Synthesis and Properties of a Ternary Polyacrylate Copolymer Resin for the Absorption of Oil Spills

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ABSTRACT: A high-oil-absorption resin of a ternary copolymer for the absorption of oil spills was successfully prepared by suspension polymerization, and characterizations of the oil-absorption resin were also examined in this study. The high-oil-absorption resin, a ternary copolymerized long-chain polyacrylate with styrene (St), butyl methacrylate (BMA), and stearyl methacrylate (SMA) as the monomers and synthesized by suspension polymerization, was introduced. The oil-absorption resin of St/BMA/SMA was characterized by Fourier transform infrared spectrometry. The particle morphology of the resin was observed by scanning electron microscopy. The effects of different polymerization technological parameters, such as the mass ratios of the monomer, the benzoyl peroxide initiator, and the crosslinking agent of divinylbenzene; the sort and concentrations of the dispersing agent of hydroxyl ethyl cellulose, sodium dodecyl benzene sulfonate, and gelatin, and the polymerization temperature, on the oil absorbency of St/BMA/SMA are discussed in detail. The optimum polymerization conditions of the St/BMA/SMA copolymer were obtained as follows: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt % (where m is the mass), temperature = 85°C. With increasing content of these factors, the oil absorbency increased at first and then decreased. Compared with binary copolymer St/BMA prepared in previous research, the highest oil absorbencies to dichloromethane were 12.80 and 23.00 g/g in the St/BMA and St/BMA/SMA copolymers, respectively. St/BMA/SMA had a higher oil absorbency and faster oil-adsorbing rate than St/BMA. The oil absorption in the oil–water mixture and the recovery of the resin were also studied in detail. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40180.

KEYWORDS: adsorption; polystyrene; porous materials

INTRODUCTION

Recently, ocean pollution by vast spills of oil is becoming a more serious environmental problem with the growth of the offshore petroleum industry and the necessity of marine oil transportation. In particular, the oily waste and pollution caused by leakage from oil tankers threatens people's survival and the environment.[1–7] For example, in 2011, the oil leak of the China National Offshore Oil Corp. covered an area of 158 km[2] and changed the quality of water from class 1 down to class 4 in a surrounding area of 840 km[2]. Therefore, oil-absorption materials have been playing an important role in various areas, for example, in industrial and environmental chemistry.[8–11]

Generally, oil-absorption materials can be divided into traditional oil-absorption materials and high-oil-absorption resins. At present, traditional oil-absorption materials, including clay, sponge, and filter paper,[12] are widely used. However, it is well known that traditional oil-absorbing materials have obvious disadvantages, such as low oil absorbency, bad oil–water selectivity, and poor oil retention. These shortcomings limit their further applications.

The first oil-absorption resin was synthesized by Dow Chemical Co. Alkyl vinyl monomers and the crosslinking agent divinylbenzene (DVB) were adopted to synthesize a kind of nonpolar, high-oil-absorption resin. Thereafter, Japanese companies, such as Sanjing Petrochemical Co. and Chumei Chemical Industry, have started to produce oil-absorption resins by this method.[13,14]

High-oil-absorption resins are a new kind of polymer material used for successfully dealing with organic reagents and oily wastewater.[15–17]

High-oil-absorption resins, being low-crosslinking-degree polymers, are copolymerized by lipophilic monomers, such as alkene and acrylate, which contain a three-dimensional (3D) network structure, in which the absorbed oil molecules exist in the form

of van der Waal's forces. Oil-absorption materials have many virtues of a large amount of oil absorption: fast oil absorption, selective absorption of oil and water, excellent oil retention, and so on.[18] So, it will be a new type of high-performance absorption material to be used in place of traditional oil-absorbing materials.

Alkene and acrylate have been widely used as monomers to prepare high-oil-absorbing resins. Xu et al.[19] used methyl methacrylate, butyl methacrylate (BMA), and hydroxyl ethyl methacrylate as monomers to synthesize an oil-absorbing resin through suspension polymerization. This kind of resin mainly contained physical crosslinking instead of chemical crosslinking. The absorbency to toluene of the resin was 12.59 g/g.[19] Huang and Xiao[20] at first prepared an oligomer with styrene (St), BMA, and 2,2-azobisisobutyronitrile. Then, the DVB crosslinker, isopropyl alcohol porogen, and ammonium persulfate initiator were fed into the mixture to produce latex by emulsion polymerization. The absorbency to toluene of the latex reached 20.78 g/g.[20]

After all, if the oil absorbency of resins is expected to improve, it is important to select several suitable monomers and a simple polymerization process and to optimize the conditions of polymerization to synthesize high-oil-absorption resins.

In this study, a high-oil-absorption resin of a ternary copolymerized long-chain polyacrylate of St/BMA/stearyl methacrylate (SMA) synthesized by suspension polymerization was introduced. The influencing factors on the oil absorbency of the high-oil-absorption resin were studied in detail; these included the monomer mass ratio, water/oil mass ratio, concentrations of the crosslinking agent and initiator, type and amount of dispersing agent, and polymerization temperature. The oil absorption and the recoveries of resin were also studied.

EXPERIMENTAL

Materials

St (analytical reagent grade, Damao Chemical Reagents Co., Tianjin, China), BMA (analytical reagent grade, Dimao Chemical Reagents Co., Tianjin, China), and SMA (analytical reagent grade, Tianjiao Radiation Curing material Co., Ltd., Tianjin, China) were freshly distilled *in vacuo*. DVB (chemical pure grade, Guangfu Fine Chemical Industry Research Institute, Tianjin, China) was used as the crosslinking agent. Benzoyl peroxide (BPO; analytical reagent grade, Kewei Co, Tianjin University, Tianjin, China) was used as the initiator. Gelatin (analytical reagent grade, Century Yinfeng Technology Development Co., Ltd., Beijing, China), sodium dodecyl benzene sulfonate (SDBS; chemical pure grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and hydroxyl ethyl cellulose (HEC; chemical pure grade, Bangcheng Chemical Industry, Shanghai, China) were used as dispersing agents. Deionized water was adopted as the polymerization medium.

