Synthesis and Characterization of a High Oil-Absorbing Magnetic Composite Material

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ABSTRACT: The high oil magnetic composite resin, which is a low crosslinking resin, was synthesized by conventional suspension copolymerization in the present work. The effect of the monomer ratio, crosslinker, initiator, modified Fe_3O_4, and reaction time on oil absorptivity of the resin and defined optimum reaction condition were studied. The highest oil absorptivity of the resin was about 20 g/g in chloroform and 10.5 g/g in toluene when the extent of modified Fe_3O_4 was 5%. Infrared (IR), X-ray diffractometer (XRD), synthetic themoanalyzer, laser particle size analyzer, and vibrating-sample magnetometer (VSM) were used to study the properties of the oil-absorbing magnetic composite resin. The magnetic composite resin can be recovered after conveniently and rapidly absorbing oil by magnetic separation techniques without excluding other mechanical techniques. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 894–900, 2004

Key words: crosslinking; separation technique; magnetic polymers; magnetic separation; copolymerzation

INTRODUCTION

An ever increasing volume of petroleum products used worldwide has brought with it a proportionate increase in the number of accidental or deliberate hydrocarbon oil spills. In open bodies of water, rivers, harbors, lakes, and oceans, it is a serious pollutant. Large spills can be positively disastrous to birds and perimarine life, and even small spills can foul beaches. There is an exigent need to develop an adequate and efficient process for removing this oil. Various materials, such as brick clay, silicon dioxide, activated carbon, paper pulp, polypropylene fiber, polyurethane foam, and oil absorbing resin, have been widely used to absorb oil spilled on water. Among them, the capability of oil-absorbing resin is seen to be superior to other ordinary materials.[1–4] It can be made granular, sheeted, or as an emulsion, and can be applied not only to environmental protection, but also to agriculture, medicine, and industry. It is this broad range of possible applications that has led to recent interest in this system.

In this work, we synthesize high oil-absorbing magnetic composite resin by suspension copolymerization combining high oil-absorbing resin with Fe_3O_4. It has hydrophilicity and a gel-type structure consisting of an elastic crosslinking three-dimensional network and interstitial space that does not dissolve in oil but swells in oil. It can remove a great variety of oil from the surface of water and only absorbs oil and not water. To conveniently and rapidly recover the resin after absorbing oil, Fe_3O_4 particles were added so that magnetic separation techniques can be used without excluding other mechanical techniques. To improve the affinity between inorganic Fe_3O_4 nanoparticles and the monomer or its polymer, and improve the Fe_3O_4 particle dispersivity in the resin, oleic acid was used for the surface modification of magnetic particles (Fe_3O_4); the oleic acid molecule adsorbs on the surface of Fe_3O_4 particles by action of hydrogen bond or coordination linkage.[5]

EXPERIMENTAL

Materials

Butyl methacrylate (Xin-Guang Chemical Reagent Factory, Peking, China) and divinylbenzene (DVB) (Chemical Reagent Company, Shanghai, China) were purified by washing with 5% aqueous sodium hydroxide (Tian-Feng Chemical Reagent Company, Tianjing, China), dried by anhydrous $CaCl_2$ (Chemical Reagent Factory, Tianjin, China) and distilled under a vacuum. Benzoyl peroxide (BPO) (Kang-Wei Chemical Reagent Factory, Shanghai, China) was dissolved in $CHCl_3$ (Second Chemical Reagent Factory, Tianjin, China) and precipitated by adding an equal volume of MeOH (Fu-Chen Chemical Reagent Company, Tianjin, China). Lauryl acrylate was synthesized using the

method described by Rehber and Fisher.[6] Potassium nitride (Fu-Cheng Chemical Reagent Company, Tianjin, China), four hydrous ferrous chloride (Shuang-Chuan Chemical Reagent Factory, Tianjin, China), potassium hydroxide (Chemical Reagent Company, Tianjin, China), oleic acid (Chemical Agent Factory, Xi'an, China), gelatin glue (Chemical Reagent Factory, Shanghai, China), chloroform (Second Chemical Reagent Factory, Tianjin, China), toluene (Chemical Reagent Company, Tianjin, China), kerosene and machine oil (market-selling, Lanzhou, China). These chemicals were purified using standard procedures.

