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β-Cyclodextrin-based oil-absorbent microspheres: Preparation and high oil absorbency

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ABSTRACT

This article reports the preparation and evaluation of polymeric microspheres as a new class of oil-absorbent (POAMs). Based on our earlier oil-absorbents, the present microspheres contained β-cyclodextrin (β-CD) moieties as both cross-linking agent and porogen agent, and showed exciting high oil absorbency, fast oil absorption speed and good reusability. Such microspheres were prepared via suspension polymerization with octadecyl acrylate and butyl acrylate as co-monomers, β-CD derivative as cross-linking agent, 2,2′-azoisobutyronitrile as initiator and polyvinylalcohol as stabilizer. Oil absorbency of the POAMs was, for CCl_4, 83.4; $CHCl_3$, 75.1; xylene, 48.7; toluene, 42.8; gasoline, 30.0; kerosene 27.1; and diesel, 18.2 g/g (oil/POAMs). Saturation oil absorption reached within 3 h in CCl_4. The POAMs exhibited high oil retention percentage (>90%), and can be reused for at least 10 times while keeping oil absorbency almost unchanged.

1. Introduction

Water pollution caused by oil spills and organic pollutants has become one of the most serious environmental problems in the last several decades (Maki, 1991; Mortita, Higuchi, & Sakata, 1987). Therefore, the synthesis of highly efficient cleanup materials (oil-absorbents) for recovery of spilled oils over water has been gathering ever-growing attention (Atta, El-Hamouly, Sabagh, & Al Gabr, 2007; Ballabh, Trivedi, & Dastidar, 2006; He, Ding, Deng, & Yang, 2012; Ibrahim, Wang, & Ang, 2010; Judson et al., 2010; Tecon et al., 2010; Trivedi & Dastidar, 2006; Wu & Zhou, 2009a), due to their high absorbency, fast absorption speed, and good absorption selectivity toward oils over water. A great number of oil-absorbents have been reported in literature (Atta, El-Ghazawy, Farag, & Abdel-Azim, 2006; Atta, El-Ghazawy, Farag, El-Kafrawy, & Abdel-Azim, 2005; Farag & El-Saeed, 2008; Jang & Kim, 2000; Kim, Chung, Ha, Kim, & Cho, 1999; Kulawardana & Neckers, 2010; Likon, Remškar, Ducman, & Švegl, 2012; Medeiros, Oliveira, Sansiviero, Araujo, & Lago, 2010; Shan, Xu, Weng, & Huang, 2003; Wang, Zheng, & Wang, 2012; Wu & Zhou, 2009b; Zhou & Chuai, 2010; Zou, Zhao, Ge, Lei, & Luo, 2012). However, there are still some disadvantages in particular the low practical applicability in the traditional oil-absorbents. Thus new oil-absorbents are still highly required.

Our previous studies demonstrate that incorporating β-cyclodextrin (β-CD) moieties into polymeric oil-absorbents can dramatically improve the oil absorbency of the absorbents (Ding, Li, Jia, Deng, & Yang, 2011; He et al., 2012), partly due to the large voids inside the oil-absorbents provided by the bulky β-CD moieties. However, some limitations—the tedious synthetic process, the high cost of the β-CD derivative (He et al., 2012), and the difficulty in handling of the absorbents in bulk (Ding et al., 2011)—should be overcome before realizing practical applications. In the present study, we designed and prepared new polymeric oil-absorbent microspheres (POAMs), not only successfully circumventing the limitations mentioned above but more interestingly keeping the high oil absorbency, fast oil absorption speed, and good reusability of the oil-absorbents. Suspension polymerization technique was adopted to prepare the POAMs (He et al., 2012). For preparing such POAMs, a more efficient and more easily available β-CD derivative was utilized instead of the earlier one (Ding et al., 2011). Crosslinking agent content and monomer feed ratio are crucial factors to prepare oil-absorbents with remarkable oil absorbency (He et al., 2012). Accordingly, these two factors together with another two vital affecting factors, i.e., initiator content and stabilizer content were investigated in detail to determine the optimal preparing parameters and further to optimize the properties of the POAMs. These investigations provide important insights for further designing and creating novel oil-absorbents. According to their superior properties, the present POAMs are expected to find some practical applications for instance in recovering spilled oils and cleaning waste water.

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2. Experimental part

2.1. Materials

Butyl acrylate (BA, Beijing Chemical Reagent Co.) was distilled under reduced pressure before use. 2,2′-Azobisisobutyronitrile (AIBN, Beijing Chemical Reagent Co.) was recrystallized from ethanol, dried under vacuum at room temperature, and stored in an amber bottle. β-Cyclodextrin (β-CD, Alfa Aesar), octadecyl acrylate (ODA, Aldrich), and polyvinylalcohol (PVA, Beijing Chemical Reagent Co.) were used as received without further purification. β-CD-A (the modified β-cyclodextrin as cross-linking agent in the present study, as structurally presented in Scheme 1) was synthesized and characterized according to our earlier report (Ding et al., 2011). The average substitution degree of the hydroxyl groups on the outside surface of β-CD was about 4. Gasoline and diesel were obtained from Sinopec Beijing Yanshan Company. Kerosene was obtained from Alfa Aesar. Freshly deionized water was used in all the experiments.