Synthesis of St/BMA/SMA

St/BMA/SMA copolymerization was carried out in a 500-mL, four-necked flask, which was equipped with a thermometer, stirrer, and condenser. A typical procedure was as follows: the dispersing agents (HEC, gelatin, and SDBS) were dissolved in a

Table I. Detailed Experimental Formulas for the Preparation of Two Optimal Resins with Various Factors According to This Process

Resin	$m_{St}/m_{monomer}$ (wt %)	$m_{BMA}/m_{soft\ monomer}$ (wt %)	Oil absorbency (g/g)
A4	50	60	23.00
B17	60	—	12.80

Preparation conditions: $m_{water}/m_{oil} = 3{:}1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$.

given weight of deionized water. Then, the solution was injected into a flask that was immersed in a water bath held at 60°C by a thermostat. The required amounts of BPO, DVB, and freshly distilled monomers were fed into the reactor to start the polymerization. The system was sealed under N_2. After 30 min, the water bath was heated up to a specified temperature. The reaction was carried out under stirring for about 8.5 h. The copolymer obtained was decanted, washed with heated ethanol/deionized water several times, and dried at 85°C *in vacuo* for 24 h until a constant weight was reached. The resulting product was the St/BMA/SMA copolymer.

The St/BMA/SMA samples were numbered A1–A7 with different St mass ratios; A8–A14 with different ratios of BMA; A15–A21 with water/oil mass ratios; A22–A27 with different amounts of crosslinking agent; A28–A33 with different amounts of initiator; A34–A48 with different amounts of HEC, gelatin, and SDBS; and A49–A54 with different polymerization temperatures. However, the St/BMA samples were numbered B1–B7, B8–B14, B15–B20, B21–B26, B27–B41, and B42–B47. Table I shows the detailed experimental formulas for preparing the two optimal resins (A4 and B17) with various factors according to previous processes.

Characterization

Fourier Transform Infrared (FTIR) Spectrometry. The FTIR spectra of the resins were recorded on a Bio-Rad FTS135 FTIR spectroscope (test conditions: potassium bromide pellets, wavelength range = 4000–400 cm^{-1}).

Scanning Electron Microscopy (SEM). The particle morphology of the resins was observed with SEM (Philips XL_30). The samples were sputter-coated with an Au film before the examination.

Oil-Absorption Test. The oil absorbency (Q) was determined by the following procedure. A quantity of dried resin was weighed, put into a filter bag, and placed in dichloromethane (CH_2Cl_2) for 24 h. Then, the filter bag with the resin was immediately taken out, rinsed for 1 min, and then reweighed. The oil absorbency was calculated according to the following equation:

$$Q = (M_2 - M_1)/M_1 \tag{1}$$

where M_1 is the weight of the resin before oil absorption and M_2 represents the weight of the resin after oil absorption.

Meanwhile, the oil absorbency of resins in the oil–water mixture (5% oil) was tested.

Kinetics of Oil Absorption. The procedure was carried out every 1 h according to the procedure described in the previous section.

Recycling of the Resins. A certain amount of dried resin (whose weight was M_1) was put into dichloromethane for 24 h. The oil absorbency was tested in accordance to the previous procedure. Then, the saturated oil-absorbing resin was placed in ethanol for 5 h to extract the dichloromethane from the resin, dried in a vacuum oven at 80°C for 24 h, and reweighed. The recovery ratio of the resin [W (%)] was calculated according to the following equation:

$$W = \frac{M_3}{M_1} \times 100 \tag{2}$$

where M_3 is the weight of the dried resin after recovery.

At the same time, the mixture of ethanol and dichloromethane was added to water, and the mixed solution was placed in a separating funnel for 30 min. Dichloromethane was recovered and weighed. The recovery ratio of dichloromethane [R (%)] was calculated according to the following equation:

$$R = \frac{M_4}{M_2 - M_1} \times 100\% \tag{3}$$

where M_4 represents the weight of dichloromethane recovered.

The previous steps were repeated 10 times.

RESULTS AND DISCUSSION

Characterization of the High-Oil-Absorption Resins

FTIR Characterization. The FTIR spectra of the resins are given in Figure 1. It was apparent that there was a characteristic absorption peak of the asymmetric bending vibrations of C—H at 1453 cm^{-1}. The presence of the peak at 759 cm^{-1} confirmed that the high-oil-absorption resins contained a benzene ring. The characteristic absorption bands of C═O appeared at 1724 cm^{-1}, and that of C—O appeared at 1184 cm^{-1}. These characteristic absorption peaks confirmed that St and BMA were in a copolymerization reaction with the high-oil-absorption resins. However, the characteristic absorption bands appeared at 2917 cm^{-1}, which corresponded to the aliphatic C—H bond and unsymmetrical stretching vibrations of —CH$_3$ groups, and at 2852 cm^{-1}, which was due to the aliphatic C—H symmetrical stretching vibrations of —CH$_2$ groups of the 17 —CH$_2$ of SMA in St/BMA/SMA.

