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β-Cyclodextrin-based oil-absorbents: Preparation, high oil absorbency and reusability

Lei Ding[a,b], Yi Li[a,b], Di Jia[a,b], Jianping Deng[a,b,*], Wantai Yang[a,b,*]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

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ABSTRACT

This article reports the first oil-absorbents consisting of β-cyclodextrin (β-CD) and showing high oil absorbency. To prepare such oil-absorbents, a β-CD derivative (β-CD-A) was synthesized and then underwent copolymerizations with octadecyl acrylate (ODA) and butyl acrylate (BA) in the presence of AIBN as initiator, yielding a cross-linked oil-absorbent. Herein β-CD-A served simultaneously as a co-monomer, cross-linking agent, and pore-forming agent. The oil-absorbent containing CD moieties showed much higher oil absorbency (CCl_4, 79.1 g; $CHCl_3$, 72.8 g; xylene, 43.7 g; and toluene, 45.7 g/g oil-absorbent) when compared with that without CD (CCl_4, 11.7 g; $CHCl_3$, 13.6 g; xylene, 16.5 g; and toluene, 19.2 g/g oil-absorbent). The desorption and the reusability of the oil-absorbents were quantitatively investigated, demonstrating the absorbents can be used for at least six times. The present oil-absorbents are expected to find practical applications particularly in the recovery of spilled oils and the treatment of wastewater.

1. Introduction

Cyclodextrins (CDs) are obtained by the degradation of starch, one of the most common natural polymers. They are cyclic oligosaccharides consisting of 6 (α), 7 (β), or 8 (γ) glucopyranose units joined together by 1,4-α-linkages forming a torus-shaped ring structure (Saenger et al., 1998; Szejtli, 1998). β-Cyclodextrin (β-CD) has 7 primary hydroxyl groups in 6-position located at the narrow side of the torus and 14 secondary glucopyranose hydroxyl groups located at the wider side of the torus (Ritter & Tabatabai, 2002). β-CD has been widely used in organic chemistry and polymer chemistry owing to its ability to form host/guest complexes by inclusion with suitable hydrophobic molecules (Deng, He, Wu, & Yang, 2008a; Ding, Jiao, Deng, Zhao, & Yang, 2009; Klink & Ritter, 2008; Rimmer & Tattersall, 1999). Meanwhile, β-CD has also been widely used for the preparation of hydrogels and nanogels (Daoud-Mahammed et al., 2009; Manakker, Vermonden, Morabit, Nostrum, & Hennik, 2008; Wang et al., 2007). We have also prepared thermosensitive hydrogels by using hydroxypropyl-β-cyclodextrin (HP-β-CD)/glycidyl methacrylate (GMA)/*N*-isopropylacrylamide (NIPAM) system via a novel one-step method (Deng, Wu, He, & Yang, 2008b). However, despite the enormous applications of CD mentioned above, no report has been found yet in literature to be focused on using β-CD for the preparation of oil-absorbent.

With the industrial development, environmental pollution resulting from oily sewages and oil spills cannot be ignored any more (Maki, 1991). During the past several decades, great interests have been focused on the development of highly efficient cleanup materials for oils on water, for instance, activated carbon, polypropylene fibers or fabrics, melt-blown polyesters, polyurethane foam, etc. Among them, oil-absorbent is widely regarded as the best cleanup material for absorbing oils because of the relatively fast oil absorption rate, large oil absorbency, and good absorption selectivity of oil over water. Many researchers have made significant contributions towards the progress on the synthesis of oil-absorbent (Farag & El-Saeed, 2008; Jang & Kim, 2000a, 2000b; Kim, Chung, Ha, Kim, & Cho, 1999; Medeiros, Oliveira, Sansiviero, Araujo, & Lago, 2010; Shan, Xu, Weng, & Huang, 2003a, 2003b; Shimizu, Koshiro, Yamada, & Tada, 1997; Zhou & Chuai, 2010). Atta and coworkers reported some oil-absorbents based on polyisobutylene/octadecyl acrylate copolymers (Atta, El-Ghazawy, Farag, & Abdel-Azim, 2006), cinnamoyloxyethyl methacrylates/isooctyl acrylate (Atta, El-Ghazawy, Farag, El-Kafrawy, & Abdel-Azim, 2005), and reactive α-olefins/maleic anhydride (Atta & Arndt, 2005; Atta, El-Hamouly, Sabagh, Al, & Gabr, 2007a, 2007b). Zhou et al. prepared 4-*tert*-butylstyrene-EPDM-divinylbenzene graft terpolymer and investigated the oil absorption properties (Wu & Zhou, 2009a, 2009b; Zhou & Cho, 2001, 2002, 2003). Kulawardana and Neckers (2010) reported a photoresponsive oil-absorbent using bis(methacryloylamino)azobenzene

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* Corresponding authors. Tel.: +86 10 6443 5128; fax: +86 10 6443 5128.
E-mail addresses: dengjp@mail.buct.edu.cn (J. Deng), yangwt@mail.buct.edu.cn (W. Yang).

