials

Divinylbenzene (DVB; from Aladdin Chemistry, China) was purified by washing three times with 5 wt% sodium hydroxide solution followed by three times with deionized water. Porogen poly (butylmethacrylate) (PBMA, $M_w = 590,000$ or $67,000$) was prepared in our laboratory. The molecular weight of PBMA was determined from solution viscosity measurements at 25°C . Butylmethacrylate (BMA), ammonium persulfate (APS), and sodium bisulfite (SHS) were all purchased from Sinopharm Chemical Reagent Co. Ltd. Sorbitan monooleate (Span80) was obtained from Kermel Chemical Reagent Factory, China. All above were used without further purification.

2.2. Polymerization

The oil phase was prepared by mixing porogen, BMA, DVB and Span 80 in a 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer and purged by N_2 bubbling for 20 min. Then, 32 ml of deionized water (the volume ratio of deionized water in the system is 80%) was added drop-wise to the oil phase with constant stirring under N_2 atmosphere. The emulsion developed as a viscous white fluid or paste. After that, ammonium persulfate and sodium bisulfate as a redox initiator system was injected into the system and stirring was prolonged for another 15 min to allow homogenization of the emulsion. Subsequently, the emulsion was transferred to a polyethylene centrifuge tube, and then heated at 40°C in an oven for 48 h. The obtained solid materials were then treated via Soxhlet extraction with respective ethyl acetate and absolute ethyl alcohol for each 12 h and dried to constant mass in vacuum. The porous resins were designated as Resin-HIPE-N, Resin-HIPE-C/X, Resin-HIPE-L/X and Resin-HIPE-H/X, according to their respective porogen type, N: no porogen, C: cyclohexane, L: lower M_w macromolecular PBMA ($M_w = 67,000$), H: higher M_w macromolecular PBMA ($M_w = 590,000$) and X: porogen content (%) accounts for the total weight of monomer and porogen.

2.3. Scanning electron microscopy (SEM)

Scanning electron microscope used in the morphology study of the obtained samples was JEOL (JSM-5510LV). The specimens were coated with gold under vacuum for the SEM observation. The diameter of the voids or windows was measured on the basis of SEM images.

2.4. Surface properties

N_2 adsorption/desorption isotherms were determined at 77.3 K on a Micromeritics ASAP 2010 apparatus after the samples were vacuum-dried at 313 K overnight. Specific surface areas were calculated by the Brunauer–Emmet–Teller (BET) equation. Pore surface

areas and pore volumes were obtained based on the Barrett–Joyner–Halenda (BJH) method using the analysis of the adsorption branch of the isotherm [22].

2.5. Oil absorbency

The oil absorbency of porous resins was determined following ASTM F726–81. Approximate 0.3 g of dried resin particles with the diameter of $\sim 0.4\text{ cm}$ were placed into a stainless steel mesh, and then immersed in toluene or chloroform at room temperature. After given time, the mesh with the sample was picked up from the oil, drained for 20 s, tapped with filter paper to remove excess oil from the mesh, and then reweighed. The oil absorbency was calculated by the following equation:

$$W = \frac{m_2 - m_1}{m} \quad (1)$$

where W was oil absorbency of each sample, m_2 was the weight of the sample and the mesh after absorption, m_1 was the weight of the dried sample and the mesh, and m was the weight of the dried sample. Triplicate measurements were performed and the average values reported.

The absorption kinetics of samples was studied by tracing the weight with time in the above measurements.

2.6. Oil retention

The fully oil-absorbed porous resins, weighed as m_3 , were centrifuged at the speed of 3000 rpm for 5 min, and then the porous resins were weighed as m_4 . The oil retention was calculated by the following formula [15]:

$$R = \frac{m_4}{m_3} \quad (2)$$

2.7. Reusability

The dried samples were immersed in chloroform and toluene to reach the saturated oil absorbency at room temperature. The fully oil-absorbed samples were dried in vacuum at room temperature for 24 h to remove the oil thoroughly. Then, the resin was retested the absorbency [23].

3. Results and discussion

3.1. Morphology and structure of the porous resins

SEM images of resins are shown in Fig. 1. The resins obtained via the PolyHIPE route, Resin-HIPE-N, were found to have cellular structure (Fig. 1a). This type of cellular structure is called voids herein (first-order pore structure), denoted as “V” in figures. As a comparison, the resin via bulk polymerization (Resin-Bulk) did not show any pores (images omitted). Intensively, the cellular structure is a partially open-cell structure, seeing the “W” positions in figures. That is, there are some windows (the second-order pore structure) in the cell wall, which connect the adjacent cells. The interface-initiated polymerization in HIPE polymerization process only produces the partially open-cell structures of Resin-HIPE-N, similar to the previous reports [18,24].

However, the windows are very limited in number in light of the present process. It is essentially true that the window structure will accelerate the oil absorption rate because it will make the voids connected each other. Oil will therefore easily stream from one void into others deep into the core of resin through the window tunnels. Otherwise, the oil would be absorbed through diffusion route without the window structure. Ostensibly, it will take more time for resin to realize saturation absorption via the diffusion

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