2.2. Preparation of poly(ODA-co-BA) oil-absorbent microspheres via suspension polymerization

The poly(ODA-co-BA) oil-absorbent microspheres (POAMs) were prepared via suspension polymerization. Firstly, PVA was dissolved in 100 mL deionized water in a 250 mL three-neck flask, which was equipped with a mechanical stirrer (stirring speed, 300 rpm), a reflux condenser, and a gas inlet pipe. Then, a mixture of monomers, initiator, and crosslinking agent of predetermined amount was introduced in the PVA aqueous solution under nitrogen atmosphere. After degassing for 1 h, the reaction system was heated to 60 °C and polymerized for 12 h. Finally, the products were collected as white microspheres, washed with acetone and deionized water, and dried in a vacuum oven at 50 °C till a constant weight. The yield of the POAMs was found to be quantitative under optimized conditions, indicating that the composition of the microspheres kept nearly the same as the feed ratio of the monomers. The as-prepared microspheres were approx. 1.5 mm in diameter.

2.3. Oil absorption test

All the oil absorption testing methods were similar to our earlier reports (Ding et al., 2011). Taking chloroform as example, a given amount of oil-absorbent sample (m_1) was put into a filter bag and immersed in chloroform at room temperature for 12 h. The chloroform was renewed every 2 h. The filter bag containing the sample was taken out from chloroform and dried at 60 °C for 24 h. Then the sample was weighed and this weight was recorded as m_2. The crosslinking degree was calculated by the following equation:

$$\text{Crosslinking degree} = \frac{m_2}{m_1} \times 100\% \tag{1}$$

A quantity of about 0.02 g of dried oil-absorbent sample (after removing the uncrosslinked polymer chains) with known weight (m_3) was put into a filter bag and immersed in an oil (CCl_4, $CHCl_3$, xylene, toluene, gasoline, diesel, and kerosene) at room temperature. After a predetermined time (12 h is needed for full oil absorbency), the filter bag with the sample was lifted from the oil and drained for 1 min. Then the sample was immediately taken out and weighed and this weight was recorded as m_4.

Oil absorbency was calculated by the following formula:

$$\text{Oil absorbency} = \frac{m_4 - m_3}{m_3} \tag{2}$$

It should be noted herein that all the oil absorbency values in the Figures below were statistical data. They were average values of three repeated oil absorption test procedures.

To investigate the oil absorption of the POAMs over water, the major procedure was the same as stated above. The filter bag with the POAM sample (m_3) was immersed in a mixture solvent (oil/water = 1/1, v/v) under stirring. After a predetermined time, the sample bag was lifted and drained for 1 min. Then the sample was immediately taken out and weighed. This weight was also marked as m_4. The oil absorbency was also determined following formula (2).

A quantity of about 0.02 g of dried oil-absorbent sample weighed beforehand was put into a filter bag and immersed in an oil at room temperature for 12 h. Then the filter bag with the sample was lifted from the oil and drained for 1 min. The sample was immediately taken out, weighed, and the weight was recorded as m_5. Afterward, the sample was immersed into 200 mL anhydrous ethanol for another 12 h. Then the filter bag with the sample was lifted from ethanol and drained for 1 min. The sample was immediately taken out, weighed, and the weight was recorded as m_6. The oil desorption rate was calculated by the following formula:

$$\text{Oil desorption rate} = \frac{m_5 - m_6}{m_5} \times 100\% \tag{3}$$

In order to investigate the oil retention ability of the POAMs, oil retention percentage was defined as follows. The fully swollen oil-absorbent microspheres with a total weight of m_7 were centrifuged at a centrifugal speed of 1000 rpm for 5 min, and then the microspheres were weighed as m_8. Where m_0 represents the initial dry weight of the oil absorbent microspheres, the oil retention percentage could be calculated by the following formula:

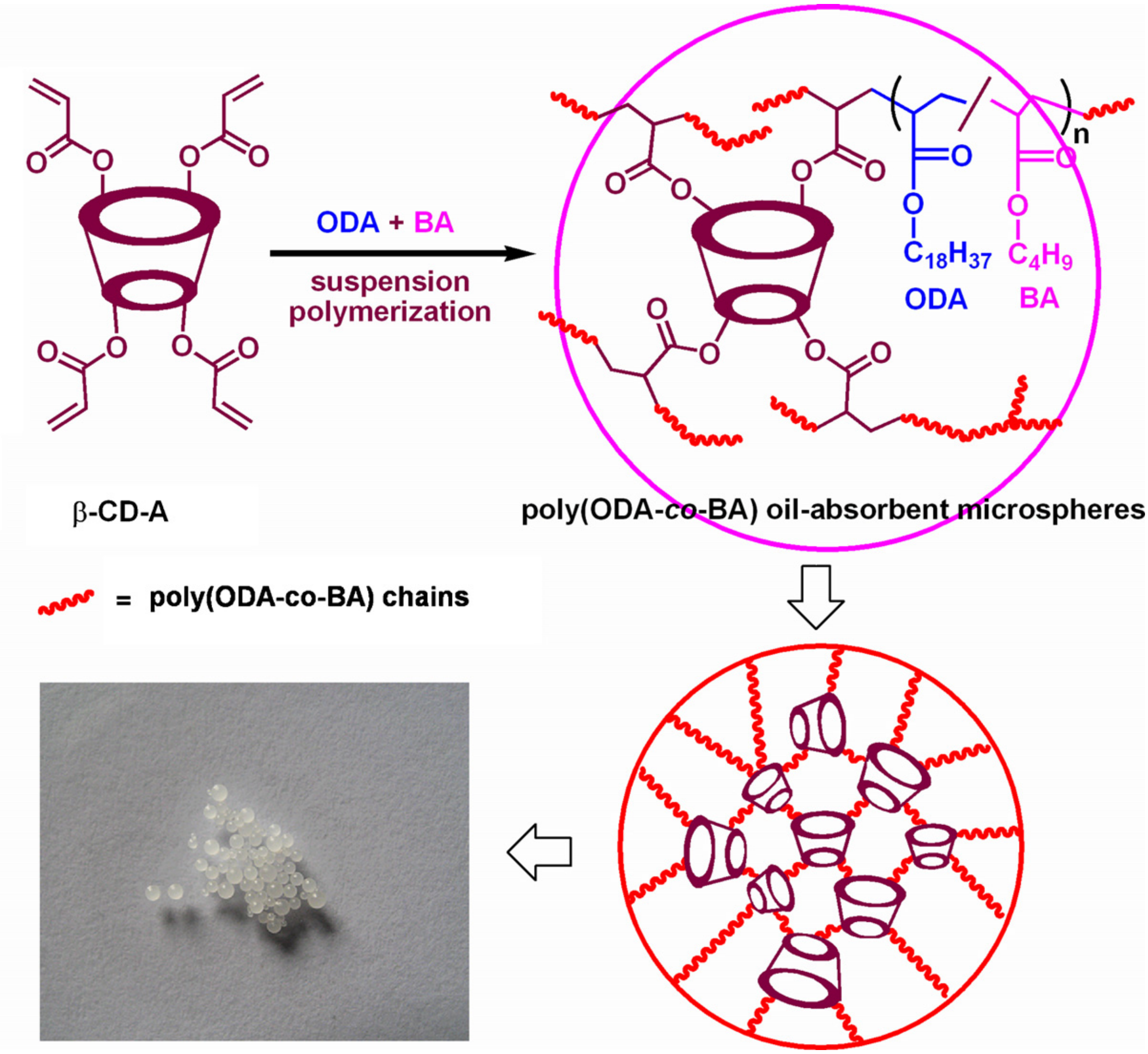
$$\text{Oil retention percentage} = \frac{m_8 - m_0}{m_7 - m_0} \times 100\% \tag{4}$$

3. Results and discussion

3.1. Preparation of poly(ODA-co-BA) oil-absorbent microspheres (POAMs)

The POAMs were prepared following Scheme 1, in which the major components constituting the POAMs are also presented. It is well known that crosslinking is responsible for the formation of three-dimensional network structures which are of great importance for the formation of organogels, hydrogels, and oil-absorbents. In our previous study (Ding et al., 2011) dealing with oil-absorbents containing β-CD moieties, the β-CD derivative, β-CD-A (Scheme 1), was proved to be an efficient crosslinking agent for the preparation of β-CD-based oil-absorbents with good three-dimensional architectures. Taking into account the relatively much easier synthesis of β-CD-A than β-CD-MA (He et al., 2012), which was also used for successfully preparing oil-absorbent spheres, β-CD-A was selected as crosslinking agent in the present work to prepare β-CD-based POAMs. β-CD-A underwent copolymerization smoothly with octadecyl acrylate (ODA) and butyl acrylate (BA) with AIBN as initiator and PVA as stabilizer via suspension polymerization, forming the expected POAMs in quantitative yield.

A typical photograph of the POAMs before absorbing oil is shown in Fig. 1A. The POAMs produced via suspension polymerization were rather uniform in diameter (approx. 1.5 mm). For a comparison of the POAMs before (Fig. 1A) and after absorbing oils, the photographs of POAMs after absorbing CCl_4, $CHCl_3$, xylene, toluene, gasoline, kerosene and diesel are presented in Fig. 1B–H, respectively. The POAMs after absorbing oils (Fig. 1B–H) became considerably larger (diameter, 5–12 mm) when compared to the original dry POAMs (Fig. 1A), providing a visually clear observation of the high oil absorbency of the POAMs. More importantly, the



Scheme 1. The preparing schematic and major components constituting POAMs.

oil-absorbed POAMs could maintain very well the spheric morphology and the absorbed oils did not flow out from the POAMs, clearly demonstrating the high strength and toughness of the POAMs even after absorbing oils.

In order to optimize the structure, composition, and properties of the POAMs, some affecting factors including monomer feed ratio and the concentrations of initiator and stabilizer were investigated in detail, as to be discussed below.

