

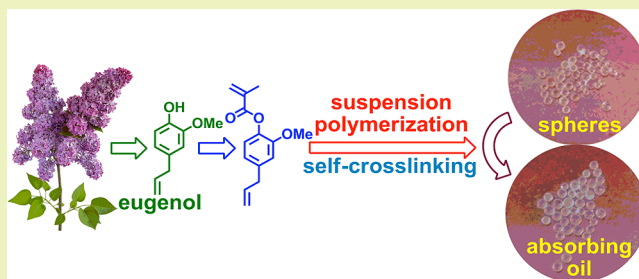
Renewable Eugenol-Based Polymeric Oil-Absorbent Microspheres: Preparation and Oil Absorption Ability

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Supporting Information

ABSTRACT: This article reports a novel type of polymeric microspheres derived from a renewable biomass, eugenol, via a facile and effective suspension polymerization approach. On the basis of eugenol and methacryloyl chloride, we first synthesized and then structurally identified the monomer eugenyl methacrylate (E-MA). By using E-MA as the sole monomer and simultaneously as the cross-linking agent, we successfully prepared cross-linked polymeric microspheres through suspension polymerization in aqueous media with 2,2-azoisobutyronitrile (AIBN) as the initiator and poly(vinyl alcohol) (PVA) as the stabilizer. The resulting microspheres were obtained in high yield with diameters ranging 500–800 μm and exhibited remarkably large oil absorbency in a relatively high speed. The microspheres can be reused for at least five times with little change in maximum absorption. The preparative strategy for the polymeric microspheres can be taken as a versatile platform for preparing more functional polymeric microspheres, which are expected to find significant applications in environmental protection and other fields.

KEYWORDS: Eugenol, Oil absorbent, Microspheres, Suspension polymerization



INTRODUCTION

Polymeric materials derived from renewable natural resources have attracted ever-growing interest due to the common concerns for finite availability of petroleum resources and environmental problems. Therefore, a variety of sustainable sources have been explored so far for preparing polymers. The most intensively investigated sustainable sources include vegetable oils,^{1–3} terpenes,⁴ rosins,⁵ phenols,^{6,7} etc. The resulting polymers were investigated for significant applications with elastomers as typical examples.^{8–10} Eugenol (4-allyl-2-methoxyphenol) is a major phenolic component in clove oil and is relatively cheap.¹¹ Clove is commercially cultivated in Indonesia, India, Sri Lanka, and southern China. Eugenol is soluble in organic solvents but slightly soluble in water. Accordingly, β -cyclodextrin was used to make it soluble in water by forming inclusion complex.¹² Eugenol and the derivatives have been widely used in dental materials for improving bioactivity¹³ and used as antioxidant¹⁴ for active packaging.¹⁵ Eugenol was also used to prepare polyacrylate materials.¹⁶ More recently, biobased polymer resins were created based on eugenol, like polybenzoxazines,¹⁷ thermosetting resins,¹⁸ polyesters,¹⁹ and cyanate esters.^{20,21} In another study, eugenol was covalently attached to polyacetylene main chains to develop novel functional materials simultaneously showing optical activity and fluorescence.²² Taking into consideration the easy availability and especially the biomass nature, eugenol holds large potentials to be explored for constructing functional polymer materials. In the present study,

we prepared a novel category of polymeric microspheres based on eugenol, and the obtained microspheres exhibited large oil absorbency and are expected to find practical applications in wastewater treatment.

