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Synthesis Optimization and Performance Test of Environmentally Friendly Renewable Poly(HMA-*co*-BMA-*co*-MA) Oil Absorbing Microspheres

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Abstract

In this study, butyl methacrylate (BMA), methyl acrylate (MA), cetyl methacrylate (HMA) as monomers, cetyl trimethyl ammonium bromide (CTAB) as dispersant, benzoyl peroxide (BPO) as initiator,N, n-methylene diacrylamide (MBA) as crosslinking agent, A kind of ternary oil absorbing resin was prepared by suspension polymerization. The range of long chain monomer (HMA), initiator (BPO), crosslinking agent (MBA) and surfactant (CTAB) was optimized by single factor experiment, and the best resin Poly (HMA-co-BMA-Co-MA) was obtained by orthogonal experiment design. The structure was analyzed by FR-IR, the microstructure of the resin was observed by SEM, and the stability of the resin was evaluated by TG. The experiment showed that the influence degree of reaction factors was as follows: long chain monomer amount > initiator amount > crosslinking agent amount > dispersant amount. The optimal synthesis conditions were: long chain monomer =25wt%, initiator =1wt%, crosslinking agent =1.1wt%, dispersant =0.030g.

Keywords

Acrylate; Suspension Polymerization; Oil-absorbing Resin; Orthogonal Experiment.

1. Introduction

With economic progress and industrial technology, oil spills, waste water from oilfield operations and organic chemicals discharged by petrochemical companies have led to a gradual increase in oily waste water pollution[1,2]. In particular, light oils, represented by chloroform, tend to accumulate in groundwater, are harmful to the environment and have mutagenic and teratogenic effects on human cells[3]. As a result, researchers have focused on developing effective methods to remove oil spills and organic chemicals from water[4]. In general, oil-absorbing materials are used to capture oil in water and to separate the oil-water miscible phase quickly and effectively[5].

With the in-depth research on oil-absorbing materials, synthetic acrylate oil-absorbing resins with porous and reticulated structure have good oil retention, fast adsorption, environmental friendliness, strong oil absorption and easy recovery[6]. Acrylic ester oil absorbing resins are divided into synthetic resins and composite resins, synthetic polymer resins are the basis of composite materials, and the adsorption properties of composite resins are inextricably linked to the performance of the underlying synthetic resin. Liang et al[7] synthesized a porous (butyl methacrylate/octadecyl acrylate) copolymer by suspension polymerization with a maximum oil absorption of 23.5 g/g against toluene. Zhang et al[8] prepared a MnO2/(n-butyl acrylate - butyl methacrylate - methacrylate - methyl methacrylate) resin with grafted MnO2, which showed an increase of 9.39g/g and 10.12g/g to 25.89g/g and 34.56g/g for toluene and chloroform respectively. Yan et al[9] successfully prepared an acrylate oil-absorbing resin by suspension polymerization using biomorphic MgO nanoparticles as inorganic components. The

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results showed that the resin adsorbed 28.22, and 10.44 g/g of chloroform, toluene and gasoline, respectively. in addition, the oil absorption rates for chloroform and toluene were 17.23 g/g and 6.82 g/g, respectively, when m(MgO)=0 wt%.

However, the base resins reported in the literature today are crudely optimized, generally have low adsorption properties and poor recyclability, thus affecting the development of composite resin performance. Therefore, the development and optimization of a base synthetic resin with excellent performance is one of the main issues currently faced.

In this study, a synthetic resin with excellent properties was successfully prepared by suspension polymerization using acrylate series as monomers. In addition, the resin was optimized by single-factor experiments, combined with an orthogonal test design, and finally, the resin properties were explored.

2. Experimental Section

2.1. Experimental Reagents and Apparatus

Butyl methacrylate (BMA), methyl acrylate (MA), cetyl trimethyl ammonium bromide (CTAB), benzoyl peroxide (BPO), N,N-methylenebisacrylamide (MBA), toluene, styrene, chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and anhydrous ethanol were purchased from Chengdu Kelong Chemical Reagent Factory. Cetyl methacrylate (HMA) was purchased from Beijing MREDA Technology Company Limited. All the reagents used were analytically pure, and the experimental water was deionized water.