3.2. *Effects of cross-linking agent content on oil absorbency*

As mentioned above, cross-linking is of great significance for the preparation of oil-absorbents containing cross-linked architectures. Accordingly, the amount of cross-linking agent, i.e., β-CD-A, in the present polymerization system was particularly investigated. To study the relationship between oil absorbency and the content of β-CD-A, a series of POAMs with varied β-CD-A content (from 4 to 10 wt%, based on the total mass of the two co-monomers) were prepared, with all other polymerization parameters remaining constant. The investigation results are presented in Fig. 2.

For all the four examined oils in Fig. 2, with increasing the β-CD-A content the oil absorbency of the POAMs increased first, reached a maximum, and then decreased. This observation could be explained as follows. β-CD-A acted as crosslinking agent in the present polymerization systems. A low content of β-CD-A gave rise to POAMs containing many soluble segments, such as linear polymers and polymer chains insufficiently cross-linked. The cross-linking degree calculated by formula (1) was very low (from 40% to 58% when the β-CD-A content ranged from 4 to 7 wt%). That is to say, the cross-linking density of the POAMs was also low, which in turn resulted in low oil absorbency. Moreover, the oil-absorbed POAMs could not maintain the spheric morphology well, also providing an evidence for the assumption that the POAMs were inefficient in cross-linking. However, an excess of β-CD-A caused a too densely cross-linked network (the cross-linking degree increased from 58% to 86% when the β-CD-A content increased from 7 to 10 wt%), which was also not favorable for increasing the oil absorbency of the POAMs. Thus, only an appropriate β-CD-A content could provide a maximum value in oil absorbency, namely, 7 wt% of β-CD-A based on the total mass of the two co-monomers, as observed in Fig. 2. It should be noted that the effects of crosslinking agent in the present system were similar to the earlier investigated systems (He et al., 2012). Nevertheless, in the latter the most suitable amount of β-CD-MA was found to be 10 wt% (He et al., 2012).

3.3. *Effects of monomer feed ratio on oil absorbency*

Monomer feed ratio directly affects the affinity of the oil-absorbents for oils. It also affects the effective network volume of the cross-linked architecture in POAMs, which undoubtedly in