SEM Characterization. The St/BMA/SMA copolymer with a low crosslinking degree was polymerized by hydrophilic monomers. It was chosen here as an oil-absorption resin because of its compatibility of the polymer chains with the organic solvents and the 3D networked structures which played a key role in the swelling of the resins.[21] The mechanism of the oil-absorption resin could be interpreted to be a solvation process of polymer chain segments. The swelling of the high-oil-absorption resin was caused by the existing 3D network structure and the solvation of hydrophilic groups in polymer chains and oil molecules. According to the polymer elastic mechanics model, it is known that the polymer chains would slowly rebound in a certain extent of stretching when the resins were fully swelled. Finally, the chains reached a thermodynamic equilibrium state, which relied on the elastic rebounding force.
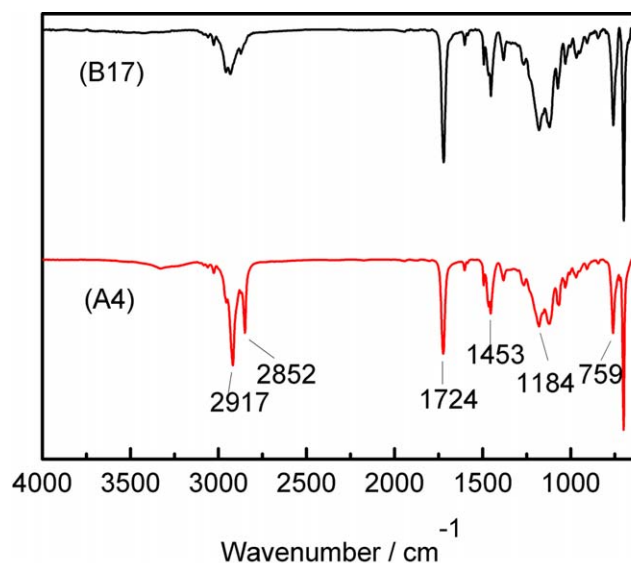
Figure 1. FTIR spectra of A4 and B17. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The morphology of the crosslinked resin influenced the oil absorption of the resins.

The SEM microphotographs of the St/BMA and St/BMA/SMA copolymers prepared by polymerization are displayed in Figure 2. Compared with St/BMA, the particle morphology of St/BMA/SMA was different, as shown in Figure 2(b). The surface of St/BMA/SMA presented a rough structure. The rough surface structure led to a large surface area, which was beneficial to the absorption of more solvent.

Kinetics of Oil Absorption. The initial process of oil absorption was affected by molecular diffusion when the resin was put into the oil. When a small amount of oil molecules entered the resins, the polymer chain segments were still intertwined, not stretched, although they began to solvate. With increasing oil molecules, the solvation of the polymer chain segments was enhanced, and the segments stretched. The oil-absorption process starting from the thermodynamic imbalance to the equilibrium state was determined by the Flory–Huggins equation, which is named the thermodynamic impetus equation when a junction of covalent bond combination is fixed in a network.

The kinetics of oil absorption is shown in Figure 3. At first, the rate of the oil absorption of the two kinds of resins was very fast. The rate of A4 was relatively faster than that of B17. The changes in the oil-absorption resins were less obvious as the time increased beyond 12 h.

The kinetics of oil absorption of the resins are illustrated in Figure 4. A4 had a higher swelling degree than B17 with the same quantity.

Effects of Various Factors on the Oil Absorbency

Effect of the Monomer Mass Ratio. The type and mass ratio of the monomers affected the oil affinity to the resin and the effective network volume, which influenced the oil absorbency.[7] In this study, St/BMA was prepared with St and BMA through suspension polymerization, whereas St/BMA/SMA was prepared
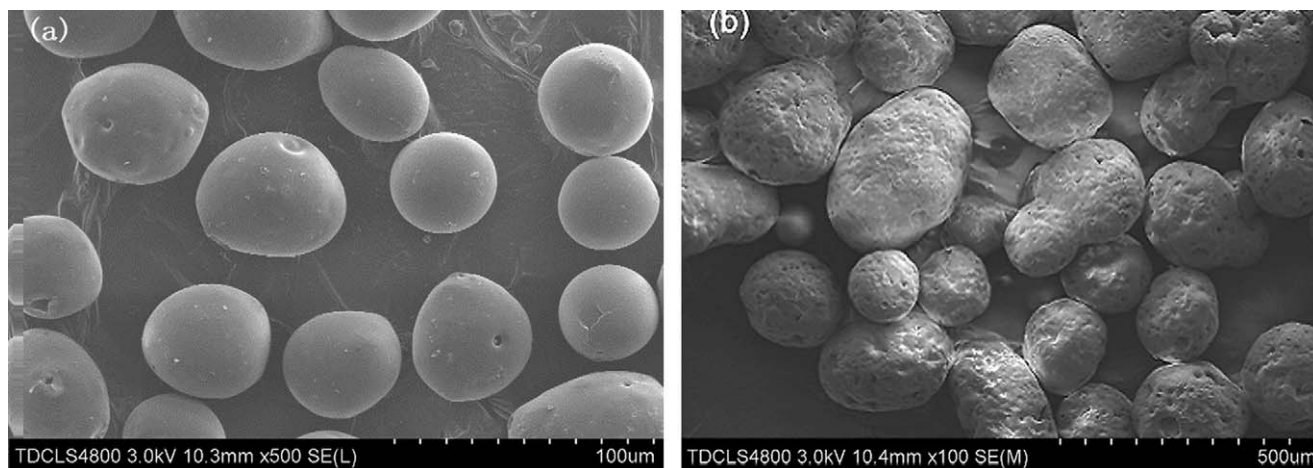
Figure 2. SEM microphotographs of (a) B17 and (b) A4.

with St, BMA, and SMA as monomers. BMA and SMA were soft monomers, whereas St was a hard monomer.

The effect of the St-to-monomer mass ratio on the oil absorbency is shown in Figure 5. It indicates that the sorption efficiency increased at first and then decreased with increasing St mass ratio; this demonstrated maximum efficiencies of 11.64 g/g at a mass ratio of 60% in St/BMA and 23.00 g/g at 50% in St/BMA/SMA.