Polymeric absorbent materials have been extensively investigated in removal of the oil from oil spill sites, largely contributing to preventing environmental pollution. Polypropylene, polyacrylates, polystyrene, and silicones are widely used to establish polymeric absorbents.^{23–26} Besides the intensively studied polymers above, some new polymers and polymer systems also have been created recently. Yang et al.²⁷ prepared renewable oil absorbents derived from poly(melamine formaldehyde). More recently, carbon nanotubes²⁸ and (reduced) graphene oxide were used as special additives for preparing advanced adsorbents.²⁹ Polymeric nanocomposites also showed potential uses in oil spill recovery.³⁰ To improve the recyclability, magnetic polymer sorbents were fabricated by Li et al.³¹ In addition to constructing novel polymer architectures, surface modification of commercial polymers, for example, melamine sponges, also attracted attention.³² Our previous studies demonstrate that incorporating β -cyclodextrin moieties in polymeric oil absorbents can dramatically improve oil absorbency of the absorbents.^{33–35} Nonetheless, polymeric oil absorbents also demonstrated some drawbacks including

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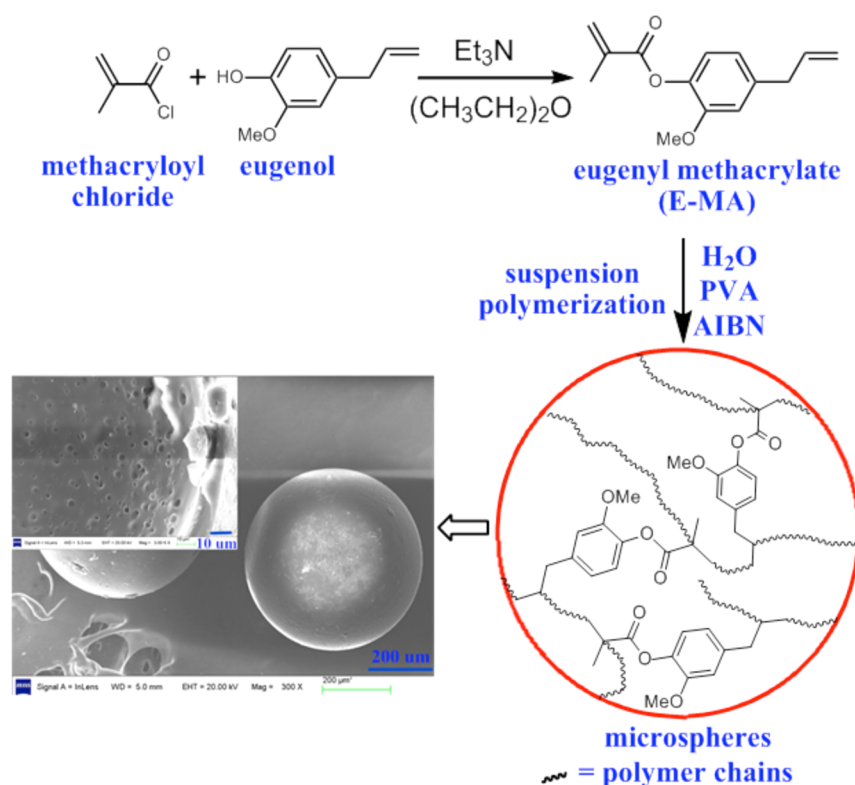


Figure 1. Schematic presentation of the strategy for preparing polymeric microspheres starting from eugenol and SEM images of the prepared polymer microspheres. Inset in the SEM image is the partially enlarged microsphere.

complicated preparation process, high cost, and nonrenewable resources, which limits the practical applications of polymer oil absorbents.

Eugenol as an important member of biomass and has never been utilized for preparing polymer microspheres yet. In the present study, we took renewable eugenol as raw material to prepare oil-absorbent microspheres by powerful suspension polymerization technique.³⁶ Of special notice is that in the present case additional cross-linking agent is not required for forming cross-linked microspheres because the monomer derived from eugenol (E-MA, Figure 1) was found to play the role of cross-linking agent. Therefore, the present pioneering study is encouraging, not only providing an unprecedented type of polymeric microspheres but also opening up new applications of eugenol.

EXPERIMENTAL SECTION

Materials. All the chemicals, unless otherwise noted, were obtained from Aldrich. Eugenol was used as received without further purification. Methacryloyl chloride (Alfa Aesar) and triethylamine were purified by distillation under reduced pressure. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol, dried under vacuum at room temperature, and stored in an amber bottle. Poly(vinyl alcohol) (PVA, polymerization degree 1750 ± 50) was purchased from Aldrich. Gasoline and diesel were obtained from Sinopec Beijing Yanshan Company. Kerosene was bought from Alfa Aesar. Peanut oil was received from Yihai Kerry Food Marketing Co. Water was freshly deionized before use.