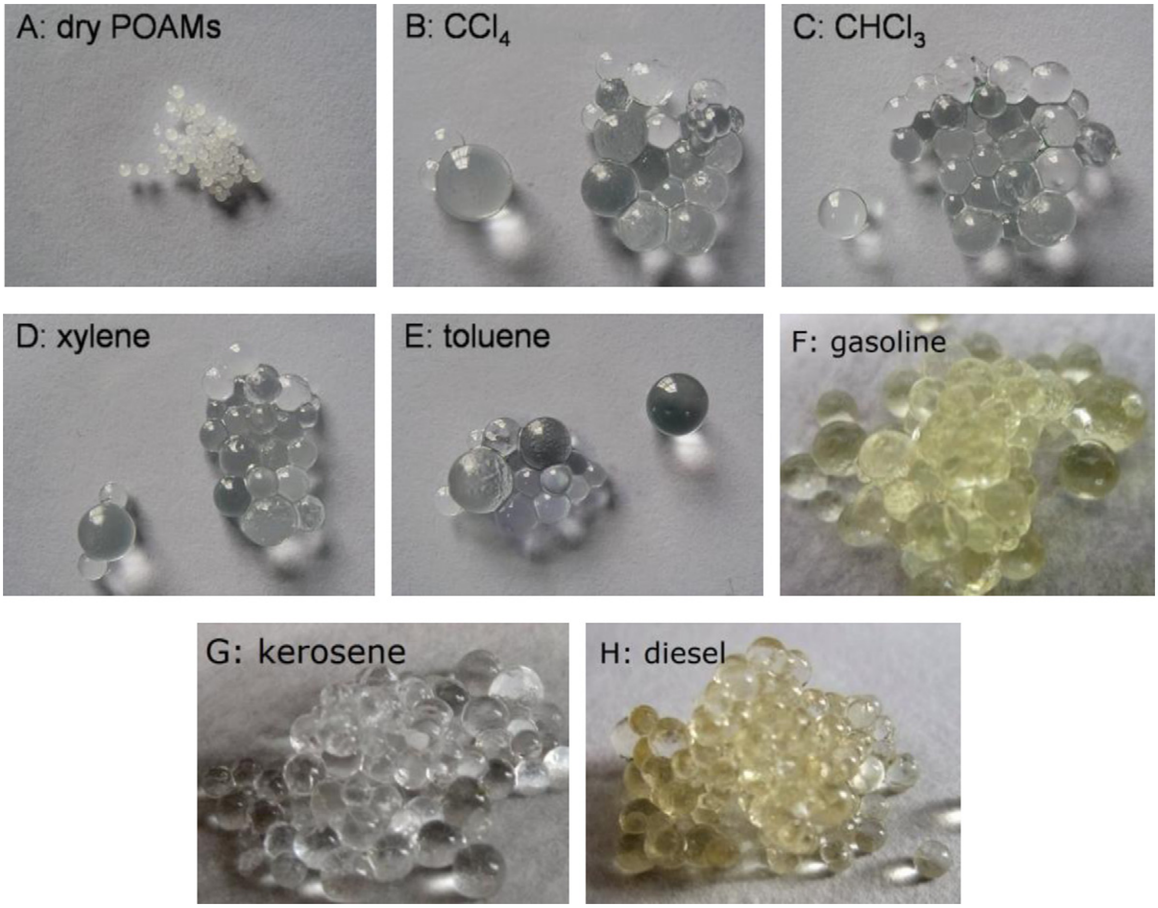


Fig. 1. Typical photographs of the POAMs (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as crosslinking agent, 2 wt% PVA as stabilizer and ODA/BA = 50/50, in mol): (A) before absorbing oils and after absorbing (B) CCl_4; (C) $CHCl_3$; (D) xylene; (E) toluene; (F) gasoline; (G) kerosene; (H) diesel.

turn influences the oil absorption process and oil absorbency of the POAMs (Jang & Kim, 2000; Shan et al., 2003). Fig. 3 illustrates the relationship between oil absorbency and the monomer feed ratios. As shown in Fig. 3, for all the four oils there was a maximum value in oil absorbency when the BA content was 50% in mol. When the BA content was lower than 50%, namely, more ODA was used in this polymerization system, the effective network volume of the formed POAMs decreased due to the presence of long alkyl chains in ODA units. Therefore, the oil absorbency was relatively lower. In contrast, when the BA content was larger than 50%, namely, the amount of ODA used in the polymerization system was less than that of BA, the hydrophobicity of the POAMs decreased since the relatively lower hydrophobicity of BA units than that of ODA units. Additionally, the driving force for oil absorption was mainly due to van der Waals interactions between the oil-absorbents and the oils.

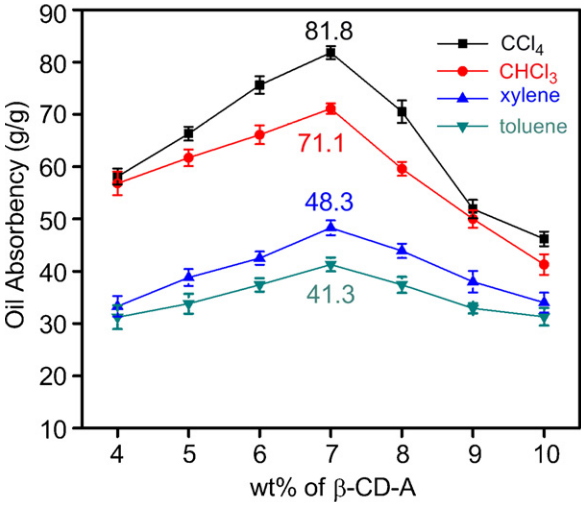


Fig. 2. Effects of cross-linking agent (β-CD-A) content on oil absorbency of the POAMs (using 3 wt% AIBN as initiator, 1 wt% PVA as stabilizer, and ODA/BA = 50/50, in mol) in four oils.

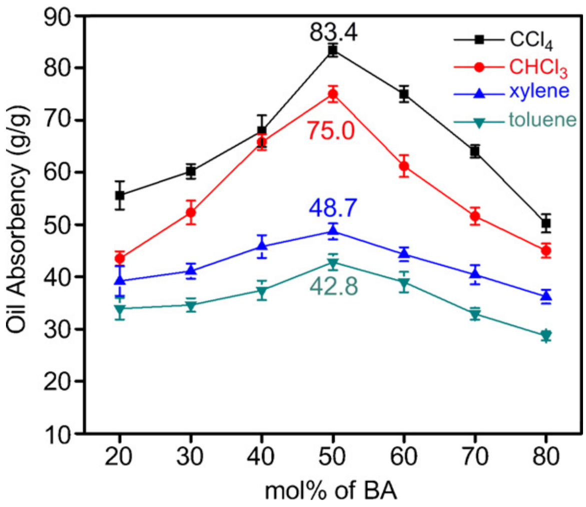


Fig. 3. Effects of BA content on oil absorbency of the POAMs (using 3 wt% AIBN as initiator, 7 wt% β-CD-A as crosslinking agent and 1 wt% PVA as stabilizer) in four oils.

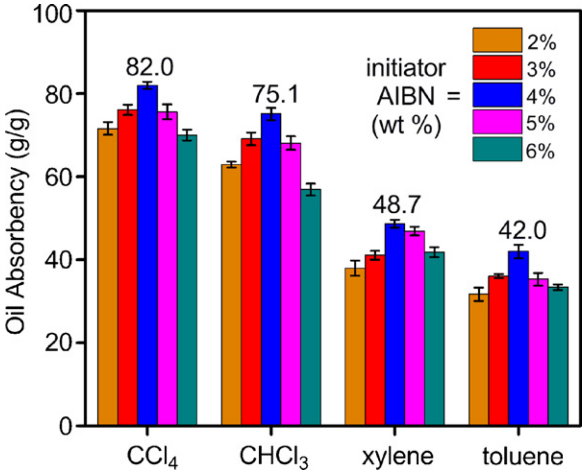


Fig. 4. Effects of initiator (AIBN) concentration on oil absorbency of the POAMs (using 7 wt% β-CD-A as cross-linking agent, 1 wt% PVA as stabilizer, and ODA/BA = 50/50, mol/mol) in four oils.