2.2. Synthesis of Poly(HMA-BMA-MA)

Poly (HMA-co-BMA-co-MA) oil-absorbing resin esters were synthesized by suspension polymerization with methyl methacrylate, butyl methacrylate and cetyl methacrylate. A certain amount of monomer acrylate (HMA, BMA, MA) mixed solution was weighed into a beaker with constant pressure funnel and set aside; subsequently, a quantity of surfactant (CTAB) was added to 45 mL of deionized water and sonicated at 35°C for 15 min until completely dissolved; at the same time, a quantity of crosslinker (MBA) and initiator (BPO) was weighed into the system; the reaction was carried out by slowly adding the monomer mixture at a rate of 1 sec/drop. After the reaction, the resin was washed four times with anhydrous ethanol and deionized water, and finally dried in a constant temperature blast oven at 40°C for 8h.

2.3. Performance Tests

The performance of the oil-absorbing resin was evaluated by the weight method. 0.3 g of dried resin was immersed in 15 mL of volatile organic solution (toluene, styrene, chloroform, carbon tetrachloride) and after a certain time the resin was removed and drained until no droplets dripped off, the residual volatile organic matter was removed from the surface with paper and weighed. Three parallel sets of experiments were performed for each adsorption. The adsorption multipliers were calculated by the following equation.

$$Q = \frac{m_1 - m_0}{m_0}$$

Q: resin saturation rate, g/g

m_0: mass of resin before adsorption, g

m_1: mass of resin after adsorption, g

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3. Results and Discussion

3.1. Optimization of the Synthesis of Poly (HMA-co-BMA-co-MA) Resins

The amount of long-chain monomer, cross-linker, initiator, surfactant and reaction temperature of acrylate synthetic resins all affect their adsorption properties. This study was carried out to optimize the synthesis of the resin by a combination of single-factor and orthogonal experiments.

3.1.1. Effect of Long-chain Monomers on Resin Adsorption Performance

The amount of long-chain acrylate monomer directly affects the oil absorption multiplier of the resin. The effect of the amount of HMA on the oil absorption multiplicity of oil absorbent resins was investigated by introducing the long-chain monomer HMA at w(MA):w(BA) = 1:1. The results are shown in Figure 1. When the amount of HMA was in the range of 15-30 wt%, the oil absorption multiplier tended to increase as the amount of HMA increased; when the amount of HMA exceeded 30 wt%, the oil absorption multiplier decreased following the continuous increase in its amount. This is because the initial introduction of long-chain monomers into the synthetic system increases the lipophilicity of the synthetic resin[12], leading to an increase in its oil adsorption multiplicity; and if the HMA content is too high, the effective internal mesh structure of the resin is reduced, which in turn reduces the adsorption performance of the resin. When the HMA content was 0 wt%, the oil adsorption multipliers of the resin for toluene and chloroform were 14.5 g/g and 17.2 g/g respectively; while when the HMA reached 30 wt%, the adsorption multipliers were 23.5 g/g and 32.5 g/g, which increased the adsorption capacity by 62.1% and 89.1% year-on-year.

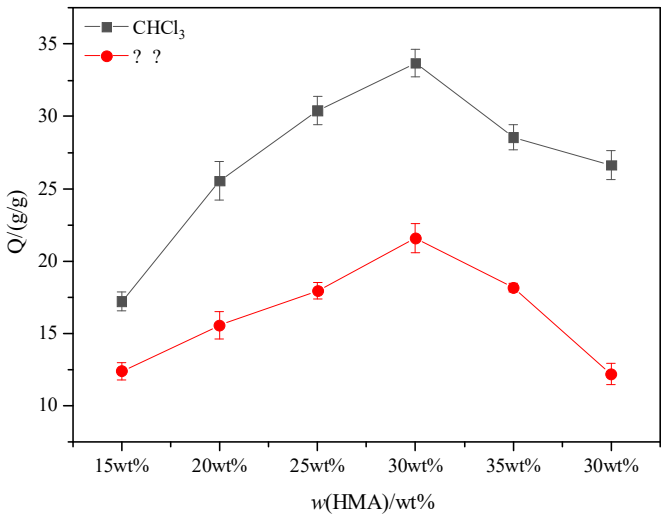

Figure 1. Effect of the amount of long chain monomer (HMA) on the oil absorption multiplicity