Analyses

Thermal stability was examined with a synthetic themoanalyzer (ZRY-2P, Shanghai) at a scanning rate of 10°C/min in air. Size distribution analysis of the magnetic composite resin was carried out by using a MS 2000 laser particle size analyzer (Malvern, UK). A crystallographic study was performed on the Fe_3O_4 powder by D/max 2400 X-ray diffractometer (XRD; Rigaku, Japan) by using $CuK\alpha$ radiation. The average size of the Fe_3O_4 particle was deduced by using the Scherrer formula.[7] The infrared (IR) spectroscopy of the samples was recorded on a spectrometer (IFS 120HR; Bruker, Germany), while a vibrating-sample magnetometer (VSM Japan, VSM-5S-15) was used to study the magnetic properties of the samples at room temperature. The values of kinematic viscosity of kerosene and machine oil were determined by YN-7 full-automatic kinematic viscosity instrument (China) at 40°C.

PREPARATION OF SAMPLES

Preparation of Fe_3O_4 nanoparticle

KNO_3 solution was added to $Fe(OH)_2$ colloid solution, which was synthesized from $FeCl_2 4H_2O$ solution and KOH solution mixed in a known ration at the stirring speed of 1600 rpm. After the mixture was aged at 90°C for 7 h, Fe_3O_4 particles were obtained by centrifugation and then washed with $1M$ HNO_3 and distilled water.

Surface organic modification of magnetic iron oxide particle

The Fe_3O_4 nanoparticles were modified by oil-soluble surfactant oleic acid at 90°C for 1 h. The modified Fe_3O_4 was then washed with anhydrous ethanol.

Preparation of the composite resin

A given weight of gelatin glue was dissolved in a known volume of distilled water in a 250-ml round-
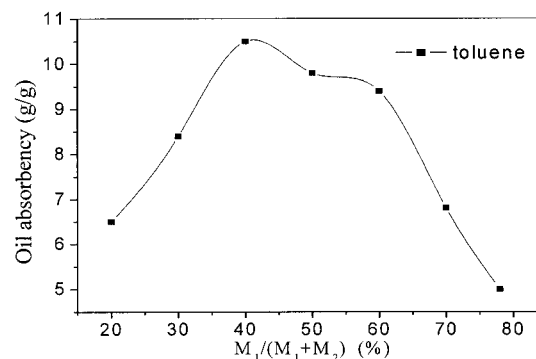

Figure 1 Relation between composition of monomer and oil absorbency. M_1: butyl methacrylate; M_2: dodecyl acrylate. Crosslinker: 0.27%; initiator: 1.7%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C.

bottomed flask equipped with a thermometer, a stirrer, a gas inlet pipe, and a reflux condenser. The mixture of butyl methacrylate and lauryl acrylate with DVB crosslinker was then added to the flask with BPO and modified Fe_3O_4. After 7 h of suspension reaction at the stirring speed of 200 rpm under nitrogen atmosphere at 90°C, the prepared composite resin was collected by filtration when the solution was cooled, then washed with hot water, and dried in a vacuum oven until a constant weight was reached.

Speed of oil absorption and oil absorption power

The sample was immersed in various oils for given time periods at room temperature and then taken out from the oil. The excess oil on the resin surfaces was removed by tissue paper. The oil absorbing sample was then weighed. The equation $(w_1 - w_2)/w_2$ could be used to evaluate the oil absorptivity, where w_1 is the weight of the oil absorbing sample and w_2 is that of the sample before immersion.