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as a photoresponsive surface cross-linker. In spite of these interesting works, new oil-absorbent systems are still required to largely improve the properties, in particular the oil-absorbency and the reusability of oil-absorbents.

In this study, we attempted to incorporate the bulky β-CD molecules into the network of oil-absorbent. For this end, a β-CD derivative containing polymerizable C=C bounds (β-CD-A) was prepared as the first step. β-CD-A plays three-fold roles herein, that is, as a co-monomer and as a cross-linking agent for the free radical polymerization, and also as a carrier to introduce CD moieties into the network. Bulky CD moieties are expected to provide the desired pores for the resulting oil-absorbent to adsorb oils, and meanwhile the hydrophobic cavities inside the CD are also in theory helpful for oil absorption. Interestingly, we found that the thus-prepared oil-absorbent (poly(ODA-*co*-BA)) showed much higher oil absorbency both in the pure oils and in the oil/water mixtures than that of oil-absorbents without CD moieties. More importantly, we found that most of the absorbed oils in the oil-absorbents can be desorbed simply by extracting with ethanol and the oil-absorbents can be reused for at least 6 times. We believe that the present oil-absorbents will be of great importance for oil-recovery and wastewater treatment. Other more applications can also be expected from them.

2. Experimental part

2.1. Materials

Butyl acrylate (BA) was purchased from Beijing Chemical Reagent Corp. and distilled under reduced pressure before use. Water was freshly deionized before use. 2,2′-Azoisobutyronitrile (AIBN) was purchased from Beijing Chemical Reagent Corp. It was recrystallized from ethanol, dried under vacuum at room temperature, and stored in an amber bottle. β-Cyclodextrin (β-CD) was obtained from Alfa Aesar. Octadecyl acrylate (ODA) was purchased from Aldrich. Acryloyl chloride was purchased from Beijing Sanshengtengda Corp. They were used without further purification. Divinyl benzene (DVB-55, 55% mixture of isomers, technical grade, Aldrich), trimethylolpropane trimethacrylate (TMPTA, technical grade, Aldrich) were used as received. Potassium hydroxide (KOH), acetone, dimethyl sulfoxide (DMSO) and all the other reagents were obtained from Beijing Chemical Reagent Corp. and used as received.

2.2. Characterization

The chemical structure of the modified β-cyclodextrin (β-CD-A) was determined by FT-IR spectroscopy and NMR spectroscopy. FT-IR spectra were recorded with a Nicolet NEXUS 670 spectrophotometer (on KBr tablet). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AV600 spectrometer in D_2O at room temperature.

2.3. Synthesis of the modified β-cyclodextrin (β-CD-A)

A cross-linking agent was synthesized by the reaction of β-cyclodextrin with acryloyl chloride in the presence of potassium hydroxide. The main procedure was as follows: β-cyclodextrin (20 g, 17.62 mmol) was added into a solution of KOH (6.02 g, 107.5 mmol) in 250 ml deionized water with vigorous stirring at room temperature. After complete dissolution of β-cyclodextrin, the solution was cooled to 0 °C and then acroloyl chloride (14.3 ml, 176.2 mmol) was dropwise added in a period of 30 min. The solution was stirred at 40 °C for about 6 h. After that, the white precipitate formed during the reaction was filtered off, and the filtrate was collected. Most of the solvent was removed using a rotary evaporator and then the residue was poured into a large amount of acetone. The obtained white solid was recrystallized from water into acetone for three times to provide the product (β-CD-A). Yield: 75%, white powder. Characteristic FTIR (KBr) bands: 1723 cm^{-1} (C=O) and 1636 cm^{-1} (H–C=C). ^{1}H-NMR (D_2O, 600 MHz, 25 °C), δ: 6.23–6.42 (CH_2=CH), 5.97–6.03 (CH_2=CH), 5.05 (O–CH–O), 3.83–3.95 (C–CH–OH and C–CH_2–OH), 3.55–3.65 (C–CH–O), 2.21 ppm (CH–OH and CH_2–O*H*). ^{13}C NMR (600 MHz, D_2O), δ: 127 (CH_2=CH), 133 (CH_2=CH), 168 (C=O), 102, 81, 73, 72, 60 ppm.

2.4. Preparation of poly(ODA-co-BA) oil-absorbent

The oil-absorbent was prepared by a solution polymerization method. A mixture of monomers, initiator, cross-link agent, and DMSO at a predetermined molar ratio was introduced into a 100 ml reactor and then polymerized at 70 °C for 12 h. After polymerization, the mixture was poured into a large amount of deionized water to obtain the product, washed with acetone for three times, and then dried in a vacuum oven at 50 °C for 24 h.