3.1.2. Effect of Elicitor Dosage on Resin Adsorption Performance

The amount of initiator has a significant effect on the polymerisation rate, as well as the relative molecular mass and crosslinking degree of the resin. This is because when the amount of initiator is too small, the polymerisation rate is low, the relative molecular mass of the resin increases and the degree of cross-linking decreases, so the monomer does not polymerise completely and remains in the resin, which leads to a decrease in the oil absorption of the resin; when the initiator content is higher than 1 wt%, the oil absorption increases as the content increases and the oil absorption decreases. When the initiator content is higher than 1 wt%, the oil absorption decreases as the content increases. This is because when the amount of initiator

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used is too large, the relative molecular mass of the polymer decreases and the cross-linkage increases due to the shortening of the chain length of the macromolecular radicals, thus reducing the oil absorption of the polymer produced. The highest oil absorption is achieved when the initiator (BPO) content is 1 wt%.

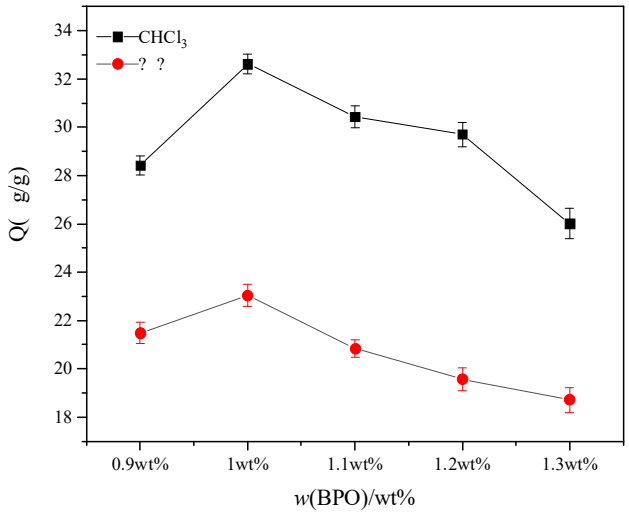

Figure 2. Effect of BPO dosage on resin oil absorption

3.1.3. Effect of Crosslinker Dosage on Resin Adsorption Performance

The spatial structure and oil absorption capacity of the resin is influenced by the amount of crosslinker, which leads to the oil absorption multiplier being affected. As shown in Figure 3, the oil absorption multiplier increases when the crosslinker content is below 1.1 wt%; the best adsorption performance is achieved at a content of 1.1 wt%; and the oil absorption multiplier decreases when the content is above 1.1 wt%. If the amount of cross-linking agent is too small, the cross-linking density is also small, resulting in a lower oil absorption rate. In addition, the resin appears viscous and has no strength, so its separation and post-processing becomes very difficult. As the amount of crosslinker increases, the oil absorption capacity also increases. However, when the amount of crosslinker used is too high, the oil absorbency decreases because the increase in crosslinking inhibits the expansion of the polymer space network, which reduces the effective network volume and oil capacity of the polymer.

3.1.4. Effect of Surfactant Dosage on Resin Adsorption Performance

The surfactant has good affinity for both oil and water phases, and also reduces the water-oil interfacial tension, which facilitates droplet dispersion and prevents droplet viscosity and aggregation. As shown in Figure 4, with the increase of surfactant dosage, the oil adsorption multiplier tends to gradually increase and then decrease, with the adsorption performance reaching a peak at 0.030 g of surfactant. This is due to the fact that when the dosage of dispersant is too small, the phenomenon of agglomeration will occur as the monomer droplets cannot be well dispersed and no particles will be produced. When the dosage of dispersant increases, the system has a good dispersion effect; when the dosage is too large, the particles of the product are not uniformly distributed and the size of the particles is relatively small, and the gelatin produced after oil absorption by the particles is low in strength, unshaped and difficult to collect after oil absorption, which indirectly affects the adsorption performance.