The existence of St contributed to the formation of a kind of structure that had a rigid backbone and was easily extended. In fact, the introduction of St into the copolymer particle improved the stability of the network and increased the probability of a St molecule contacting the resin; this led to increased sorption efficiency when the amount of St was increased. On the other hand, the St reduced the affinity of the resin to oil.[22] So the optimum mass ratios of St were 60% in St/BMA and 50% in St/BMA/SMA.

Compared with St/BMA, St/BMA/SMA had a higher oil absorbency because of the network properties of the resins. The higher oil absorbency was determined by a hard skeleton and easy extending network. St as a hard monomer provided the rigidity of the network, but the composition of the soft parts, such as BMA and SMA, affected the relaxation of the network. St/BMA/SMA, consisting of BMA and SMA, had a softer network and better relaxation; these were helpful for oil penetration. Although the affinity of the long chain of SMA to the oil seemed outstanding, the effective network volume of SMA was smaller than that of BMA. Therefore, a reasonable proportion of SMA to BMA promoted the oil absorbency.

To St/BMA/SMA, the mass ratio of BMA to the soft monomer also affected the oil absorption.

Figure 6 shows the relation between the ratio of BMA to the soft monomer and the oil absorption. The oil absorbency increased initially, reached a top value, and then decreased sharply with the increasing mass ratio of BMA to the
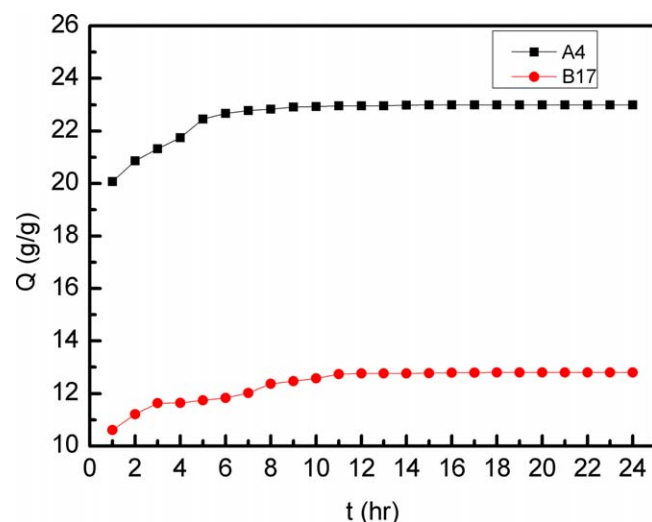

Figure 3. Kinetics of the oil-absorption comparison between A4 and B17. t = time of oil absorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Swelling curve of A4 and B17: (a) dried B17, (b) wet B17 swollen in dichloromethane for 24 h, (c) dried A4, and (d) wet A4 swollen in dichloromethane for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
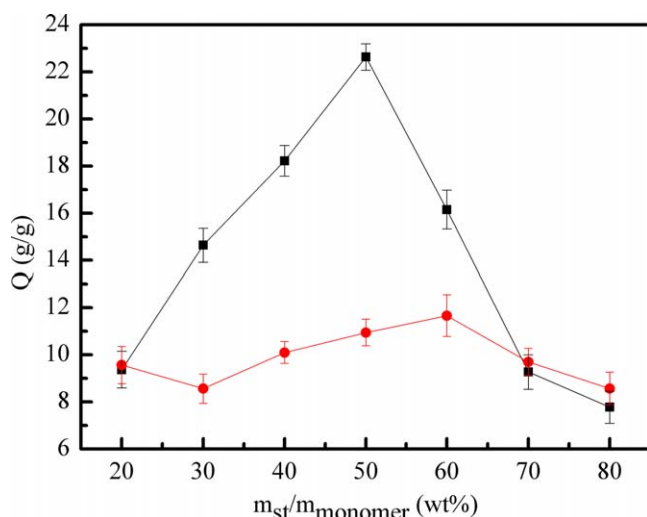
Figure 5. Relation between the mass ratio of St to the monomers and oil absorbency: (■) A1–A7: $m_{BMA}/m_{soft\ monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$ and (●) B1–B7: $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

soft monomer. The oil absorbency reached its maximum of 22.58 g/g at a ratio of BMA to the soft monomer of 60%. SMA had a better affinity to oil than BMA because of its long chain, whereas the effective network capacity of SMA was lower than that of BMA. Thus, we needed to adjust the ratio of BMA to SMA to construct a 3D network, which had good affinity to oil and a greater effective capacity.
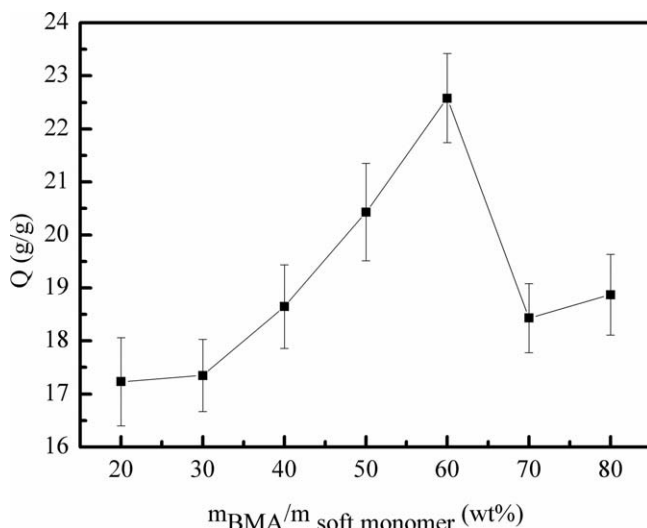
Figure 6. Effect of the oil absorbency on the mass ratio of BMA to soft monomers. A8–A14: $m_{St}/m_{monomer} = 50$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$.
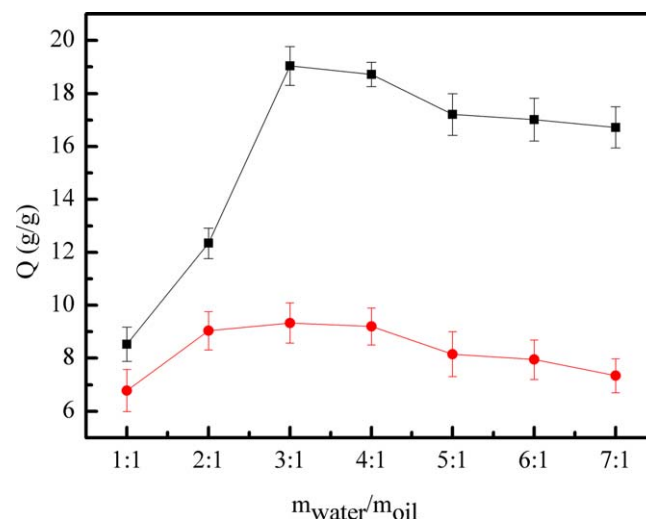
Effect of the Water/Oil Mass Ratio. The water phase referred to the deionized water and dispersing agents, and the oil phase consisted of a mixture of monomers, crosslinking agent, and initiator. Figure 7 illustrates the relationship between the oil absorbency and the different water/oil mass ratios.