2.5. Cross-link degree

For some oil-absorbents in literature, soluble fraction (*SF*) (Atta et al., 2005, 2006, 2007a, 2007b) or gel fraction (*GF*) (Zhou & Cho, 2002) was measured to investigate the cross-linking of the absorbent networks. In the present study, cross-link degree (*D*) of the oil-absorbents was determined in a similar way to characterize the oil-absorbents. 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 cross-link degree (*D*) was calculated by the following equation:

$$D = \frac{m_2}{m_1} \times 100\% \qquad (1)$$

2.6. Oil absorption test

2.6.1. Oil absorbency

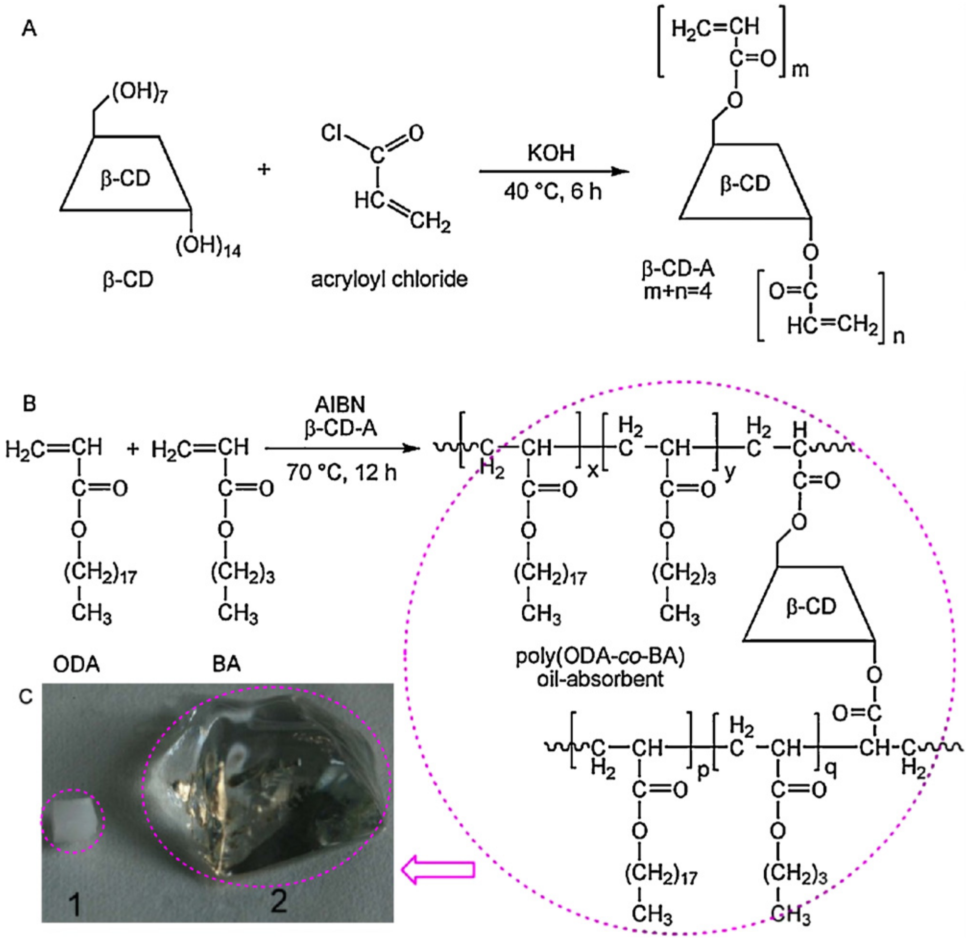
The oil absorbency (Q) was determined by the method reported in literature (Atta et al., 2005, 2006, 2007a, 2007b; Kulawardana & Neckers, 2010; Wu & Zhou, 2009b; Zhou & Cho, 2001, 2002). A quantity of about 0.02 g of dried oil-absorbent sample with known weight (m_3) was put into a filter bag and immersed in four different oils (tetrachloromethane, chloroform, xylene, and toluene) 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 oils and drained for 1 min. Then the sample was immediately taken out and weighed. The oil absorbency was calculated by the following formula:

$$Q = \frac{m_4 - m_3}{m_3} \qquad (2)$$

where Q represents the oil absorbency; m_3 and m_4 are the weights of the oil-absorbent before and after oil absorption, respectively.

2.6.2. Oil desorption rate

In order to investigate the reusability of the poly(ODA-*co*-BA) oil-absorbent, a new parameter, oil desorption rate, was defined in this paper. 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 oils 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



Scheme 1. Synthesis route of (A) β-CD-A and (B) poly(ODA-*co*-BA) oil-absorbent. (C) Photographs of the poly(ODA-*co*-BA) oil-absorbent (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent, and ODA/BA = 50/50 in mol): (1) before and (2) after absorption of $CHCl_3$.

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 (R) was calculated by the following formula:

$$R = \frac{m_5 - m_6}{m_5} \times 100\% \qquad (3)$$

3. Results and discussion

3.1.1. Strategy for preparing the oil-absorbent

The poly(octadecyl acrylate-*co*-butyl acrylate) [poly(ODA-*co*-BA)] oil-absorbent was prepared following the strategy depicted in Scheme 1. Firstly, some of the hydroxyl groups of β-CD were substituted by reacting with acryloyl chloride to provide a multi-acrylate-terminated β-CD (β-CD-A) as a cross-linking agent for the preparation of oil-absorbent. Then, β-CD-A was copolymerized with octadecyl acrylate (ODA) and butyl acrylate (BA) using AIBN as a free radical initiator to obtain the designed poly(ODA-*co*-BA) oil-absorbent containing β-CD moieties. More details will be presented later on.