Recovery of floating oil

One gram of composite resin was left floating for 4 h on the bath, which contained 1500 ml water and 4 ml kerosene. A magnet was engaged to grip the magnetic resin after absorbing and then the resin was swilled out by water or scratched by a bar without magnetism. By such means, about 98% resin containing absorbing kerosene was obtained. It suggests that an electric magnet can be used to grip the composite resin after absorbing for recovering the oil from the water. This magnetic composite material can also be used to recover leaked oil of maritime accident.[1] The ability of resin for recovery of floating oil based on the state of residue of oil on the water surface was evaluated. With the composite resin treatment, complete absence of residual oil on water surface shows that the resin
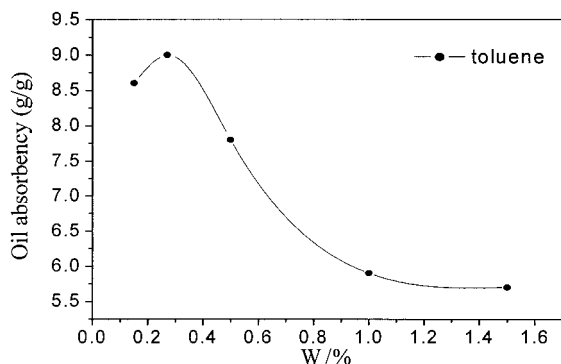
Figure 2 Relation between the amount of crosslinker and oil absorbency. $M_1/(M_1 + M_2)$: 60%; initiator: 2%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C.

Figure 4 Relation between the reaction time and oil absorbency. $M_1/(M_1 + M_2)$: 40%; crosslinker: 0.27%; initiator: 1.7%; modified Fe_3O_4: 5%; T: 90°C.

has a high recovery of floating oil and is easily separated from the polluted water by magnetic separation.

RESULTS AND DISCUSSION

Characterization of the samples

Effect of monomer ratio

Figure 1 exhibits the relation between the monomer ratio and the oil absorption. It can be seen that the oil absorption curve was a peak with respect to the percentage of butyl methacrylate monomer. Adding butyl methacrylate changes the network structure of the resin and increases the interstitial space, so oil absorption increases; however, if the percentage is too great, the oil absorption reduces, because the lipophilicity is much worse than that of lauryl acrylate.[8] Oil absorption reached its highest value of 10.5 g/g at 40% butyl methacrylate, as shown in Figure 1.

Effect of amount of crosslinker

The effect of the amount of crosslinker is shown in Figure 2. The amount of crosslinker directly affects
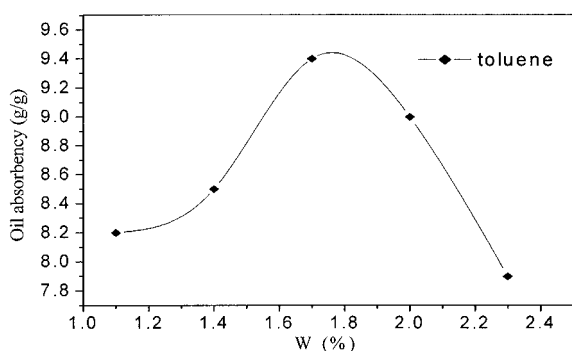
interstitial space in the resin. If the amount of crosslinker is too great, the crosslinking degree increases and the network space in the resin decreases. As a result, the oil absorption reduces, which is consistent with the Flory theory mentioned in this article. By contrast, if the amount of crosslinker is too small, density reduces and the ratio of soluble resin increases, so the oil absorption again decreases. The resin has the best oil absorptivity when the interstital space is at its optimum value. Figure 2 shows that this occurs at 0.27% crosslinker by weight.

Effect of amount of initiator

Figure 3 shows the relation between the amount of initiator and the oil absorptivity. The oil absorption is the highest when the amount of initiator is 1.7%. The amount of initiator affects molecular weight between cross bonding of resin, which affects content of networks. In the other studies,[9–11] where the oil absorbing resin is free of modified Fe_3O_4, the optimum amount of initiator is about 1%. The reason, perhaps,