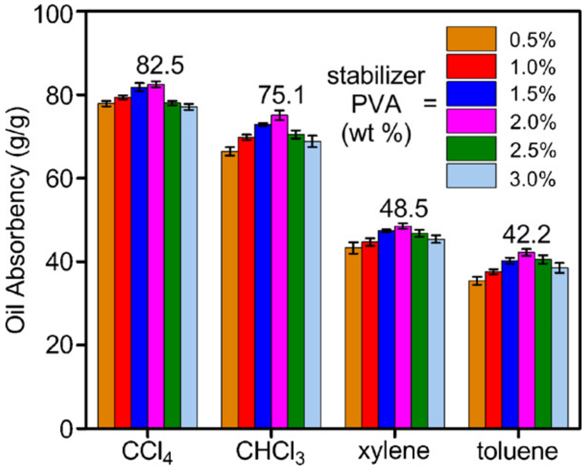


Fig. 5. Effects of stabilizer (PVA) content on oil absorbency of the POAMs (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent, and ODA/BA = 50/50, mol/mol) in four oils.

So a moderate increase in the ODA content resulted in an increase in oil affinity and oil absorbency of the POAMs. Based on the investigations in Fig. 3 and the discussions above, the optimized monomer feed ratio is ODA/BA = 50/50 in mol.

3.4. *Effects of initiator concentration on oil absorbency*

To investigate the effects of initiator concentration on oil absorbency of the POAMs, we prepared POAMs with varied AIBN content (from 2 to 6 wt%, based on the total mass of the two co-monomers), keeping all other variables constant. The relevant results are depicted in Fig. 4. With increasing AIBN concentration, the oil absorbency initially increased, arrived to a maximum value, and then decreased again. The optimum AIBN concentration was found to be 4 wt% based on the weight of the two co-monomers. The concentration of initiator played big roles in the reaction rate, molecular weight of the macromolecular chains constituting the absorbent, and the cross-linking degree in the POAMs. Too much initiator generated too many active species. This resulted in a fast reaction rate, short polymeric chains, densely cross-linked network, and finally a lower oil absorbency of the POAMs. Nevertheless, when the POAMs were prepared at a too low initiator concentration, long polymeric chains and loosely cross-linked network would be formed, also resulting in a decrease in the oil absorbency. Therefore, an appropriate AIBN concentration was determined as 4 wt% in the present study.

3.5. *Effects of stabilizer content on oil absorbency*

A stabilizer is frequently required to prepare POAMs with uniform diameters via suspension polymerization. The amount of stabilizer affected the diameter of the POAMs and also had a slight influence on the oil absorption behaviors. In more detail, when the PVA content increased from 0.5 to 3.0 wt%, the microsphere diameters decreased from approx. 2.1 mm to approx. 0.7 mm. Fig. 5 displays the relationship between the oil absorbency and the stabilizer content. It can be seen from Fig. 5 that oil absorbencies of the POAMs changed slightly for all the four oils when the PVA content increased from 0.5 to 3.0 wt%. In more detail, when the PVA content was 2.0 wt% based on the weight of the two co-monomers, the thus-prepared POAMs had maximum oil absorbencies toward all the four examined oils. When the concentration of PVA was lower than 2.0 wt%, the obtained POAMs tended to coagulate and the yield of POAMs was also rather low. On the contrary, when too much PVA was used, the excess PVA would be difficult to remove thoroughly from the POAMs and thus a large part of PVA was found to remain on the surface of the POAMs. It should be pointed out herein that when PVA was 2.0 wt% and below, almost all of it can be removed by high-speed centrifugation (20,000 rpm, three times). According to the results of Fig. 5, we used 2.0 wt% PVA (based on the weight of the two co-monomers) to carry out the suspension polymerizations in the present study.

3.6. *Oil absorption speed of the POAMs*

Our earlier investigations (Ding et al., 2011) demonstrated that oil absorption speed of the poly(ODA-co-BA) oil-absorbents synthesized via solution polymerization was quite fast, and it took 6 h for the absorbents to reach a saturated oil absorbency. In the present study, we attempted to adopt suspension polymerization to prepare POAMs with further faster oil absorption speed. Interestingly, we obtained the expected POAMs under the aforementioned optimized polymerization conditions (molar ratio of 50/50 for ODA/BA, 7 wt% β-CD-A, 4 wt% AIBN and 2 wt% PVA). Oil absorbency of the POAMs as a function of immersion time in the four pure oils is presented in Fig. 6A. It is evident that the oil absorbency toward all the four oils increased upon increasing the immersion time and then leveled off after ca. 3 h. Namely, the oil-absorbent microspheres prepared via suspension polymerization method exhibited a much faster oil absorption speed when compared to their counterparts synthesized via solution polymerization. This observation is most likely originated in the large specific surface area of the POAMs, which allowed the oil molecules to diffuse inside the microspheres with much ease. Even though the two samples (oil-absorbent synthesized via solution polymerization and POAMs prepared via suspension polymerization) were different in morphology, the comparison between them in terms of oil-absorbency was favorable for us to understand more deeply the POAMs and to further optimize the structure and properties of them.