3.2. Synthesis and characterization of the modified β-cyclodextrin (β-CD-A)

In order to incorporate CD moieties into the cross-linking chains of the poly(ODA-*co*-BA) oil-absorbent, it is essential to introduce C=C groups onto the CDs. In this work, modified β-cyclodextrin (β-CD-A) was prepared via the reaction of hydroxyl groups on the outside surface of β-CD with acryloyl chloride under strong alkalinity condition (Scheme 1A). To confirm the chemical structure of β-CD-A and to investigate the average substitution degree of the hydroxyl groups on the outside surface of β-CD, we measured the ^1H and ^{13}C NMR spectra of β-CD-A in D_2O (Fig. 1). In Fig. 1A, the three peaks located at chemical shifts of $\delta = 6.42$, 6.23, and 5.97 ppm are associated with the methylene (H_a, H_b, CH2=CH–) and methylidynel protons (H_c, CH_2=CH–) of the C=C groups. The signals located at broad chemical shifts in the region of 3.55–3.65 ppm are attributable to the inner methylidynel protons between the oxygen and carbon moieties (H_d, C–CH–O), and peaks located at broad chemical shifts in the region of 3.83–3.95 are assigned to the inner methylene and methylidynel protons between the hydroxyl groups and carbon moieties ($H_{d'}$, C–CH_2–OH and C–CH–OH) on the glucose units of β-CD. The signal located at $\delta = 5.05$ ppm is attributable to the methylidynel protons between the oxygen moieties ($H_{d''}$, O–CH–O). The peak at $\delta = 2.21$ ppm corresponds to the hydroxyl protons adjacent to the methylene and methylidynel moieties (H_e, CH–OH and CH_2–OH). According to the area ratio of peak H_c to peak H_e, the average substitution degree of the hydroxyl groups on the outside surface of β-CD is determined to be about 4.0. The ^{13}C NMR spectroscopy (Fig. 1B) also provides strong evidence for the successful modification of β-CD. Compared with the ^{13}C NMR spectrum of pure β-CD, the characteristic peaks at $\delta = 127$, 133, and 168 ppm of the acrylate moieties appeared in the spectrum of β-CD-A. Thus, it can be concluded that β-CD-A with four C=C moieties has been successfully synthesized.

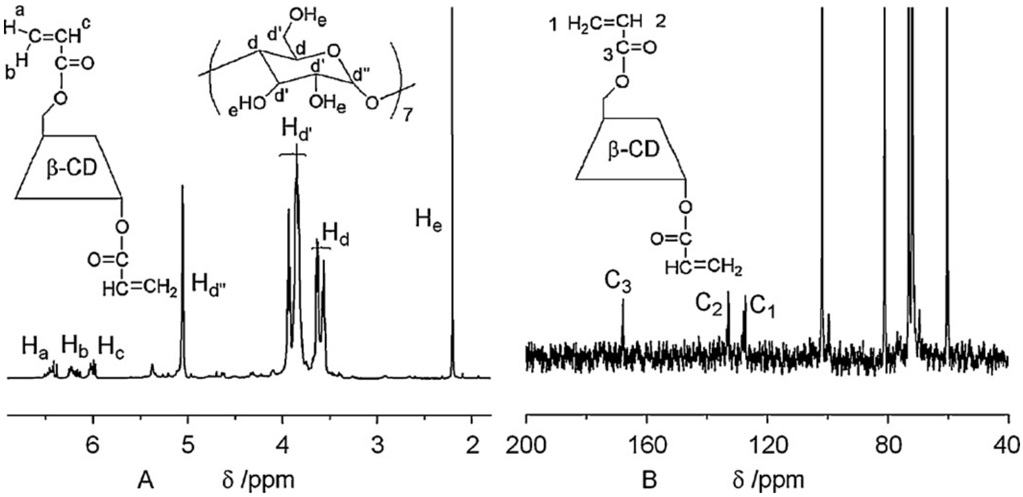


Fig. 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of the modified β-CD (β-CD-A).

3.3. Preparation and oil absorption properties of poly(ODA-*co*-BA) oil-absorbents

Cross-linking is responsible for the formation of three-dimensional network structure which is important for the preparation of organogels and hydrogels. It is also well known that elasticity and swelling properties are attributed to the presence of physical or chemical cross-links in polymer chains. In order to fabricate the expected three-dimensional architecture of the poly(ODA-*co*-BA) oil-absorbent, we designed and synthesized a novel cross-linking agent derived from β-CD in this work, namely, β-CD-A discussed above. In the subsequent copolymerizations, β-CD-A plays three-fold roles, i.e., as a co-monomer and as a cross-linking agent for the free radical copolymerizations, and also as a carrier to introduce CD moieties into the network. In addition, the incorporation of the bulky cyclodextrin molecules led to a great number of voids inside the network, which in turn is helpful to largely increase the oil absorbency, as discussed below.

