Characterization of Magnetic Poly(methyl methacrylate) Microspheres Prepared by the Modified Suspension Polymerization

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ABSTRACT: The study focuses on the characterization of the superparamagnetic microspheres of poly(methyl methacrylate) (PMMA) prepared by the modified suspension polymerization. The nano-sized oleic acid-coated magnetite particles (OMP) mixed with methyl methacrylate (MMA) monomers and divinylbenzene were employed to produce the nonporous superparamagnetic PMMA microspheres. The morphology, composition and magnetic properties of the magnetic PMMA microspheres were characterized with the scanning electron microscopy, particle size analyzer, transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, and superconductor quantum interference device. As a result, the obtained PMMA microspheres had the average particle size of 1.8–6.8 μm and magnetite content of 4.74–10.85 wt %. The corresponding saturation magnetization of the PMMA microspheres was in the range of 2.04–8.51 emu/g. The diameter of the PMMA microspheres showing the polydispersity significantly decreased with the higher weight ratio of OMP to MMA. On the contrary, the magnetite content and saturation magnetization of the PMMA microspheres would increase with the higher weight ratio of OMP to MMA. Furthermore, the distinct relationships between the characteristics of magnetic PMMA microspheres and the weight ratio of OMP to MMA have been proposed. The magnetic PMMA microspheres show the good stability in the solution with the pH region of 2.1–12.9. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 583–590, 2008

Key words: magnetite; microspheres; superparamagnetic; suspension polymerization; PMMA

INTRODUCTION

Magnetic polymer particles have caused a great interest and application in the biotechnology and medicine fields during the past years.[1,2] The magnetic microspheres, which can be effectively separated and collected in the environment of the magnetic field are appropriate to be used in the areas of the cell isolation, enzyme immobilization, protein and enzyme purification, water treatment and targeting drug.[3–8] The synthesis of the magnetic polymer particles has been proceeded via different polymerization processes, including emulsion polymerization,[9] miniemulsion polymerization,[10] dispersion polymerization,[11] suspension polymerization[12–15] and seed polymerization.[16] Among these polymerization processes, the suspension polymerization is considered simpler and more feasible for a massive production of the magnetic polymer microspheres. However, the magnetic polymer microspheres obtained from the convectional suspension polymerization usually possess a larger particle size of hundred micrometers and a broader particle size distribution resulting in the limited application.

Recently, Ma et al.[17,18] and Yang et al.[19] proposed a modified suspension polymerization for the preparation of the magnetic polymer microspheres. The novel method of the modified polymerization processes is to introduce the nano-sized oleic acid-coated magnetite particles (OMP) into the suspension polymerization system for the product of the magnetite-encapsulated polymer particles. The obtained magnetic polymer microspheres would have the particle diameter of several micrometers along with the narrow size distribution and high magnetite content. With the advantages of these characteristics, the magnetic polymer microspheres can be applied as an ideal magnetic adsorbent or carrier after the further surface modification.[17–20] Thus the efficiency and capacity of the adsorption processes are enhanced with the employment of the magnetic polymer microspheres.

In addition, the amount of the OMP used in the modified suspension polymerization is adjustable. The synthesis prescription for the polymerization process can be prepared with different weight ratios of OMP to monomers. Note that the applied weight ratio of OMP to monomers may affect the particle size and

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magnetite content of the obtained magnetic polymer spheres.[21–23] According to the previous study about the miniemulsion polymerization,[24] the result indicates that the weight ratio of OMP to monomers is remarkably influential in the magnetite content of the magnetic polystyrene nanospheres. It is clear that the particle diameter and magnetic properties are crucial for the application of the magnetic polymer spheres. However, the related research about the effect of the weight ratio of OMP to monomers on the modified suspension polymerization is still scarce.

This study investigates the preparation of magnetic poly(methyl methacrylate) (PMMA) by the modified suspension polymerization with various weight ratios of OMP to methyl methacrylate (MMA). The morphology, particle size, magnetite content, magnetic properties and yield of the prepared PMMA microspheres were characterized. Furthermore, the distinct relationships between the particle characteristics and the weight ratio of OMP to MMA were presented, which is important for the proper design of manufacturing the ideal magnetic microspheres. Therefore, this work can provide the useful information for the preparation of magnetic polymer microspheres by the modified suspension polymerization.

EXPERIMENTAL

Chemicals

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 99%), ammonium hydroxide (NH_4OH, 25%) and MMA were purchased from Merck (Darmstadt, Germany). Oleic acid was obtained from Nacalai Tesque (Kyoto, Japan). Polyvinyl alcohol (PVA) used as a stabilizer has the molecular weight of 22000 g/mol from Acros (Geel, Belgium). Methylene blue trihydrate was purchased from MP Biomedicals (Irvine, CA). Divinylbenzene (DVB) used as the crosslinker was purchased from Tokyo Chemical Industry (Tokyo, Japan). Benzoyl peroxide (BPO) used as an initiator for the polymerization was obtained from Fluka (St. Gallen, Switzerland). Hexane used as the solvent was purchased from Hayashi Pure Chemical Industries (Osaka, Japan). MMA and DVB were purified by the vacuum distillation prior to use. Other chemicals were used without any further purification.