Measurements. FT-IR spectra (KBr pellet) were measured using a Nicolet NEXUS 670 spectrophotometer. ^1H and ^{13}C NMR (nuclear magnetic resonance, 400 and 100 MHz, respectively) spectra were measured in CDCl_3 using a Bruker AV400 spectrometer at 20°C , with tetramethylsilane (TMS) as the internal standard. The morphology of the microspheres was characterized by S-4700 electron microscope

(SEM, Hitachi). Differential scanning calorimetry (DSC) was carried out with a WATERWSSL C Q100 under 50 mL/min of flowing N_2 at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was performed with a Q50 TGA at a scanning rate of $10^\circ\text{C}/\text{min}$ under N_2 . Pore analysis was carried out on a BK122W sorption analyzer.

Synthesis of E-MA. Monomer E-MA (as structurally presented in Figure 1) was synthesized and characterized according to the method in literature.³⁷ Eugenol (6.56 g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol) were dissolved in diethyl ether and then introduced into a three-necked, round-bottomed flask. Methacryloyl chloride (4.7 g, 0.045 mol) dissolved in diethyl ether was added dropwise at room temperature. The reaction mixture was stirred for about 48 h at room temperature and under nitrogen atmosphere. The mixture was filtered to remove triethylamine hydrochloride and then washed with 5% NaOH solution and deionized water three times to remove any unreacted reagents. It was then dried over anhydrous Na_2SO_4 and distilled under reduced pressure to give the crude product. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (90/10 v/v) as the eluent to give E-MA (yield, 80%).

Preparation of Oil-Absorbent Microspheres. The microspheres were prepared via the suspension polymerization approach (Figure 1). The concentrations of initiator (AIBN) and stabilizer (PVA) were found to be two key affecting factors. Our previous studies^{33–35} had investigated their effects in detail to determine the optimal preparing parameters. According to these studies, we used 2.0 wt % PVA and 4.0 wt % AIBN (based on the weight of monomer E-MA). First, 2 g of E-MA and 0.08 g of AIBN were introduced in a 250 mL three-neck flask, which was equipped with a mechanical stirrer (stirring speed, 350 rpm). After the mixture was stirred for about 10 min, a PVA aqueous solution (2 wt %, 100 mL) was added under nitrogen atmosphere. Then, the reaction mixture was subjected to vigorous stirring at a speed of 350 rpm for 30 min so that monomer droplets were well dispersed. After that, the reaction systems were heated to 60°C for 12 h. The yielded product was filtered and washed with acetone and deionized water. Finally, the microspheres were dried

in a vacuum oven at 50 °C to constant weight. The yield of the microspheres was 50 wt % under the following conditions: PVA, 2.0 wt %; AIBN, 4.0 wt %; and stirring speed, 350 rpm.

Oil Absorption Test. In the present study, all the oil absorbency values were determined based on the average values of three parallel measurements by referring to our earlier report.³⁵ Typical experimental processes are briefly stated below.

Cross-Linking Degree of Microspheres. Cross-linking degree was measured by a previously established method,³⁵ which has been widely taken to determine the cross-linking degree of oil absorbents.^{33,34,38} A given amount of the oil-absorbent microspheres (weight, m1) was put into a filter bag and immersed in excessive chloroform at room temperature for 12 h. The chloroform was renewed every 2 h. The filter bag containing the microspheres was taken out from chloroform and dried at 60 °C for 24 h. Then, the microspheres were weighed, and this weight was denoted as m2. The cross-linking degree of the microspheres was calculated by the equation, cross-linking degree = $(m2/m1) \times 100\%$. The cross-linking degree of the microspheres was determined to be 93%.