With β-CD-A as cross-linking agent, copolymerizations of ODA and BA were accomplished via solution polymerization in the presence of AIBN as initiator. The copolymerizations were investigated in detail by varying the amount of cross-linking agent, initiator concentration, and the monomer feed ratio (ODA/BA). The corresponding polymerization conditions and the absorption characteristics of the poly(ODA-*co*-BA) oil-absorbents will be discussed in detail later. Typical photographs of the poly(ODA-*co*-BA) oil-absorbent (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent and ODA/BA = 50/50, mol/mol) before and after oil absorption in $CHCl_3$ was shown in Scheme 1C. The pictures provide a visually clear observation of the high oil absorbency of the absorbents.

3.3.1. Effect of cross-linking agent content on oil absorbency

To investigate the effect of the cross-linking agent content on the oil absorbency, we prepared a series of poly(ODA-*co*-BA) oil-absorbents with varied β-CD-A contents (from 4% to 10%, based on the total mass of the two co-monomers), keeping all other conditions constant. Fig. 2 illustrates the relationship between oil absorbency and the content of β-CD-A. As shown in Fig. 2, for all the four oils used in this experiment, there was a maximum value in oil absorbency when the β-CD-A content was 7 wt%. The cross-link degree (D) of the oil-absorbents was determined using the method depicted in the experimental part. The cross-link degree increased from 44% to 70% when the β-CD-A content increased from 4% to 10%. That is to say, a lower concentration of β-CD-A (e.g. 4 wt%) would lead to such an oil-absorbent in which the cross-linked network would be too loose. Accordingly, a lower oil absorbency was observed. However, when the amount of β-CD-A exceeds 7 wt%, the oil absorbency decreases to different extents in all the four oils. It is well known that an excess of cross-linking agent will cause the formation of a too denser network of the copolymer and reduce drastically the chain length between cross-linking points, meanwhile causing an excessive decrease in the mobility of the polymeric chains (Atta et al., 2006; Jang & Kim, 2000b; Shan et al., 2003b). This is disadvantageous for the oil to flow inside the network of the absorbent and accordingly the oil absorbency is low.

3.3.2. Effect of monomer feed ratio on oil absorbency

The monomer feed ratio affects the hydrophobicity and the effective volume of the cross-linking network, and therefore affects its oil absorption process and oil absorbency (Jang & Kim, 2000b; Shan et al., 2003a; Zhou & Cho, 2002). A series of poly(ODA-*co*-BA) oil-absorbents with varied monomer feed ratios (ODA/BA = 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, mol/mol) were prepared with all other variables unchanged. The relevant oil absorption investigations are depicted in Fig. 3. It can be seen that for all the four oils examined, there was a maximum value for oil absorbency when the monomer feed ratio was 50/50 (ODA/BA, mol/mol). In

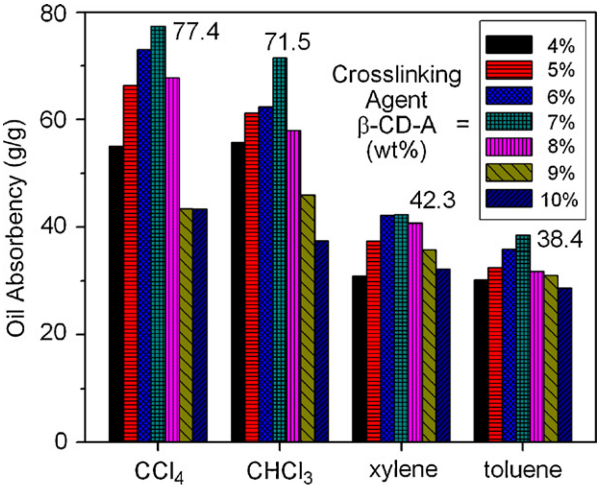


Fig. 2. Effect of cross-linking agent (β-CD-A) content on oil absorbency of the poly(ODA-*co*-BA) oil-absorbent (using 3 wt% AIBN as initiator and ODA/BA = 50/50, in mol) for four oils.

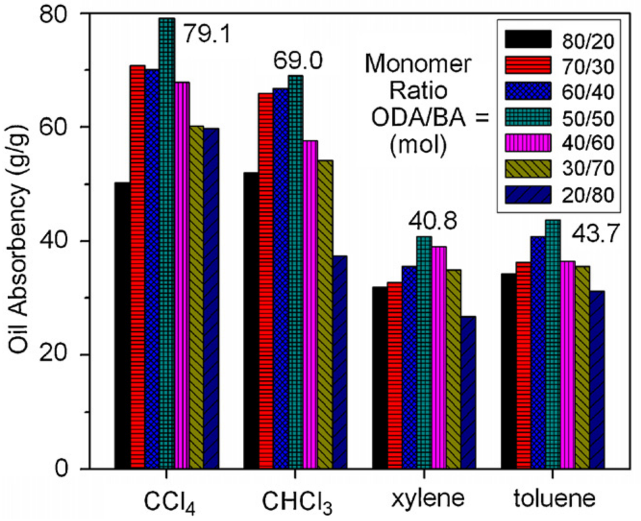


Fig. 3. Effect of monomer feed ratio (ODA/BA) on oil absorbency of the poly(ODA-*co*-BA) oil-absorbent (using 3 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent) in four oils.