Figure 3 Relation between the amount of initiator and oil absorbency. $M_1/(M_1 + M_2)$: 60%; crosslinker: 0.27%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C.
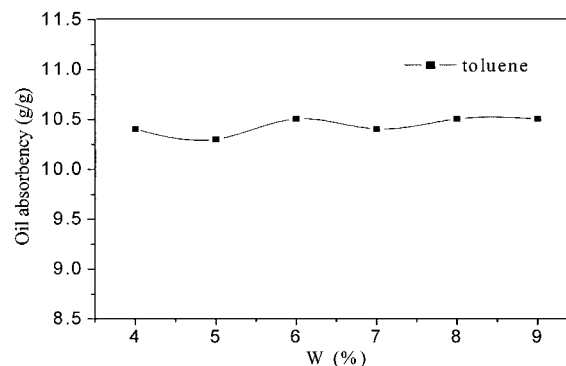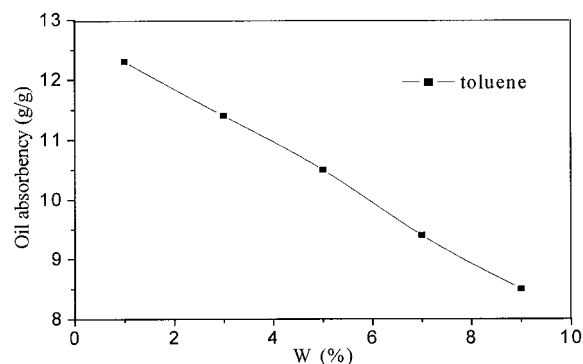

Figure 5 Relation between the amount of modified Fe_3O_4 and oil absorbency. $M_1/(M_1 + M_2)$: 40%; crosslinker: 0.27%; initiator: 1.7%; reaction time: 7 h; T: 90°C.
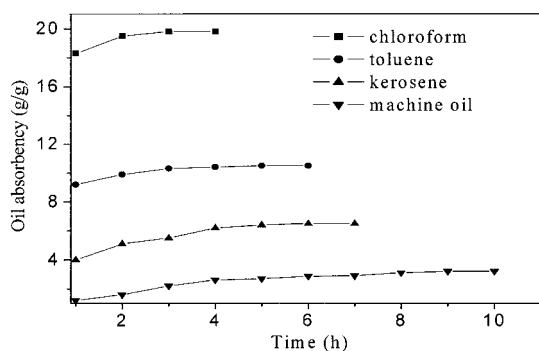
Figure 6 Relation between time and oil absorbency. $M_1/(M_1 + M_2)$: 40%; crosslinker: 0.27%; initiator: 1.7%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C.

Figure 7 Thermogravity curve of the composite resin (air, 10°C/min). $M_1/(M_1 + M_2)$: 40%; crosslinker: 0.27%; initiator: 1.7%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C.

for the higher value in this work is that the modified Fe_3O_4 retards copolymerization to a certain extent.

Effect of polymerization time

Figure 4 displays the effect of polymerization time. Prolonged polymerization time gave almost no change to the oil absorption of the composite resin. This follows the free-radical polymerization law, because molecular weight affects oil absorption of the resin greatly, and reaction time of free-radical polymerization shows nearly no influence on molecular weight of polymer.

Effect of amount of modified Fe_3O_4

The effect of the amount of modified Fe_3O_4 is shown in Figure 5. It is apparent that oil absorption by the composite resin decreased as the amount of the modified Fe_3O_4 was increased. The modified Fe_3O_4 occupied the part of the interior space of the resin and is distributed in the resin dispersedly. Even when the amount of added modified Fe_3O_4 reaches 9%, the oil absorption is as high as 8.5 g/g in toluene.

Speed of oil absorption and oil absorption power

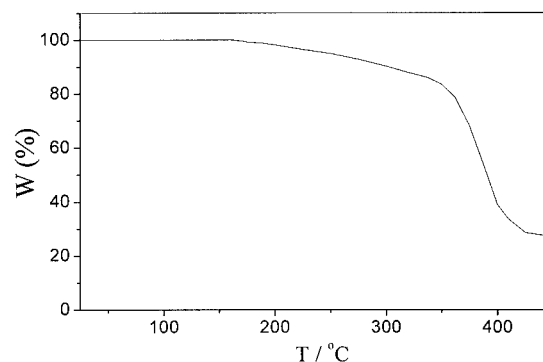Figure 6 shows the resin's absorption speed of various oils and oil absorptivities. The oil absorption of the magnetic composite resin increases with time and the absorptivities maintained at a certain level when the time is prolonged enough. The speed of oil absorption by the magnetic composite resin decreases as viscosity of oil increases. The size of the resin also affects the absorption speed too; the smaller the diameter of the resin, the greater its oil absorption speed. Solubility parameter affects oil absorbility; solubility parameter of the resin is closer to the absorbed oil; oil absorptivity is higher. The sequence of oil absorptivity is chloroform > toluene > kerosene > machine oil; time of swelling saturation has the same order as the above. After reusing 10 times, its oil absorbency is about 82% of initial value. Table I lists values of viscosity and solubility parameter of the oils.