Oil Absorbency. A quantity of about 0.02 g of dried oil-absorbent microspheres with known weight (m3) was put into a filter bag and immersed in different oils (CHCl₃, toluene, gasoline, diesel, kerosene, and peanut oil) at room temperature. After a predetermined time (12 h was taken to ensure a maximum 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 (m4). The oil absorbency was calculated by the formula, oil absorbency = $(m4 - m3)/m3$.

Oil Desorption Efficiency. The oil desorption efficiency was carried out by referring to our earlier report.³⁵ The procedure for the microspheres to absorb oils kept the same as stated above. 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 taken out from the oil and drained for 1 min. The sample was immediately weighed (m5). 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 and weighed again, and the weight was noted as m6. We experimentally demonstrated that the microspheres had a little oil absorbency in ethanol (approximately 0.04 g/g), and meanwhile, the tested oils, CHCl₃, toluene, gasoline, etc., could readily dissolve in ethanol. This is the reason for us to use ethanol as desorption agent. The oil desorption efficiency was calculated by the formula $(m5 - m6)/m5 \times 100\%$.

RESULTS AND DISCUSSION

Strategy for Preparing Eugenol-Based Polymeric Microspheres. The present study aims to prepare novel biobased polymeric microspheres by using eugenol as the major starting material. As shown in Figure 1, eugenol first reacted with methacryloyl chloride to form the designed monomer E-MA. E-MA simultaneously contains two C=C bonds, so we envision that both of the two C=C bonds may undergo free radical polymerization. This will avoid the additional use of specific cross-linking agent for the fabrication of cross-linked polymeric microspheres. Accordingly, E-MA underwent suspension polymerization in aqueous medium by using AIBN as initiator and PVA as stabilizer. The following investigations convincingly confirmed that our strategy is effective, by which an unprecedented class of polymeric microspheres were obtained, as to be reported next.

Characterizations of Monomer E-MA and Microspheres. As shown in Figure 1 and as stated in the Experimental Section, E-MA was prepared on the basis of eugenol and methacryloyl chloride in a high yield (about 80%). E-MA was characterized by FT-IR spectroscopy, for which the spectra are presented in Figure 2.

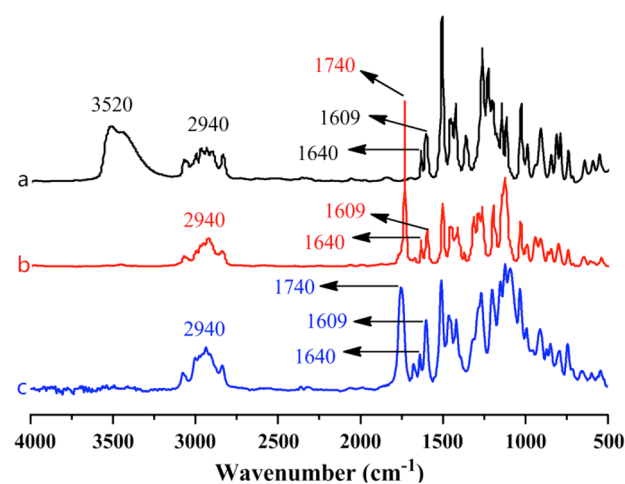


Figure 2. FT-IR spectra of eugenol (a), monomer E-MA (b), and polymer (c).

When compared to the FT-IR spectrum of the raw material eugenol (spectrum a), several characteristic peaks of E-MA can be clearly observed in spectrum b. In eugenol (spectrum a), the peaks are assigned as follows: 3520 (–OH), 2940 (methyl and methylene), 1609 (phenyl), and 1640 cm^{–1} (C=C structure). For E-MA (spectrum b), the peaks are analyzed as 2940 (methyl and methylene), 1609 (phenyl group), 1640 (C=C structures in acrylate and vinyl groups), and 1740 cm^{–1} (C=O in ester structure). Furthermore, the disappearance of the peak around 3520 cm^{–1} in E-MA indicates the transformation of –OH groups in eugenol to the ester groups in E-MA. This, together with the new peak at 1740 cm^{–1}, strongly demonstrated the successful synthesis of E-MA.