In order to investigate the oil absorption of the POAMs over water, we further measured the oil absorbencies of the POAMs as a function of immersion time in a mixture of oil and water (oil/water = 1/1, v/v), as shown in Fig. 6B. The POAMs were immersed in the mixture of oil and water under vigorous stirring in order to achieve a sufficient contact between the POAMs with the oil. The oil absorption speed of the POAMs in oil/water mixture was also faster than their counterparts (Ding et al., 2011). Within

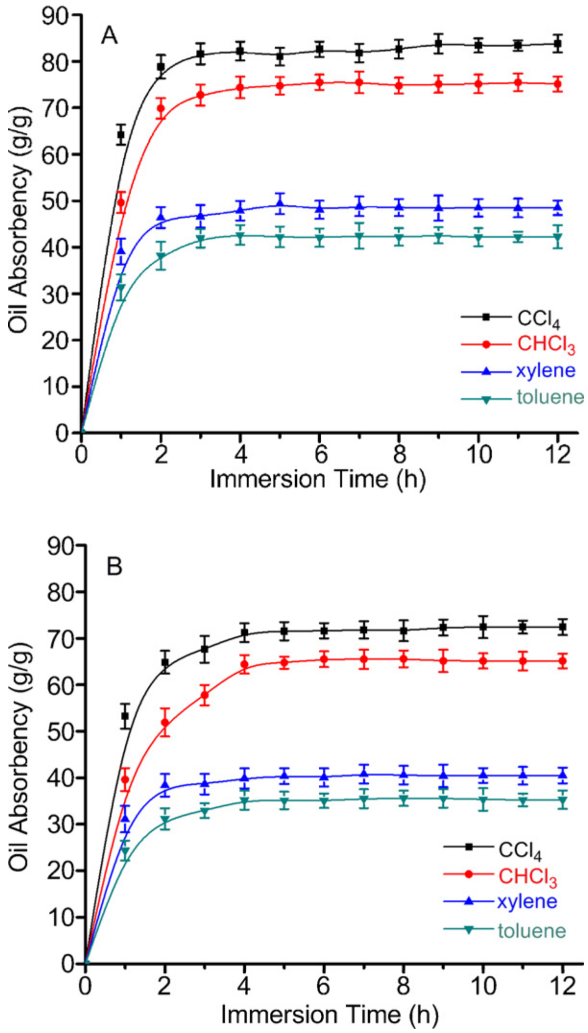


Fig. 6. Oil absorbencies of the POAMs (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as crosslinking agent, 2 wt% PVA as stabilizer, and ODA/BA = 50/50, mol/mol): (A) in four oils and (B) in the mixture of oil and water (oil/water = 1/1, v/v) as a function of immersion time.

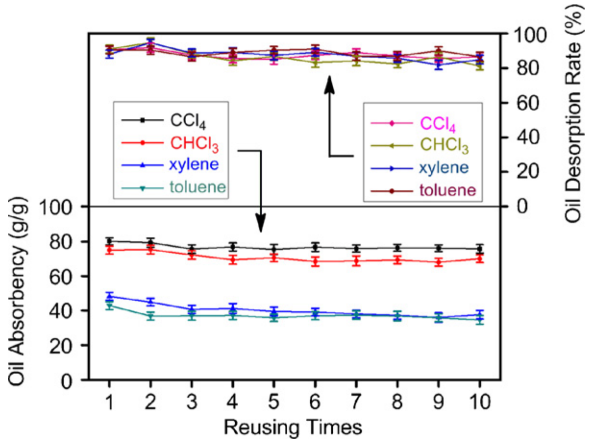


Fig. 7. Variation of (A) oil absorbency and (B) oil desorption rate of the POAMs (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent, 2 wt% PVA as stabilizer, and ODA/BA = 50/50, mol/mol) as a function of the reusing times.