this copolymerization system, the hydrophobicity of poly(ODA) is much stronger than that of poly(BA) owing to the longer pendent alkyl chains in the former. Thus, an increase in the content of ODA will result in an increase in hydrophobicity and oil absorbency of the oil-absorbent. However, the oil absorbency decreased when the content of ODA was too large, because too many ODA in the copolymer system lowered the effective network volume of the absorbent owing to the too many long alkyl groups. An appropriate addition of BA will increase the effective network volume of the absorbent to some extent, and thus, increase the oil absorbency. This was clearly observed in Fig. 3, and the optimized monomer feed ratio was found to be 50/50 (ODA/BA, mol/mol).

3.3.3. *Effect of initiator concentration on oil absorbency*

We prepared the poly(ODA-*co*-BA) oil-absorbents using AIBN as a free radical initiator. In order to study the effect of the initiator concentration, we prepared poly(ODA-*co*-BA) oil-absorbents with varied AIBN contents (from 2% to 6%, based on the total weights of the two co-monomers). Fig. 4 demonstrates the relationship between oil absorbency and the initiator concentration. For all the four oils, there was a maximum value for oil absorbency when the initiator content was 4 wt%. The initiator concentration has a significant effect on the length of the polymeric chains of the absorbent. Short polymeric chains will be formed with a high initiator concentration, which was not favorable in terms of oil absorbency. In contrast, when the oil-absorbent was prepared at a low initiator concentration, long polymeric chains will be formed. Nevertheless, too long polymeric chains are not desirable for the formation of effective cross-linking networks, and thus resulted in the decrease of the oil absorbency (Jang & Kim, 2000b; Shan et al., 2003a; Zhou & Cho, 2002). According to our investigations, the optimized initiator concentration was 4 wt% of the total mass of the two co-monomers.

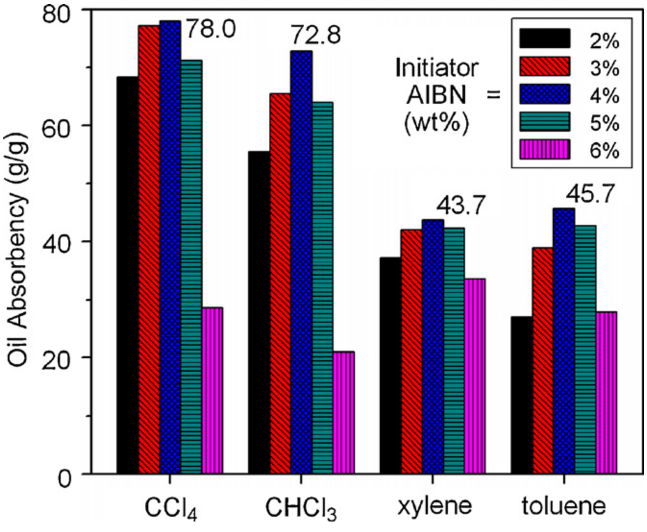


Fig. 4. Effect of initiator (AIBN) concentration on oil absorbency of the poly(ODA-*co*-BA) oil-absorbent (using 7 wt% β-CD-A as cross-linking agent and ODA/BA = 50/50, mol/mol) in four oils.