MEASUREMENT

Thermostability of the composite resin

Thermogravity of the composite resin is shown in Figure 7. The sample started to decompose at about 150°C, showing that the composite resin can be used under normal conditions.

Size distribution of the magnetic composite resin

Figure 8 exhibits size distribution of the composite resin. Its dimensions are from 50 to 2000 μm, and its average dimension is 1024 μm. It is clear that adding modified Fe_3O_4 has almost no influence on the diam-

TABLE I
Viscosity and Solubility Parameter of the Oils

	Chloroform	Toluene	Kerosene	Machine oil
Viscosity (mm²/s)	0.0365[a]	0.064[a]	1.209[b]	28.96[b]
Solubility parameter (cal/ml)$^{1/2}$	9.3[c]	8.9[c]	—	—

[a] Value of viscosity at 25°C from H. Z. Lu.[12]
[b] Value of viscosity at 40°C obtained by kinematical viscosity instrument.
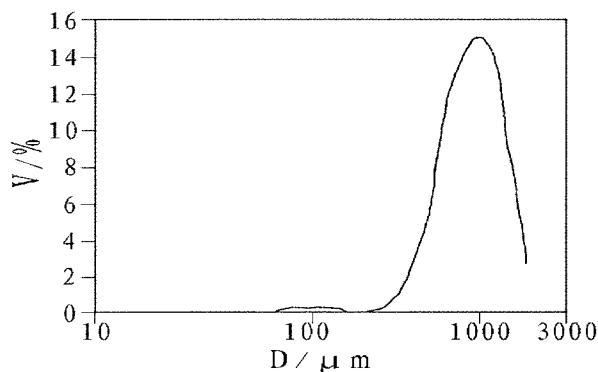[c] The data from C. R. Zheng.[13]

Figure 8 Size distribution of the magnetic composite resin. $M_1/(M_1 + M_2)$: 60%; crosslinker: 1%; initiator: 1.7%; modified Fe_3O_4: 5%; reaction time: 7 h; T: 90°C; stirring speed: 200 rpm.

eter of the magnetic composite resin. Different particle diameters can be obtained by changing the amount of dispersant and the agitating speed. Increasing the amount of dispersant and the agitating speed decreases the particle diameter.

X-ray diffraction pattern of Fe_3O_4

Figure 9 shows the XRD patterns of Fe_3O_4 nanoparticles and Fe_3O_4 modified with oleic acid. It is identified to be Fe_3O_4 by phase analysis; both (a) and (b) have spinel structure. The average size is estimated to be about 52 nm, according to the Scherrer equation. It demonstrates that crystal structure of Fe_3O_4 has no change after being modified with oleic acid.

Infrared spectra of Fe_3O_4 and modified Fe_3O_4

IR spectra of Fe_3O_4, oleic acid, and modified Fe_3O_4 are presented in Figure 10. The characteristic absorption peak of Fe_3O_4 is situated at 580 cm^{-1}, presented in Figure 10(a, c). Absorption peaks of —CO and —OH at 1710 and 2900 cm^{-1}, respectively, are in oleic acid,
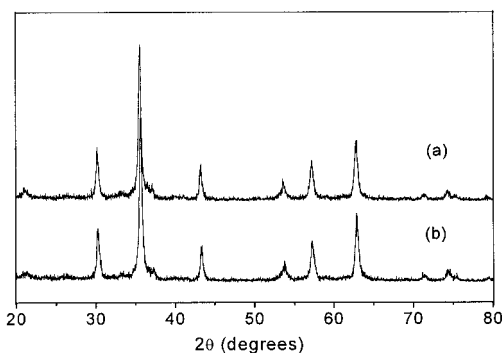