E-MA was further subjected to NMR measurement. The ¹H and ¹³C NMR spectra of it are illustrated in Figure S1 of the Supporting Information. The detailed analyses of the peaks are indicated in the spectra (¹H NMR spectrum: δ_{H} 7.26 (CDCl₃), 1.70 (H₂O)). The signals are in well agreement with the molecular structure of the monomer. This observation provides further evidence for the formation of eugenol-based monomer E-MA.

E-MA underwent suspension polymerization in aqueous system with AIBN as the initiator and PVA as the stabilizer. We found that the stirring speeds played important roles in the formation of regular microspheres. In more detail, a stirring speed of 350 rpm led to satisfactory microspheres. However, a lower stirring speed (e.g., 200 rpm) resulted in irregular spheres due to aggregation. At a much higher stirring speed (e.g., > 500 rpm), the obtained microspheres showed a wide size distribution. It should be highlighted that even in the absence of an additional cross-linking agent, the suspension polymerization provided the anticipated cross-linked polymeric microspheres in a yield of 50 wt % with 2.0 wt % PVA, 4.0 wt % AIBN, and at a stirring speed of 350 rpm. (Herein, the yield means the yield of regular microspheres rather than monomer conversion.) The cross-linking degree of the microspheres was determined to be 93%. The FT-IR spectrum of the polymer microspheres (Figure 2, spectrum c) shows that not all of the double bonds were consumed. However, we highlight that compared to the reported analogous acrylate-based polymeric microspheres³⁸ and typical suspension polymerizations for preparing cross-linked polymeric microspheres^{39,40} the present ones are advantageous in the simple polymerization system

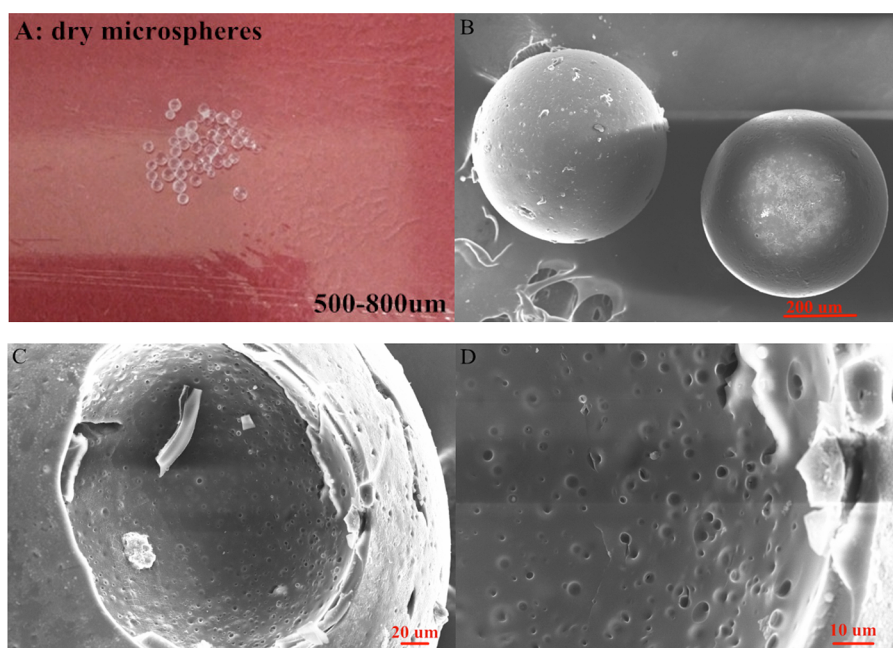


Figure 3. Photographs of the microspheres (A) and SEM images (B, C, D: scale bars are 200, 20, 10 μm , respectively).