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3.2. Resin Characterization

3.2.1. FT-IR

Figure 3 shows the infrared spectrum of the preferred resin. In Figure 3, the characteristic peaks at wave numbers 2937 and 2857 are -CH_2 asymmetric stretching and symmetric stretching vibrations, respectively; the characteristic peaks at wave numbers 1145 and 1733 indicate the presence of C-O-C and C=O structures in the ester monomer in the resin structure; the characteristic peak at wave number 1249 is a C-N stretching vibration, which indicates by the above test results that the resin structure contains a clear The results of the above tests show that the resin structure contains a clear ester-based structure, i.e. a C-N structure in which the crosslinker and the polymerized monomer combine smoothly, indicating successful polymerization of the resin.

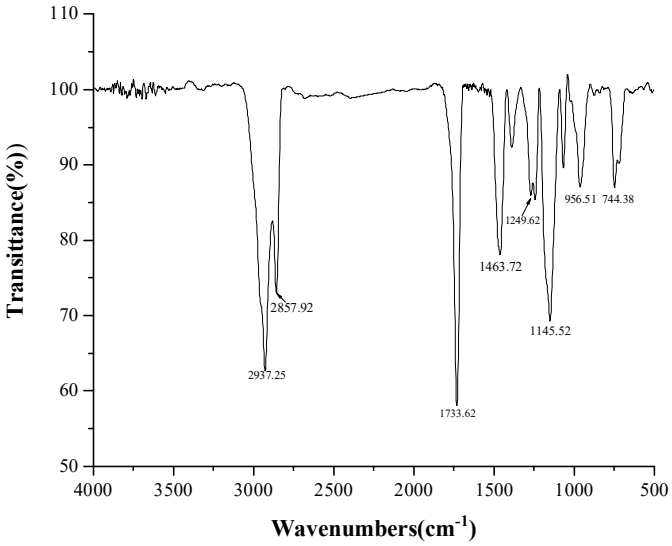

Figure 3. FT-IR spectrum of Poly (HMA-co-BMA-co-MA) resin

3.2.2. SEM

The microscopic morphology of the Poly (HMA-co-BMA-co-MA) resin was observed by SEM. As shown in Figures 4a and 4b, the resin surface is relatively rough and evenly distributed with folds. This indicates that the resin has a large specific surface area and contains some micro-pores, allowing oil molecules to diffuse into the interior.

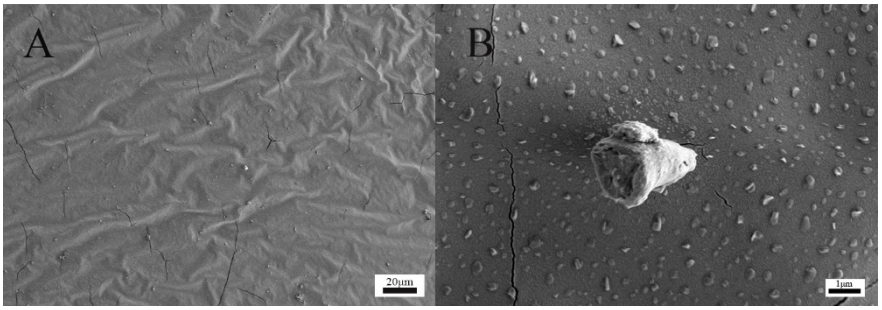

Figure 4. SEM image of Poly (HMA-co-BMA-co-MA) resin

3.2.3. TG

The TG test results for Poly (HMA-co-BMA-co-MA) resin are shown in Figure 5. The decomposition was divided into three main stages. Stage I is from 270 to 305 °C, where the resin decomposes slowly and loses 5.07% of its mass; Stage II is from 305 to 390 °C, where the short chain molecules of the polymer start to break down and lose 84.07% of their mass due to the high temperature conditions; Stage III is from 390 to 560 °C, where the resin copolymer

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decomposes completely. It can be seen that the resin has good thermal stability and is suitable for adsorption applications under conventional conditions.

