Synthesis and characterization of a sphere-like modified chitosan and acrylate resin composite for organics absorbency

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Abstract. In this study, the chitosan (deacetylation degree > 95%) was modified with vinyltriethoxysilane (A151) and became hydrophobic. The modified chitosan and acrylate resin composite can be synthesized by butyl methacrylate (BMA), butyl acrylate (BA), poly vinyl alcohols (PVA), N,N'-methylene bisacrylamide (MBA), benzoyl peroxide (BPO), and ethyl acetate under microwave irradiation. The optimal synthetic condition was as follows: the molar ratio of BA and BMA was 1.5:1, the dosage of ethyl acetate, PVA, MBA, BPO and modified chitosan were 50 wt.%, 10 wt.%, 1.5 wt.%, 2.0 wt.% and 1.0 wt.% of monomers, respectively. The adsorption capacity of the composite for CHCl₃ and CCl₄ were approximately 53 g/g and 44 g/g, respectively. The organics absorbency and regeneration of the samples were also tested, and the samples were characterized by analysis of the scanning electron microscope and simultaneous thermo gravimetric/differential thermal.

1. Introduction

The exhausted oils from industrial activities or operational maintenance of machines are usually treated by specialized firms while the disposal of waste containing oils at low concentration occurs in conventional sewage treatment systems and causes environmental damages. In order to reduce the polluting power of oily wastes, they might be treated separately before discharge [1]. In recent years, many research methods are chosen methyl acrylates as raw material; however, the adsorption capacities of acrylate resins are very low. To solve this problem, some natural materials have attracted the attention of many researchers. Asha Srinivasan researched fungus mucor roux rich with chitosan for removal oil from water [2]. H.H. Sokker, etc. reported an adsorbent, which was chitosan gelatin based on polyacrylamide compound, and showed a high adsorption capacity of crude oil from aqueous solution [3]. S.M. Sidik, etc. investigated oil palm leaves modified by lauric acid to adsorb crude oil and the maximum adsorption capacity was 1176±12.92 mg/g at 303K [4]. Chitosan is a partially acetylated glucosamine biopolymer with many useful features such as hydrophilicity, biocompatibility and biodegradability. Recently, chitosan has been also used as natural templates for the fabrication of functional inorganic oxides [5, 6]. In addition, the amino groups on the chitosan also can be used for further functionalization, such as various drugs, specific binding sites, or other functional groups [7, 8]. The aim of this study was to synthesize modified chitosan and acrylate resin composite and research

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organics adsorption performance of composite resin, because chitosan combined with methyl acrylate and butyl acrylate resins by hydrogen bond, which improved the performance of the compound material.

2. Experimental

2.1. Materials
All regents were all of analytical grade. The chitosan (deacetylation degree > 95%) was obtained from Jinan Haidebei Marine Biological Engineering Co., LTD. Benzoperoxide (BPO) is recrystallized from ethanol, dried at 60°C, and stored in a desiccator. Deionized water was used in all the experiments. Two gram of chitosan, a certain amount of A151 and 50 mL deionized water were added into a round bottom flask. The mixed solution was stirred at a certain temperature by microwave radiation. After the reaction, the sample was washed several times with deionized water and dried in the oven at 80°C, which is modified chitosan for next experiment.

2.2. Synthesis of composite
PVA was dissolved in two-neck flask under stirring at 90°C. Then the mixture included the monomers (BMA and BA), pore-forming agent (ethyl acetate), initiator (BPO), cross-linker (MBA) and hydrophobic chitosan, were injected into the PVA aqueous solution under stirring in the presence of nitrogen. The reaction mixture was kept at 80°C for 80 min by microwave irradiation (300W). The sample was washed with ethanol and deionized water, respectively. Finally, the sample was dried in vacuum oven at 60°C for 12 h.

2.3. Characterization
The IR spectra were collected using a Fourier transform infrared spectroscopy (FTIR) spectrophotometer (Nicolet iS10). The surface morphology of the samples characterized by scanning electron microscopy (SEM) was performed by S-4800 Field Emission SEM (Hitachi, Japan). Thermo gravimetric (TG) and differential thermal analyses (DTA) were carried out simultaneously using a DTG-60A instrument (Shimadzu Corporation, Japan).

2.4. Oil adsorption experiments
All tests were performed at 25°C. The absorbent was immersed in organics solution for 12 h. The sorption capacity of the absorbent was expressed in grams of the pollutant (oil or organics) absorbed by per gram of the absorbent (g/g):

\[ q_{eq} = \frac{w_e - (w_o + w_w)}{w_o} \]  

(1)

Where \( q_{eq} \) (g/g) is the sorption capacity of the absorbent, \( w_e \) (g) is the weight of the swollen state of the sample at equilibrium, \( w_o \) (g) is the weight of the dry state of the sample (initial weight), and \( w_w \) is the weight of adsorbed water (g). In the pure oil or organics medium without any water, \( w_w \) is equal to zero.