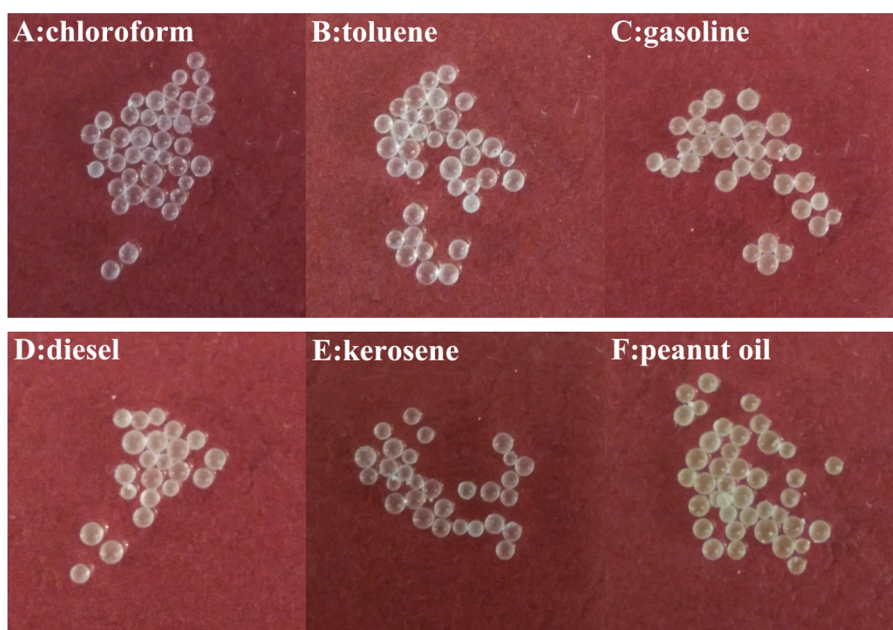


Figure 4. Photographs of the microspheres after absorbing oils.

(without specifically adding cross-linking agent) and the renewable raw material.

Figure 3A presents the photographs of the resulting microspheres at a dry state. They seem colorless, and the diameters range from 500 to 800 μm . Figure 3B–D presents typical SEM images of the microspheres for a whole one (Figure 3B) and enlarged partial view (Figure 3C and D). The SEM images show that a large number of pores were formed in the microspheres due to the cross-linking between the polymer chains (as illustratively shown in Figure 1), even though no special cross-linking agent was added.

To further characterize the porous structure of the microspheres, we used the Barrett–Joyner–Halenda (BJH) method with nitrogen as the adsorbate to measure the

microspheres' pore size and pore diameter distribution. Surface area was determined by the BET method. The related results are presented in Figure S2 of the Supporting Information. The BET specific area is 1.26 m^2/g , and the pore diameter is 6.21 nm. The pore diameter range is located mainly in 2–50 nm, indicating that the microspheres belong to mesoporous materials. Due to the absence of an additional cross-linking agent and porogen agent in the formula for preparing the microspheres, specific surface area seems to be not very high. We should mention that even for the microspheres with a specific porogen agent,⁴¹ the specific surface area (about 4.4 m^2/g) is not much higher than our microspheres without adding a porogen agent. BET data offer further evidence for the

formation of pores in the microspheres, as observed in the SEM images presented in Figure 3.

We subsequently measured the thermal stability of the microspheres, which is one of the key factors when they are considered being put into practice. The thermal stability of the prepared microspheres was characterized by thermogravimetric analysis (TGA) technique. TGA measurement was performed from room temperature to 1000 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The relevant result is presented in Figure S3 of the Supporting Information. The main polymer structure was found to decompose in the temperature range of 350–480 °C. The present microspheres show higher thermal stability than other acrylate-based polymeric microspheres (310–380 °C) reported by Ye et al.⁴² DSC analysis was also performed on the microspheres, and the relevant DSC curve is presented in Figure S4 of the Supporting Information. According to the DSC analysis, the polymer chains in the microspheres possessed a glass transition temperature (T_g) of 98 °C. It further indicates that the monomer E-MA may be utilized to prepare novel plastic materials.

Oil Absorbency of Microspheres. As shown from the SEM images in Figure 3, the microspheres range from 500 to 800 μm in size at dry state. The photographs of microspheres after being swelled in chloroform, toluene, gasoline, diesel, kerosene, and peanut oil are presented in Figure 4A–F, respectively. The microspheres became considerably larger (diameter, 2–3 mm) after absorbing oils. More importantly, the microspheres could maintain very well the spherical morphology even after a large absorption of oils, which demonstrates the high strength of the microspheres before and after swelling.