As shown in Figure 7, there was a maximum point. When the water/oil mass ratio was smaller than that at the maximum point, the oil absorbency increased with increasing water/oil mass ratio. However, the oil absorbency decreased with increasing water/oil mass ratio when the water/oil mass ratio was larger than that at the maximum point.

In the suspension polymerization, the initiator, crosslinking agent, and monomers were an oil-soluble system. When the water/oil mass ratio increased, the concentration of oil decreased. The initial increase in the oil absorbency was caused by the increased availability of space of the oil-absorption resins. However, when the concentration of the oil phase exceeded a value, the average molecular weight of the side chains increased as did the diffusivity of the monomers, and the degree of polymerization and the viscosity of the solutions increased, whereas the oil absorption decreased.

Effect of the Amount of Crosslinking Agent. The oil-absorbing process of high-oil-absorption resins is a swelling process.[7] The effects of various DVB concentrations based on the weight of the monomers on the oil absorbency are shown in Figure 8. With increasing amount of DVB, the oil absorbency increased and then decreased.

It was well known that the amount of crosslinking agent affected not only the interstitial space structures of the resins

Figure 7. Effect of the oil absorbency on the water/oil mass ratio: (■) A15–A21: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 60$ wt %, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$ and (●) B8–B14: $m_{St}/m_{monomer} = 60$ wt %, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
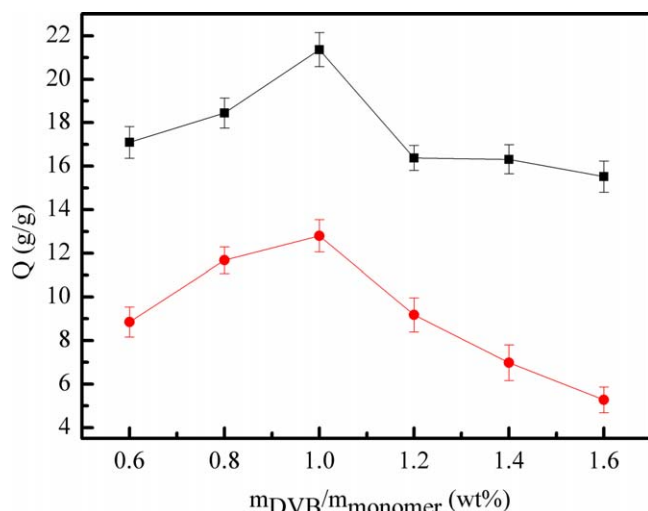
Figure 8. Effect of the oil absorbency on the amount of crosslinking agent: (■) A22–A27: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$ and (●) B15–B20: $m_{St}/m_{monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but also the particle morphology and the degree of crosslinking of the resins; this affected the oil absorbency of the resin. Reducing the amount of crosslinker increased the swelling ability, but stable networks could not form when the crosslinking density was too low.[23] The addition of too great an amount of DVB increased the crosslinking density of the resin and shortened the chain segment. This caused the molecular network spreading to be restrained and thus made the polymer network capacity decrease and blocked the chain movement. Consequently, the high oil swelling and oil retention abilities originated from the appropriate crosslinking degree of the resins.[24] As a result, the oil absorbency decreased. When the amount of crosslinking agent was 1.0 wt %, the resins had the best oil absorbency.

Effect of the Amount of the Initiator. St/BMA and St/BMA/SMA as short-chain and long-chain high-oil-absorption resins, respectively, were prepared by suspension polymerization with free-radical polymerization.

Figure 9 shows the variation in the oil absorbency relative to different amounts of initiator on the basis of the weight of the monomers. With increasing BPO concentration, the oil absorbency increased and then decreased. It was apparent that the oil absorbency was the highest when the amount of initiator was 1.5 wt %.

The amount of initiator influenced the molecular weight and crosslinking degree of the resin. Moreover, it was known that a greater amount of initiator would generate more free radical centers and increase the rate of reaction in the system. Therefore, the crosslinking degree of the polymer, and the oil absorb-

ency also increased. However, when the amount of BPO increased continuously, the crosslinking density and the network space decreased. As a result, this restrained the spread of solvent molecules into the resin and eventually reduced the oil absorbency. Thus, the lower amount of initiator improved the oil absorbency. However, when the amount of initiator was too small, the number of active centers were lower, and the reaction rate and crosslinking degree decreased; this caused a lower oil absorbency, and the resin after oil absorption lacked strength.

Effect of the Type and Amount of the Dispersing Agent. The addition of the dispersing agent in the polymerization to prepare stable and uniform particles was useful. Also, the dispersing agent had indirect effects on the molecular weight of the resins. Therefore, the proper concentration and the sort of dispersing agent not only lowered costs but also increased the oil absorbency.