Figure 9 X-ray diffraction spectrum of the samples. (a) Fe_3O_4; (b) modified Fe_3O_4 by oleic acid.
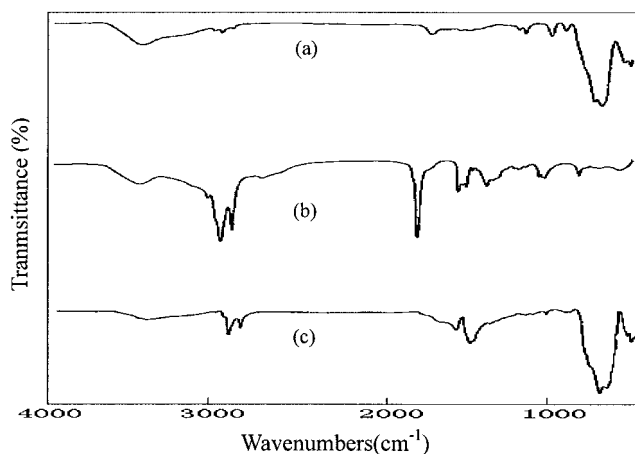

Figure 10 IR spectra of Fe_3O_4 and modified Fe_3O_4. (a) Fe_3O_4; (b) oleic acid; (c) modified Fe_3O_4.

as shown in Figure 10(b). In Figure 10(c), absorption peak of —CO shifts right to 1430cm^{-1}. Carbonyl likely combines with Fe_3O_4 particle by chemical bonding, which was consistent with the result reported by Zhu et al.[5]

IR spectra of magnetic composite resin and the resin without modified Fe_3O_4

Figure 11 shows IR spectra of magnetic composite resin and the resin free of Fe_3O_4. It is apparent that there is a characteristic absorption peak of Fe_3O_4 in Figure 11(b), and it proves that modified Fe_3O_4 is in the composite resin. The high oil-absorbing magnetic composite material was successfully synthesized by the method mentioned in this article.

Measurement of Fe_3O_4 content

A certain amount of modified Fe_3O_4 to be tested was burnt at a temperature of 600°C in a muffle furnace at
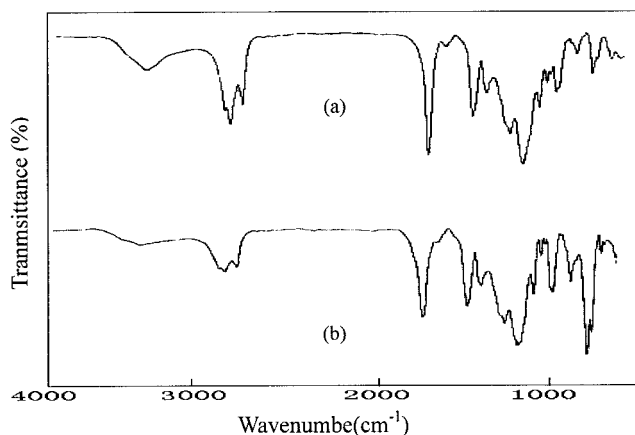

Figure 11 IR spectra of magnetic composite resin and the resin without modified Fe_3O_4. (a) magnetic composite resin; (b) resin without modified Fe_3O_4.
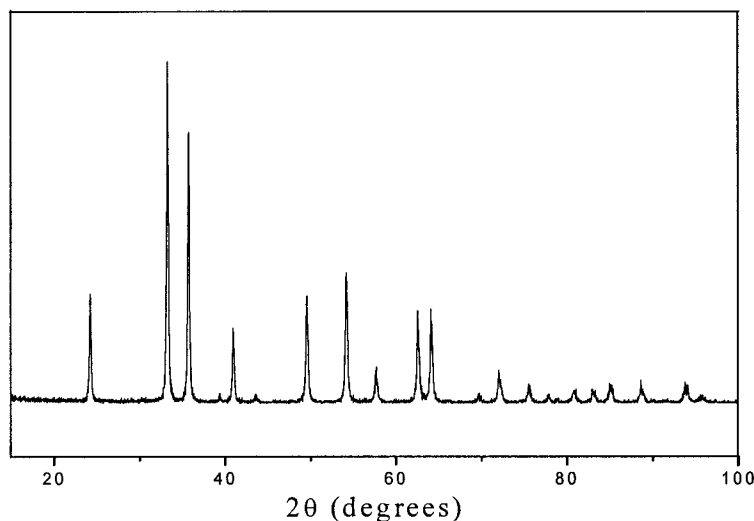
Figure 12 X-ray diffraction spectrum of a-Fe_2O_3.