Small molecules can easily diffuse inside the microspheres due to the presence of large pores in the latter. As shown in Figure 5A, the microspheres had relatively larger adsorption in chloroform and toluene, while they showed lower adsorption toward the other four common oils (gasoline, diesel, kerosene, and peanut oil). For gasoline, the lower adsorption may be explained as follows. Gasoline contained some relatively longer molecular chains. These longer molecular chains were mainly adsorbed on the surface of the microspheres and thus blocked further adsorption of other small molecules. However, we hope to point out that even for diesel and kerosene the oil absorbency by the present microspheres under investigation (diesel, 31.7 g/g; kerosene 33.8 g/g) is still much higher than the reported data in literature, for example, diesel, 18.2 g/g and kerosene, 27.1 g/g reported by Song et al.³⁵

Figure 5 also shows that the microspheres took approximately 3 h to reach saturated adsorption in the pure oils, faster than the counterparts reported by our earlier study,³³ where it took about 6 h for the oil adsorbents to reach a saturated adsorption. The reason for the faster saturated adsorption in the present microspheres is due to the special molecular structure of the monomer E-MA. E-MA acted as simultaneously monomer and cross-linking agent, which led to a uniform cross-linked structure inside the microspheres. This seems to be favorable for the microspheres to quickly reach a saturated adsorption. We further measured the microspheres' absorption toward raw oil (purchased from Aldrich), and the oil absorbency was found to be 21.6 g/g.

We propose that the microspheres may find practical applications in wastewater treatment, so we further accomplished the oil absorption tests by using the microspheres in

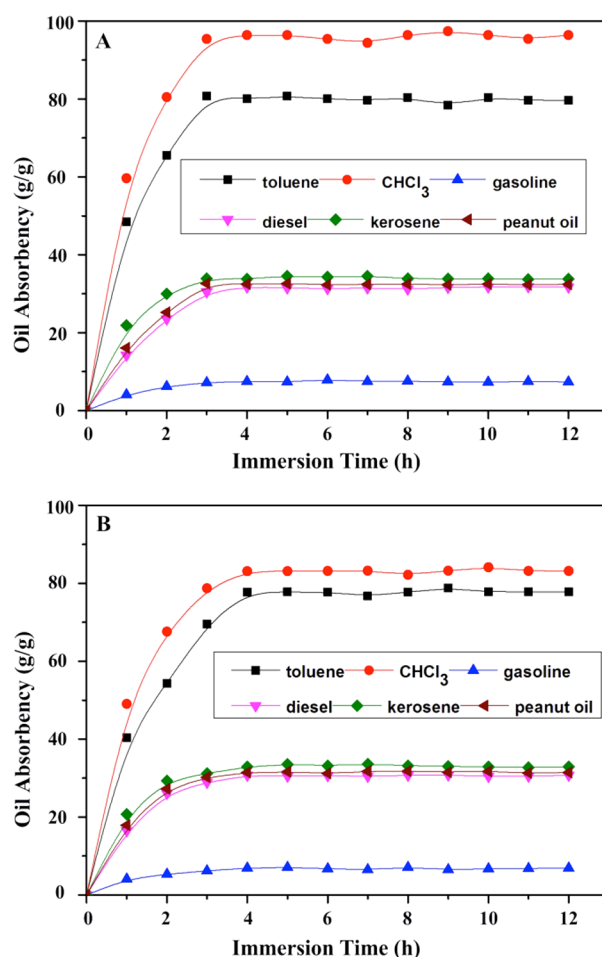


Figure 5. Oil absorbency of the microspheres in pure oils (A) and oil–water mixture (B).

oil–water mixture. Figure 5B shows the oil adsorption of the microspheres over water. In the oil–water mixture, the microspheres took about 4 h to reach saturated adsorption. Nevertheless, the oil absorbency decreased slightly compared to that in the cases of absorbing pure oils. This observation is probably due to the heterodispersion of the oils in water. Moreover, the presence of water may be undesirable for the oils to penetrate into the interior of microspheres. The density of chloroform is larger than the other oils. This most likely led to the especially large decrease in oil absorption of chloroform in the oil–water mixture.