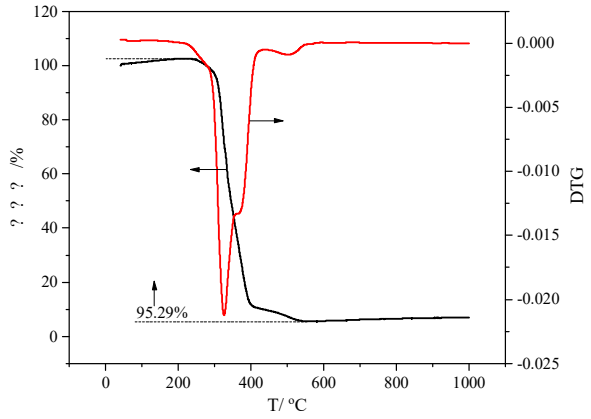

Figure 5. TG test for Poly (HMA-co-BMA-co-MA) resin

3.3. Resin Performance Testing

3.3.1. Adsorption Performance of Resins for Different VOCs

The three-dimensional spatial network structure of Poly (HMA-co-BMA-co-MA) resins gives them a good oil absorption capacity. Due to the van der Waals forces between the lipophilic groups and the liquid, oil can enter the resin. Due to the cross-linked structure, highly oleophobic resins only swell but do not dissolve in solvents [13]. When the resin is placed in oil, at first, intermolecular diffusion control plays a dominant role due to the concentration difference. When a certain amount of oil enters the resin, the polymer chains are solventised. However, the amount of oil absorbed is not sufficient to stretch the polymer chains. As more oil molecules penetrate the resin, the polymer chains are stretched; however, the cross-linked network of the resin has a tendency to recover elastically, which prevents further expansion of the resin [14], and eventually an oil absorption equilibrium is achieved.

In addition, the absorption ability of Poly (HMA-co-BMA-co-MA) to various solvents was investigated, and the results are shown in Figure 6. The oil absorption multiplicity of the resin to benzene, toluene, styrene, CH2Cl2, CHCl3 and CCl4 were 23.17, 25.59, 23.17, 25.22, 33.17 and 29.32 g/g, respectively. it can be seen that Poly (HMA-co-BMA-co-MA) has adsorption capacity for all common organic solvents and can be used in the practical treatment of common organic solvent contamination.

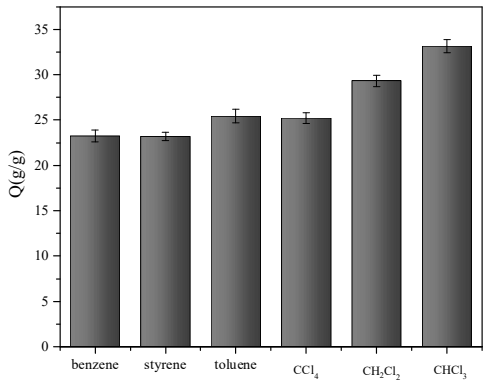

Figure 6. Adsorption performance of resin on selected VOCs

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3.3.2. Resin Regeneration and Recycling Properties

In practical applications, the regeneration and recycling performance is an important factor in the performance evaluation system of adsorbent materials, and the recycling of the resin for CHCl3 is shown in Figure 7. After four adsorption-desorption cycles, the modified resin showed an oil absorption multiplicity of 31.10 g/g for CHCl3, which was only a 5.18% decrease in oil absorption multiplicity, and the resin performance retained 82.43% after eight adsorption-desorption cycles.

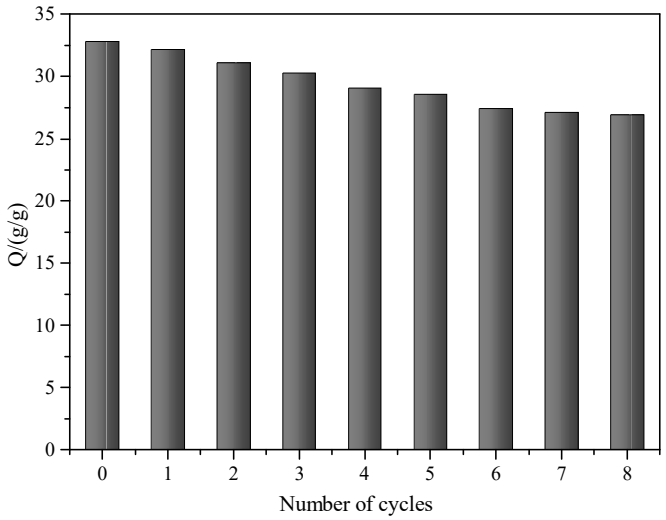

Figure 7. Cycling performance of the resin after adsorption of $CHCl_3$

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