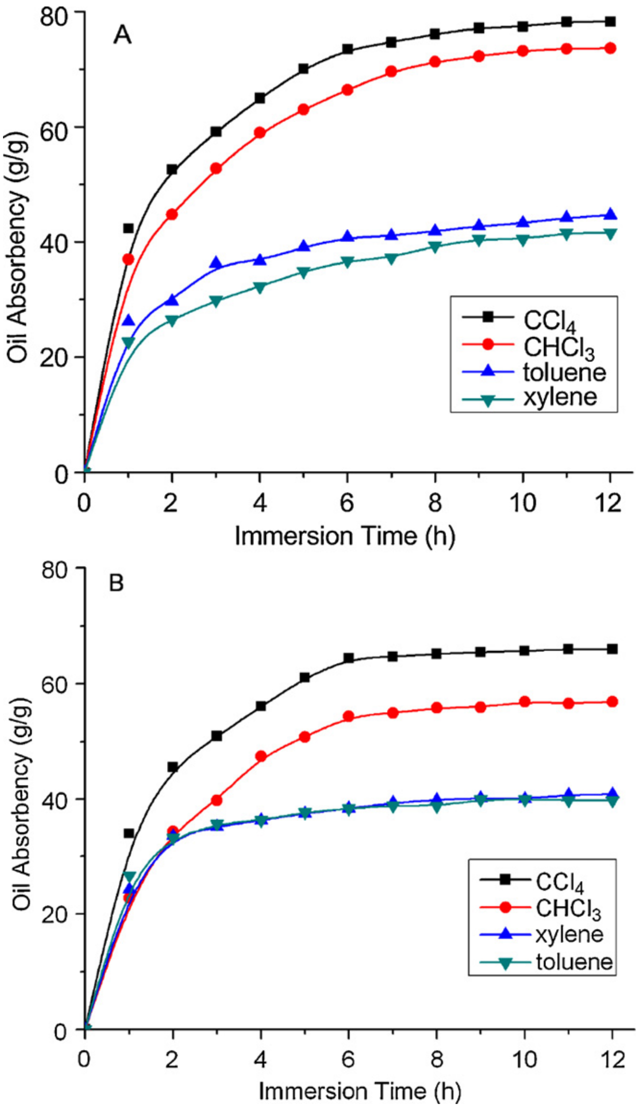


Fig. 5. Oil absorbency of the poly(ODA-*co*-BA) oil-absorbent (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent and ODA/BA = 50/50, mol/mol) (A) in four oils and (B) in the mixture of four oils and water (oil/water = 1/1, v/v) as a function of immersion time.

3.4. *Oil absorption rate of the oil-absorbent*

Fig. 5A illustrates the oil absorbency of the poly(ODA-*co*-BA) oil-absorbent (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent, and ODA/BA = 50/50, mol) in four oils as a function of immersion time. It is evident that the oil absorbency initially increased with immersion time and reached equilibrium 6 h later

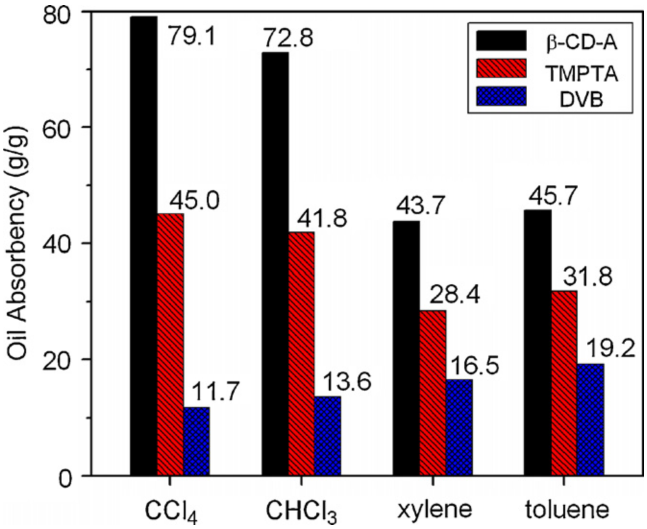


Fig. 6. Oil absorbency of the poly(ODA-*co*-BA) oil-absorbent cross-linked by β-CD-A, TMPTA, and DVB (using 4 wt% AIBN as initiator, 7 wt% cross-linking agent and ODA/BA = 50/50, mol/mol).

and remained almost constant after that. Hence, it is concluded that oil absorption rate of the poly(ODA-*co*-BA) oil-absorbents is quite fast, and it takes only 6 h for the absorbent to reach the saturated oil absorbency.

In order to investigate the potential practical applications of the oil-absorbent, we further measured the oil absorbency of the poly(ODA-*co*-BA) oil-absorbent in a mixture of different oils and water (oil/water = 1/1, v/v) as a function of immersion time. The corresponding results are shown in Fig. 5B. The oil-absorbent was immersed in the mixture of oil and water under vigorous stirring in order to make the mixture homogenous. As can be clearly observed from Fig. 5B, the oil absorption rate was also very fast even in oil/water mixtures, and after 6 h the oil absorbency reached the maximum value. However, the saturated oil absorbency of the absorbent in the oil/water mixtures was a little lower than that in the pure oils discussed above.

3.5. *Comparison between oil-absorbents with and without CD*

In order to improve the oil absorbency of the oil-absorbent, we incorporated bulky CD molecules in the poly(ODA-*co*-BA) oil-absorbent by using β-CD-A as cross-linking agent. For a comparison, we further prepared two poly(ODA-*co*-BA) oil-absorbents cross-linked by TMPTA and DVB, respectively. Both were prepared in a similar way with the exception of using TMPTA and DVB as cross-linking agent instead of β-CD-A. Fig. 6 depicts the investigations. It is evident that oil absorbency of the absorbent bearing CD moieties (CCl_4: 79.1 g/g, $CHCl_3$: 72.8 g/g, xylene: 43.7 g/g, and toluene: 45.7 g/g) is much higher than those without CD (for absorbent cross-linked by TMPTA, CCl_4: 45.0 g/g, $CHCl_3$: 41.8 g/g, xylene: 28.4 g/g, and toluene: 31.8 g/g; for absorbent cross-linked by DVB, CCl_4: 11.7 g/g, $CHCl_3$: 13.6 g/g, xylene: 16.5 g/g, and toluene: 19.2 g/g). Based on the above comparison, a conclusion can be made that oil absorbency of the oil-absorbent containing CD moieties improved dramatically owing to the incorporation of the bulky CD molecules, just as expected.