2.5. Hydrophobic test
Equation (2) is Washburn’s equation that presents the relation between a squared height of the penetrating liquid and the penetrating time [9].

\[ h^2 = \frac{\gamma \cos \theta}{2 \eta} \]  

(2)

where \( h \) (m) is the water level in tube, \( r \) (m) the average geometric radius of filling powders’ gap, \( \gamma \) (N/m) is the surface tension of liquid, \( t \) (s) is the penetrative time, \( \theta \) is the contact angles of powders, \( \eta \) (pN·s) is the viscosity of solvent.
3. Results and discussion

3.1. Hydrophobic test of modified chitosan

The chitosan powder was modified by different amounts of A151 (4, 10, 12 and 20% of the chitosan powder weight). Figure 1A showed that the original chitosan powder was hydrophilicity. After modified by a small amount of A151, the hydrophobic capability of chitosan powder was improved significantly. When A151 was 20 wt. % of the chitosan powder, the slope of curve was approximate to horizontal, it illustrated that the modified chitosan was completely hydrophobic.

Figure 1. A: Dynamic hydrophobic test of modified chitosan; B: The FTIR spectra of chitosan (a) and modified chitosan (b).

3.2. Characterizations

Figure 1B showed the FTIR spectra of chitosan and modified chitosan. Figures 1A and 1B showed the characteristic peak at 1661 cm\(^{-1}\) corresponds to C=O stretching vibration of secondary amide, the peaks at 1381 cm\(^{-1}\) and 1412 cm\(^{-1}\) are assigned to plane rocking and twisting of –CH\(_3\). In figure 1b, the peak at 765 cm\(^{-1}\) are due to C-H surface rocking vibration of -(CH\(_2\))^n- group(n<4), the strong and broad peak at 1099 cm\(^{-1}\) nearby can be assigned to C-O stretching vibration of alkyl ether. The sharp peak at 1087 cm\(^{-1}\) is assigned to C-O stretching vibration of vinyltriethoxysilane (figure 1B).

Figure 2A shows a schematic illustration of the binding mechanisms of composite resin. The surface morphologies of acrylate resin and composite resin were observed by FESEM in figure 2B and 2C, and figure 2B showed that the surface of acrylate resin was very smooth, unlike acrylate resin; composite resin (figure 2C) exhibited a rough surface, which indicated that modified chitosan had penetrated into the inner macropore of resin by combining with acrylate resin by hydrogen bond. The real photos of composite before and after adsorption organics are presented sphere-like structure in figures 2D and 2E, and there are many holes on the surface of the composite. The characterization of composite should make oil absorbency increased.

The weight loss of samples due to thermal degradation was obtained from the thermo gravimetric analysis. As shown in figure 3, it represented the TG–DTA curves of acrylate resin and composite. The resin decomposed in two consecutive steps. The first mass loss occurred in the temperature range of 67–290°C with the loss of about 20% based on the weight of resin, the second mass loss took place in the temperature range of 290–394°C with 80% loss (figure 3A). However, the first mass loss of the
Figure 2. Structural representation of composite resin (A); SEM images of acrylate resin (B) composite resin (C); The real photos of composite resin(D: before oil absorption, E: After oil absorption).

Composite resin occurred in the temperature range of 148–242°C with the loss of 5% based on the weight of resin, the second mass loss took place in the temperature range of 242–409°C with 90% loss (figure 3B). The thermostability of the composite was more than that of acrylate resin. The DTA plot showed one distinct endothermic peaks, which at 357°C corresponded to vaporization of acrylate resin, however the DTA plot of the composite showed one distinct exothermic peak (figure 3B),
because of the crosslinking of modified chitosan and acrylate resin, the forces and structures of compound resin were changed.

**Figure 3.** TG–DTA curves of acrylate resin and the composite resin (A: acrylate resin; B: composite resin).

**Figure 4.** Effect of some factors on oil absorbency.
3.3. Oil absorptivity and renewability of composite resin

Although oil absorption mechanism of oil-absorptive resin and mechanism of superabsorbent are essentially similar, but superabsorbent resins absorb water by using hydrogen bonds, and oil-absorptive resin can only absorb oil or organics by Van der Waals force between the molecules. This difference explained the reason that the oil-absorptive resins have lower absorptive ability. Hydrophobic chitosan and acrylate resin composite will change the molecular structure of the original resin network, which can improve the oil absorptive capacity and mechanical strength. In addition, oil absorption resin would achieve oil-absorption and oil-retention properties by its molecular network structures. The effects of initiator, dispersant, cross-linker and modified chitosan were shown in figure 4, results showed that the optimum synthesis condition is as follows: the dosages of cross-linker, initiator, dispersant and modified chitosan are 1.5 wt.%, 2.0 wt.%, 10 wt.% and 1.0 wt.% of monomers, respectively. Desorption of the composite was done by distillation method, then the sample was put into organics again, and then the absorption capacity was calculated. The reusability of composite was shown in figure 5. From figure 5, we can see that the composite can be repeatedly used, and the regenerative composite has good adsorption performance.

![Composite Resin and Acrylate Resin Oil Absorption Comparison](image)

**Figure 5.** Oil absorbency of acrylate resin and compound resin with the reused times at 298K.

4. Conclusions

A sphere-like modified chitosan and acrylate resin composite as efficient sorbent material for oil and organics was synthesized by suspension polymerization under microwave irradiation. From the above-mentioned results, it can be concluded that the organics adsorption performance of the composite is better than that of acrylate resin. Through the thermo gravimetric analysis, thermal decomposition and heat stability of the as-prepared sample were improved distinctly.

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