The microspheres may be recycled and reused in theory in oil absorption tests. To further elucidate this hypothesis, we subsequently restored the microspheres through a desorption process by using ethanol as the extracting agent after the first cycle use of them in oil absorption. After that, we utilized them again for absorbing oils. For clarity, we show the results in two graphs in Figure 6. As shown in Figure 6, both the maximum oil absorbency and desorption efficiency are plotted against time. It shows that even after repeated uses for five times, the microspheres still could maintain constant oil absorption. It further demonstrates that the microspheres have good reusability and could be used for at least five times. More oils will be examined in the future work. Furthermore, the interesting microspheres are expected to demonstrate further improved oil absorbency, recycling ability, and other properties

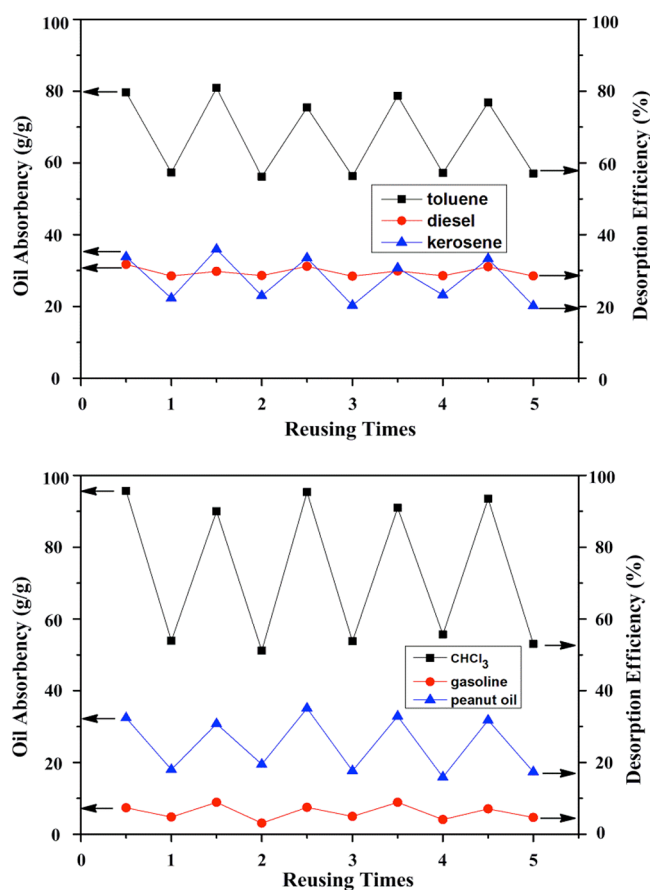


Figure 6. Recyclability of the microspheres as oil absorbent. Top: for CHCl₃, gasoline, and peanut oil. Bottom: for toluene, diesel, and kerosene.

after an optimization in composition, structure, and morphology.

CONCLUSIONS

A novel class of oil-absorbent microspheres was prepared via suspension polymerization by using eugenyl-methacrylate (E-MA) as the sole monomer in the absence of a cross-linking agent. This is the first polymeric microspheres derived from eugenol. BET and SEM techniques demonstrated the porous structure of the obtained microspheres. Oil adsorption tests demonstrated the excellent properties of high oil absorption, fast absorption speed, and reusability. Also, remarkably, the microspheres have high oil absorption and fast absorption speed of oils from water. Such novel polymeric microspheres are highly interesting because the monomer derived from renewable biomass eugenol. The microspheres are expected to find practical applications in wastewater treatment. We are currently continuing our study along this significant research direction.

ASSOCIATED CONTENT

Supporting Information

Figures of adsorption-desorption isotherms, BJH pore size distribution, and TG analysis and DSC of the microspheres. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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