3.6. *Reusability of the poly(ODA-co-BA) oil-absorbent*

The reusability of the poly(ODA-*co*-BA) oil-absorbents was investigated by measuring their oil absorbency and oil desorption properties. The relevant results are displayed in Fig. 7. After oil absorption, the oil molecules were wrapped into the network of oil-absorbent through the affinity between the oil molecules and the hydrophobic pendent groups of the absorbent. The oil-absorbent has a strong ability to protect the oil from flowing out of the network, so it is difficult to desorb the absorbed oil molecules. However, the oil can be desorbed by an extraction method. In this study, ethanol was used as an extractant for the four oils, because it is a good solvent for these oils and meanwhile almost cannot be absorbed by the oil-absorbent. The oil desorption rate was defined in the experimental part. Fig. 7A shows that, for CCl_4 and $CHCl_3$, oil absorbency of the absorbent decreased to some extents (CCl_4: from 77.2 g/g to 60.5 g/g; and $CHCl_3$: from72.8 g/g to 52.0 g/g) when the absorbent was used for six times. However, the oil absorbency was still much higher compared with that of the oil-absorbents without CD moieties (Fig. 6). In Contrast, for xylene and toluene, it seems that the oil absorbency keeps nearly constant regardless of the reused times. Fig. 7B clearly shows that the oil desorption rate was all very high (for CCl_4: >81.5%; $CHCl_3$: >77.7%; xylene: >72.3%; toluene: >72.8%). This indicated that most of the absorbing oil molecules were desorbed from the oil-absorbent, and the absorbent can be reused for at least 6 times.

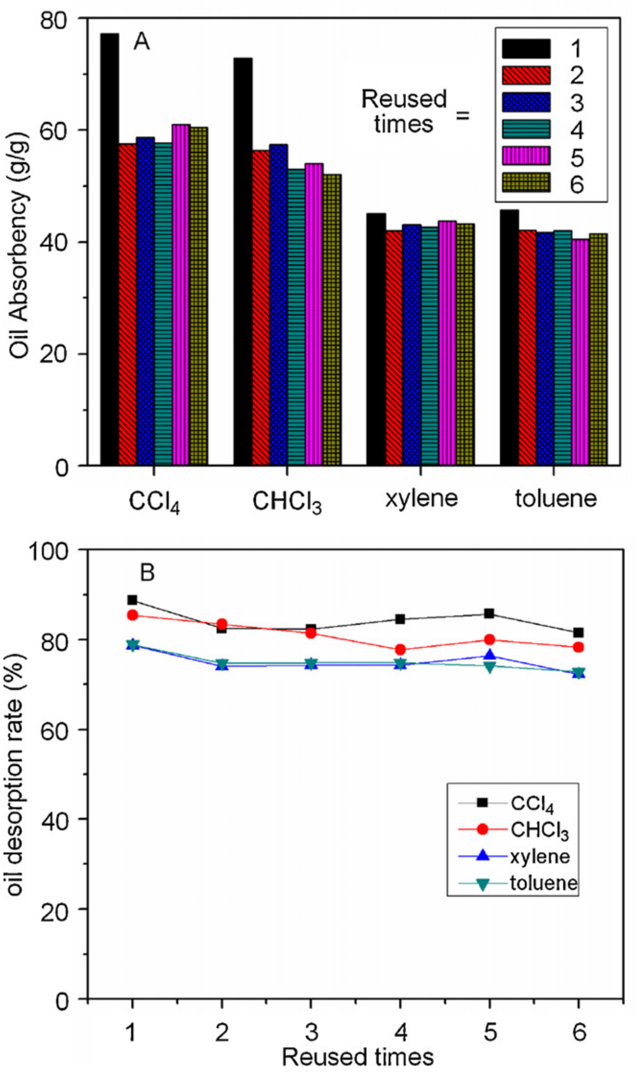


Fig. 7. Variation of (A) oil absorbency (*Q*) and (B) oil desorption rate (*R*) of the poly(ODA-*co*-BA) oil-absorbent (using 4 wt% AIBN as initiator, 7 wt% β-CD-A as cross-linking agent and ODA/BA = 50/50, mol) with the reused times.

4. Conclusions

We have successfully synthesized a novel modified β-cyclodextrin (β-CD-A) by the reaction of acryloyl chloride with β-CD. The average degree of substitution of the hydroxyl groups on β-CD is about 4.0. Poly(ODA-*co*-BA) oil-absorbents with different content of β-CD-A, AIBN, and various monomer feed ratio were prepared using the as-prepared β-CD-A as a cross-linking agent. The optimized recipe (molar ratio of 50/50 for ODA/BA, 7 wt% β-CD-A, 4 wt% AIBN) for the absorbent was obtained according to the oil absorption test. The thus-prepared oil-absorbents containing CD moieties shows much higher oil absorbency than that of those without CD. The poly(ODA-*co*-BA) oil-absorbent can be reused for at least 6 times according to the investigation of the reusability of the absorbent, and showed quite fast oil absorption rate and good oil absorbency in the mixture of oil and water, which is superior in terms of wastewater treatment. We believe that the present technique will find some practical applications in the near future. The present research is ongoing along this way.

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