In this study, composite dispersing agents that consisted of HEC, SDBS, and gelatin were used to prepare stable and uniform particles.

HEC was synthesized with alkali cellulose and ethylene oxide, and the solution viscosity increased with decreasing temperature and was suitable for a higher temperature reaction. Uniform particles, which had a smooth surface and micropores, were formed in the presence of HEC. Gelatin was dissolved in hot water and provided a very good protection ability to the particles and a weak dispersability. So a mixture of gelatin and an anionic surfactant, such as SDBS, could often be used as a dispersing agent in polymerization. The particles were good at oil absorption in the presence of a microporous structure.
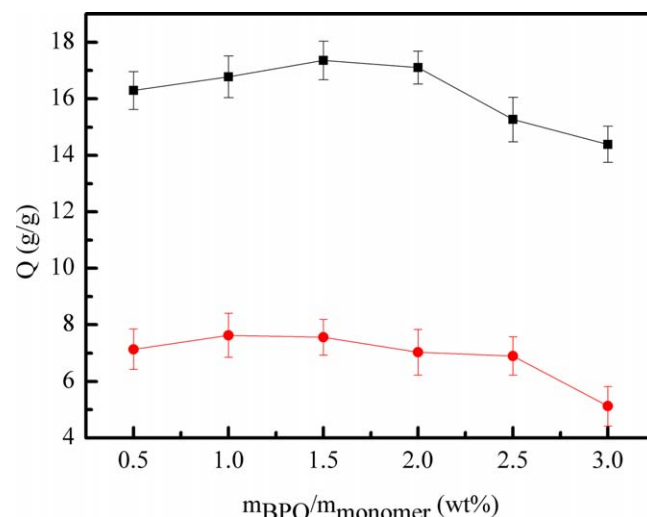
Figure 9. Effect of the oil absorbency on the amount of initiator: (■) A28–A33: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$ and (●) B21–B26: $m_{St}/m_{monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
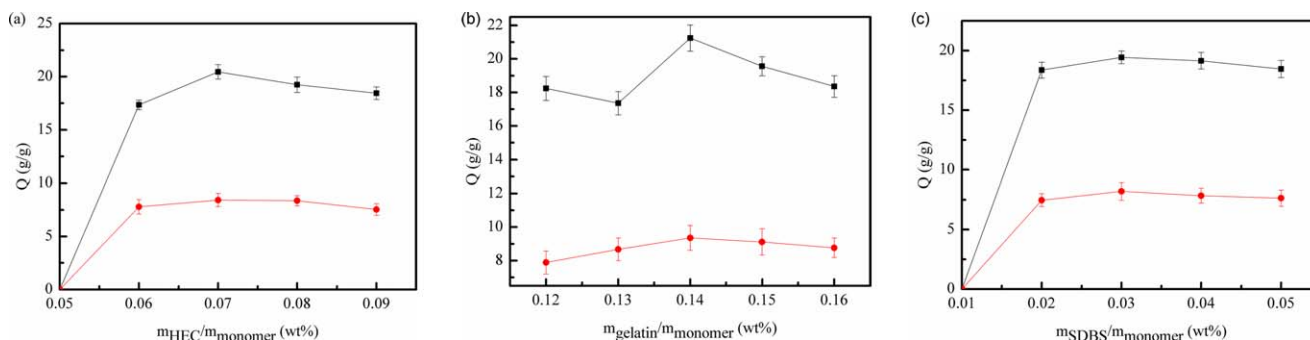
Figure 10. T Effect of the oil absorbency on the amount of (a) HEC, (b) gelatin, and (c) SDBS: (■) A34–A48: $m_{St}/m_{monomer}$ = 50 wt %, m_{BMA}/m_{soft} $_{monomer}$ = 60 wt %, m_{water}/m_{oil} = 3:1, $m_{DVB}/m_{monomer}$ = 1.0 wt %, $m_{BPO}/m_{monomer}$ = 1.5 wt %, and T = 85°C and (●) B27–B41: $m_{St}/m_{monomer}$ = 60 wt %, m_{water}/m_{oil} = 3:1, $m_{DVB}/m_{monomer}$ = 1.0 wt %, $m_{BPO}/m_{monomer}$ = 1.5 wt %, and T = 85°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thus, in this experiment, the HEC and gelatin composite, with the addition of the third component, SDBS, was used as a dispersing agent to prepare stable and uniform particles.

The relation between the amount of the dispersing agent and oil absorbency is demonstrated in Figure 10(a–c). When the concentration of dispersing agent was low, the product tended to form large particles and hardly absorbed oil. With increasing concentration, the oil absorbency increased. The dispersing agent was soluble in water and increased the viscosity of water and could partly remain on the surface of the resins. The particles of the resins were small, and the resins that absorbed oil could not recover and regenerate.

Effect of the Polymerization Temperature. The initiator of BPO completely reacted at 70–95°C because, at 60–85°C, it decomposed into radicals.

The effect of the polymerization temperature on the sorption efficiency is illustrated in Figure 11. We observed that the maximum values of oil absorbency were 10.02 g/g in St/BMA and 19.31 g/g in St/BMA/SMA, respectively. The oil absorbency of the resin increased with increasing polymerization temperature up to 85°C, after which it started to decrease.