constant weight. The oleic acid in the sample was removed, and Fe_3O_4 was completely converted into α–Fe_2O_3. It can be proved by XRD analysis shown in Figure 12. The remains were weighted; the content of Fe_3O_4 in the modified Fe_3O_4 was calculated indirectly. It was repeated three times. As a result, the average content of Fe_3O_4 is 93.7% in the modified Fe_3O_4.

Magnetic properties of Fe_3O_4

The hysteresis loop measured by VSM at room temperature is plotted in Figure 13; as can be seen; the Fe_3O_4 nanoparticle is magnetic, not superparamagnetic. For fields higher than a certain H, the material is magnetized to saturation. The oil-absorbing resin added to the modified Fe_3O_4 is expediently recovered by magnetic separation techniques without the other mechanical techniques. Magnetic property of the final magnetic composite resin can be controlled by the amount of modified Fe_3O_4.
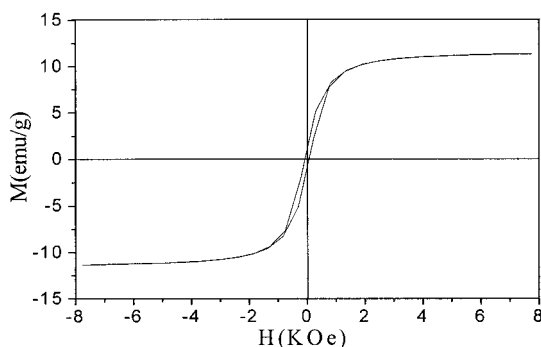

Figure 13 M–H hysteresis loop of Fe_3O_4 particles measured by VSM at room temperature.

OIL ABSORPTION MECHANISM

The prepared resin is a low crosslinking magnetic composite resin using high oil absorbing resin and Fe_3O_4. Oil absorption is a result of interaction between its lipophilic group of the resin and oil molecules. It possesses three-dimensional hydrophobic networks that were caused by crosslinking. It can swell various oils, not dissolve it. It is different from water absorption resins. The latter had much greater absorption power than that for the former, because the oil absorbing resin absorbs oil by van der Wahl force, while the water absorbing resin absorbs water depends on the action of hydrogen bond. According to Flory theory,[14] oil absorptivity of the resin can be expressed as

$$\theta^{5/3} \cong \frac{(1/2 - X_1)/V_1}{V_e/V_o}$$

where θ is the times of the absorbed oil; V_1 is molal volume of the resin; V_e/V_o is the crosslinking density of the resin; and X_1 is interaction parameter between oil and the resin. While being added, modified Fe_3O_4 distributing in the resin dispersed and occupied part of the interior space,[15] and its oil absorption decreased a little.

CONCLUSION

A simple method of high oil-absorbing magnetic composite was studied by using a method of conventional suspension polymerization. It combined high oil-absorbing resin with magnetic separation technology, because its magnetic character can be collected by magnetic means (electromagnet, permanent magnet arrangements) in a short time and according to our

experiments to collect almost 100% of the spilled oil on the surface of water. The surface of Fe_3O_4 was modified with surfactant oleic acid; as a result, it improved the affinity between the magnetic particles (Fe_3O_4) and the monomer or its polymer. Fe_3O_4 particles dispersed distribution in the oil-absorbing resin, and adding modified Fe_3O_4 has almost no influence on the diameter of the magnetic composite resin. The magnetic property of the final magnetic composite resin can be controlled by the amount of modified Fe_3O_4. The highest oil absorption of the composite materials is about 20 g/g for chloroform and 11 g/g for toluene or so when the extent of the modified Fe_3O_4 is 5% by weight, and oil absorption of the resin without adding the modified Fe_3O_4 can absorb 23 g/g for chloroform and 15g/g for toluene.[16] Five percent (weight) content of the modified Fe_3O_4 has no obvious influence on the oil absorptivity of the resin.

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