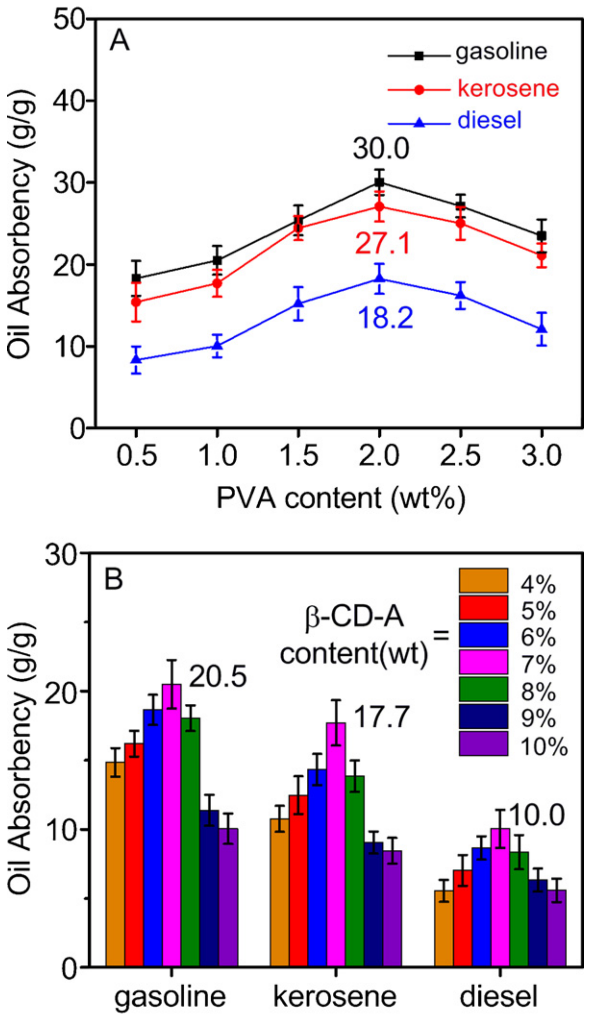


Fig. 8. Oil absorbencies of the POAMs in three petroleum derivatives (using 4 wt% AIBN as initiator and ODA/BA = 50/50, mol/mol): (A) varied PVA content (7 wt% β-CD-A as cross-linking agent); (B) varied β-CD-A content (1 wt% PVA as stabilizer).

4 h, the POAMs reached the saturated oil absorbency. Nevertheless, the oil absorbency decreased slightly when using oil/water mixture instead of pure oil. This might be explained by the fact that oils dispersed in water could not easily diffuse from the external surface of the POAMs into the interior of the network.

3.7. Investigation of the reusability of the POAMs

Our earlier study (Ding et al., 2011) on the reusability of poly(ODA-co-BA) oil-absorbent demonstrated that most of the absorbed oils could be desorbed from the oil-absorbent. The absorbent could be reused for at least 6 times. In the present study, the reusability of the POAMs was also quantitatively investigated in a similar manner. The oil absorbency and oil desorption rate of the POAMs (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as crosslinking agent, 2 wt% PVA as stabilizer, and ODA/BA = 50/50, in mol) as a function of reusing time are presented in Fig. 7. The oil absorbencies of the POAMs stayed almost constant even after reusing for 10 times. In addition, the oil desorption rates calculated according to formula (3) for all the four oils were all remarkably high (for CCl_4, >92.7%; $CHCl_3$, >90.6%; xylene, >90.9%; toluene, >93.3%). When compared to our previous β-CD-based oil-absorbents, the oil desorption rates of the present POAMs were largely increased.

The oil retention property of the POAMs was further investigated. In practice, the oil-absorbed POAMs were expected to maintain well the absorbed oils during transferring to avoid secondary pollution. The oil retention percentage was calculated according to formula (4) described above. The oil retention percentage for CCl_4, $CHCl_3$, xylene, and toluene was 90.7%, 90.8%, 91.2%, and 94.4%, respectively. This demonstrated that most of the absorbed oil could be stored in the POAMs even after the POAMs were centrifuged at a high speed. Hence, the POAMs were expected to find some practical applications owing to the interesting reusability and oil retention performances, together with the excitingly high oil absorbencies.

3.8. Oil absorbency of petroleum derivatives

We further selected three types of petroleum derivatives and investigated the oil absorbency of them by the POAMs. The photographs of POAMs after absorbing gasoline, kerosene and diesel are presented in Fig. 1F–H. For the three petroleum derivatives, the effects of stabilizer content on oil absorbency are shown in Fig. 8A. The results are similar to those described above (Fig. 5). The oil absorbency of the POAMs changed slightly when the PVA content increased from 0.5 to 3.0 wt%. Furthermore, when the PVA content was 2.0 wt%, the POAMs reached maximum oil absorbencies toward the three petroleum derivatives. In particular for gasoline, the maximum oil absorbency was 30.0 g/g. The oil absorbency of the POAMs with varied β-CD-A content is presented in Fig. 8B. Increasing the β-CD-A content led to such a change in the oil absorbency of the POAMs: it initially increased, reached the maximum, and then decreased again. This observation is also similar to the investigation in Fig. 2 (discussed above). Accordingly, the POAMs also demonstrate considerable oil absorbency toward the three petroleum derivatives. After optimizing the compositions and structures of the POAMs, high oil absorbency toward the petroleum derivatives are anticipated. Further investigations along this direction are currently ongoing in our lab.

4. Conclusions

A series of poly(ODA-co-BA) oil-absorbent microspheres was synthesized via suspension polymerization. The effects of synthetic conditions on oil absorbency of the POAMs were investigated in detail. The optimized recipe for synthesizing POAMs was as follows: molar ratio of 50/50 for ODA/BA, 7 wt% β-CD-A, 4 wt% AIBN, and 2 wt% PVA. The POAMs demonstrated high oil absorbency toward the four examined oils, fast oil absorption speed both in pure oil and in the mixtures of oil and water, high oil retention percentage, and remarkable reusability. The POAMs also demonstrate considerable oil absorbency toward petroleum derivatives. Accordingly, we expect that the as-prepared POAMs could find some practical applications as materials for instance in the recovery of spilled oils and in the treatment of waste water.

Acknowledgments

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