It was a well-known fact that an increase in the polymerization temperature enhances the rates of initiation, leads to the formation of more basic chains, and thereby increases the free volume and decreases the flow activation energy of macromolecules. This provides the polymer with enough moving space for oil.[25] However, when the polymerization temperature is too high, the decomposition rate of the initiator is too fast to produce too many polymerization active centers. This causes the low molecular weight of high-oil-absorption resins and the decrease in the oil absorption.
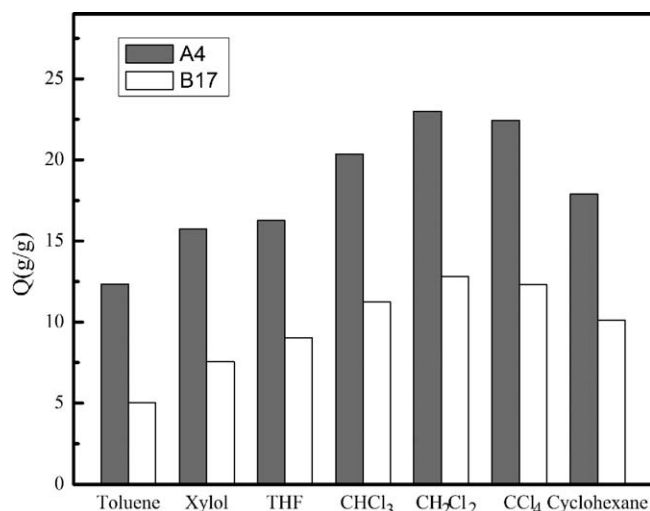
Absorbency of the Resin to Different Solvents. The absorbency of the copolymer resin to different oils is illustrated in Figure 12. It was evident that the oil absorbency of the ternary resin [tetrahydrofuran (THF) = 16.27 g/g, xylol = 15.74 g/g, toluene = 12.34 g/g, CH_2Cl_2 = 23.00 g/g, carbon tetrachloride (CCl_4) = 22.56 g/g, chloroform = 20.35 g/g, cyclohexane = 18.23 g/g] was higher than that of the binary resin (THF = 9.04 g/g, xylol = 7.56 g/g,

toluene = 5.02 g/g, CH_2Cl_2 = 12.80 g/g, CCl_4 = 12.31 g/g, chloroform = 11.24 g/g, cyclohexane = 10.12 g/g).

The monomers affected the oil affinity of the resins, the network structure, and so on, which directly influenced the oil-absorption process. Generally, the oil affinity of the long-chain alkyl ester was better than that of the short-chain alkyl ester. On the other hand, the long-chain alkyl ester formed effective physical crosslink points, which were conductive for the resin to spread the network structure. Therefore, the ternary copolymer resin showed better oil absorbency. In addition, the absorbency of the copolymer resin to different solvents was different. It could be explained that the polarities of a variety of solvents were different. The nearer the solubility parameters were,
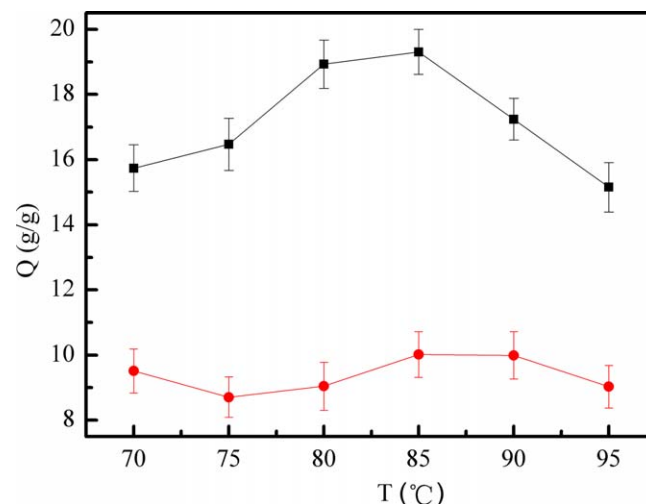
Figure 11. Effect of the oil absorbency on the reaction temperature: (■) A49–A54: $m_{St}/m_{monomer}$ = 50 wt %, $m_{BMA}/m_{soft\ monomer}$ = 60 wt %, m_{water}/m_{oil} = 3:1, $m_{DVB}/m_{monomer}$ = 1.0 wt %, $m_{BPO}/m_{monomer}$ = 1.5 wt %, $m_{HEC}/m_{monomer}$ = 0.07 wt %, $m_{SDBS}/m_{monomer}$ = 0.03 wt %, and $m_{gelatin}/m_{monomer}$ = 0.14 wt % and (●) B42–B47: $m_{St}/m_{monomer}$ = 60 wt %, m_{water}/m_{oil} = 3:1, $m_{DVB}/m_{monomer}$ = 1.0 wt %, $m_{BPO}/m_{monomer}$ = 1.5 wt %, $m_{HEC}/m_{monomer}$ = 0.07 wt %, $m_{SDBS}/m_{monomer}$ = 0.03 wt %, and $m_{gelatin}/m_{monomer}$ = 0.14 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
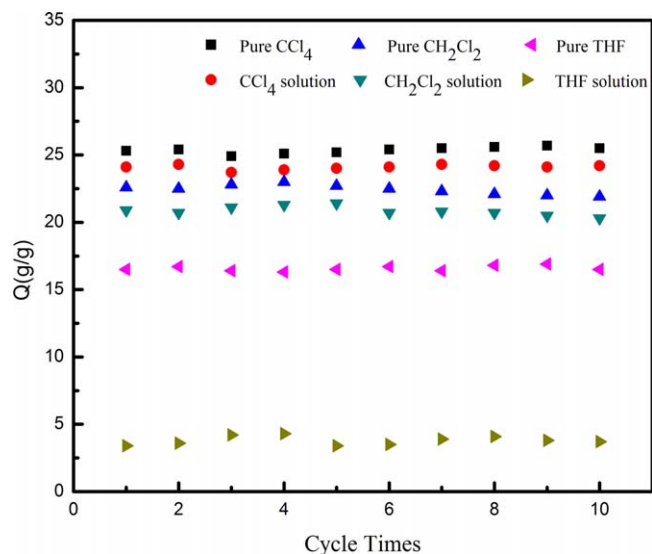
Figure 12. Absorbency of A4 and B17 for different solvents. (A4) $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 50$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$ and (B17) $m_{St}/m_{monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$.

the better the compatibilities of the polymer chains and the solvent were.

Oil Absorption of the Resin in the Oil–Water Mixture. The oil–water mixture was designed to simulate oily wastewater in the actual environment and was used to investigate the difference of the oil absorption of the resin in pure oil and actual oily wastewater.

The resin was reused 10 times in water solutions of CCl$_4$, CH$_2$Cl$_2$, and THF, respectively. The oil absorbency in the oil–water mixture is illustrated in Figure 13. The results show that the oil absorbencies in the water solutions of CCl$_4$ and CH$_2$Cl$_2$ were almost the same as the absorbency in the corresponding pure solvent. However, the oil absorbency in the water solution of THF was much lower than that in pure THF. This could be explained by the fact that CCl$_4$ and CH$_2$Cl$_2$ were not soluble in

Figure 13. Oil absorbency of resin A4 in different water solutions: (■) A4: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 50$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and $T = 85°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water, whereas THF was easily soluble in water. That indicated it was difficult for the resin to extract THF from water.

Recycling of the Resin
In this experiment, the oil-absorption resin was reused 10 times. The oil absorbency of the resin each time was studied in dichloromethane [CH$_2$Cl$_2$; see at Figure 14(a)]. The oil absorbency of the resin was around 20 g/g without obvious changes during recycling; this indicated that recycling did not affect the oil absorption of the resin.

Figure 14(b) shows the recovery ratio of the resin. A small part of the resins were lost after each cycle; this was in an acceptable range.

The resin saturated by dichloromethane was extracted by ethanol to get a mixed solution of ethanol and dichloromethane. Dichloromethane was separated from the aqueous phase by the addition of water to the mixed solution. The recovery ratio of
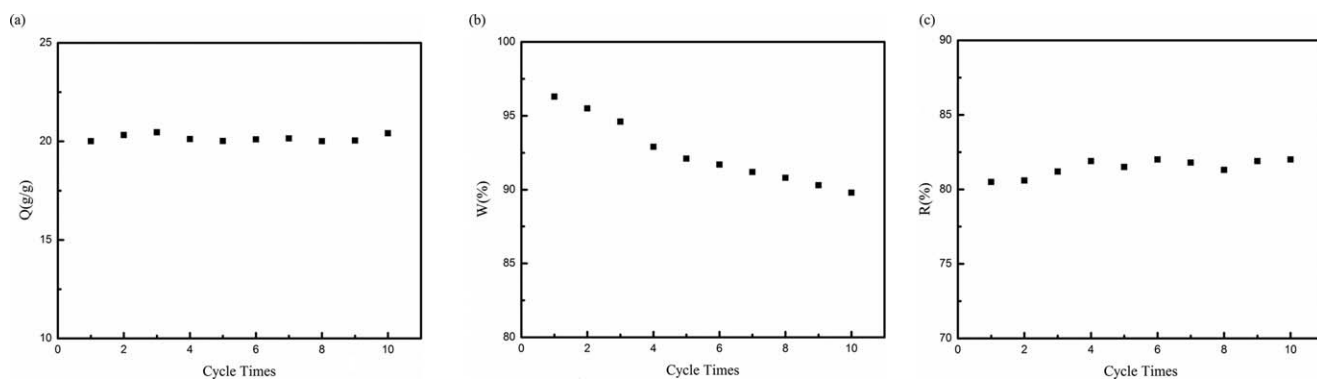
Figure 14. Recycling of the resin A4: (a) absorbency of A4 in each cycle, (b) recovery ratio of A4 in each cycle, and (c) recovery ratio of dichloromethane in each cycle.

dichloromethane is illustrated in Figure 14(c). The ratio remained at about 82%. As a result, the high-oil-absorption resins had a high oil absorbency, the recovery ratio of the resin, and the recovery ratio of dichloromethane, which confirmed the good recycling ability of the polyacrylic microspheres in the short term.

CONCLUSIONS

An St/BMA/SMA copolymer resin was synthesized by suspension polymerization. The effects of the monomer mass ratio, water/oil mass ratio, concentration of the crosslinking agent, concentration of the initiator, kind and concentration of the dispersing agent, and polymerization temperature on the oil absorbency have been discussed. The oil absorbency comparison of the long-chain high-oil-absorbing resin of St/BMA/SMA and the short-chain St/BMA copolymer were investigated. In the St/BMA copolymer, the optimum polymerization conditions were as follows: $m_{St}/m_{monomer} = 60$ wt %, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt %, and temperature $(T) = 85°C$. The optimum polymerization conditions of the St/BMA/SMA copolymer were obtained as follows: $m_{St}/m_{monomer} = 50$ wt %, $m_{BMA}/m_{soft\ monomer} = 60\%$, $m_{water}/m_{oil} = 3:1$, $m_{DVB}/m_{monomer} = 1.0$ wt %, $m_{BPO}/m_{monomer} = 1.5$ wt %, $m_{HEC}/m_{monomer} = 0.07$ wt %, $m_{SDBS}/m_{monomer} = 0.03$ wt %, $m_{gelatin}/m_{monomer} = 0.14$ wt % (where m is the mass), and $T = 85°C$. The oil phase was added to reaction system 20 min later. The highest oil absorbencies to dichloromethane were 12.80 and 23.00 g/g in the St/BMA and St/BMA/SMA copolymers, respectively. Compared with the high-oil-absorption resins of the binary copolymer prepared by suspension polymerization, the high-oil-absorption resins of the ternary copolymer had a higher oil absorbency. The resin had a good recycling ability, which confirmed that the resin has the potential to be applied in the treatment of oily wastewater.

ACKNOWLEDGMENTS

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