Preparation of OMP

The coprecipitation method was carried out for the preparation of nano-sized OMP. 23.5 g $FeCl_3 \cdot 6H_2O$ and 8.6 g $FeCl_2 \cdot 4H_2O$ were dissolved in 500 mL deionized water in the condition of continuous nitrogen purge. The temperature of the solution was maintained at 85°C and then 27.8 mL NH_4OH was added rapidly. Subsequently oleic acid was gradually dropped into the solution within 10 min. The stirring speed was controlled at 600 rpm until the block-like magnetite (Fe_3O_4) gel appeared. The obtained magnetite gel as the aggregate of the OMP was cooled to the room temperature and washed several times with the deionized water. Three different weight ratios of oleic acid to magnetite in the values of 0.443, 0.886, and 1.33 were executed to study the magnetic properties of the OMP.

Preparation of magnetic PMMA microspheres

The magnetic PMMA microspheres were prepared by the modified suspension polymerization. 2 g BPO, 95 mL MMA, 10 mL DVB, and 30 mL Hexane along with different weights of the magnetite gel were mixed to form the organic phase, which was strongly agitated and then subjected to ultrasonication for 3 min to assure the homogeneous dispersion of the OMP. One may note that the OMP with higher weight ratio of oleic acid to magnetite are more hydrophobic and compatible with the organic phase. However, the magnetization of OMP would decrease with the increase of the weight ratio of oleic acid to magnetite, as discussed later in this study. As a result, the OMP with the weight ratio of oleic acid to magnetite of 0.886 is chosen in the synthesis of magnetic PMMA microspheres because of the proper compatibility and magnetization.

Four different weight ratios of OMP to MMA monomers in the values of 0.0526, 0.105, 0.158, and 0.263 were employed in this work. It should be mentioned that the preparation of the organic phase in the condition of higher weight ratio of OMP to MMA is more laborious because of the conspicuous aggregation of OMP. The water phase was consisted of 25 g PVA, 5 mL methylene blue trihydrate, and 1000 mL deionized water. Then the two phases were mixed by the stirring speed at 600 rpm and continuous nitrogen purge in the reactor equipped with four vertical baffles. The temperature of the synthesis solution was increased from 45 to 55°C within 1 h, then maintained at 60°C for 2 h, and finally held at 70 and 80°C for 1 h each. After the synthesis process was completed, the magnetic PMMA microspheres were separated from the solution by a magnet and washed by the deionized water and acetone in turn to remove the attached stabilizer and other impurities on the particle surface.

Characterization of OMP and magnetic PMMA microspheres

The morphology and size of magnetic PMMA microspheres were observed by scanning electron micros-

copy (SEM, JEOL, model JEOL-5610, Tokyo, Japan) and particle size analyzer (PSA, Brookhaven, model 90plus, New York, NY). The porosity of the magnetic PMMA microspheres is estimated by the mercury porosimeter (Micromeritics, model Autopore 9520, Norcross, GA). In addition, the transmission electron microscopy (TEM, JEOL, model JEOL-2000EX, Tokyo, Japan) was utilized to investigate the dispersity of OMP in hexane and the morphology of the microtomed magnetic PMMA microspheres. The crystal structure of the magnetite was analyzed by the wide angle X-ray diffraction (XRD, Rigaku, model DmmaxB, Tokyo, Japan). The magnetite content of OMP and magnetic PMMA microspheres was measured from the curves of thermogravimetric analysis (TGA, DuPont, model SDT2960, Wilmington, DE). The magnetization curves of the dried samples were recorded with the superconducting quantum interference device (SQUID, Quantum Design, model MPMS-XL7, San Diego, CA). Furthermore, the dissolution of the encapsulated OMP of magnetic PMMA microspheres is tested by immersing into the aqueous solution with the pH value of 0.2–12.9 for a week. The pH value of the aqueous solution is adjusted by adding the hydrochloric acid or sodium hydroxide. The concentration of the ferric ions dissolved in the solution is measured by the atomic absorption spectrum (Perkin–Elmer, model 3300, Waltham, MA).

RESULTS AND DISCUSSION

Appearance and particle size of magnetic PMMA microspheres

The morphology of magnetic PMMA microspheres with different weight ratios of OMP to MMA are shown by the SEM micrographs (Fig. 1). It is apparent that the particles are with spherical shape; moreover, the nonporous surface of the particles is demonstrated by using the mercury porosimeter. The particle size of the magnetic PMMA microspheres is in the order of several micrometers and seems to increase with the smaller weight ratio of OMP to MMA. For the precise statistics of the particle size, the histograms of particle size distribution of the samples measured by the PSA are indicated in Figure 2. The size of the magnetic PMMA microspheres is found polydisperse with a small trail. The average diameters of the magnetic PMMA microspheres are 6.8, 3.8, 2.8, and 1.8 μm with the relative

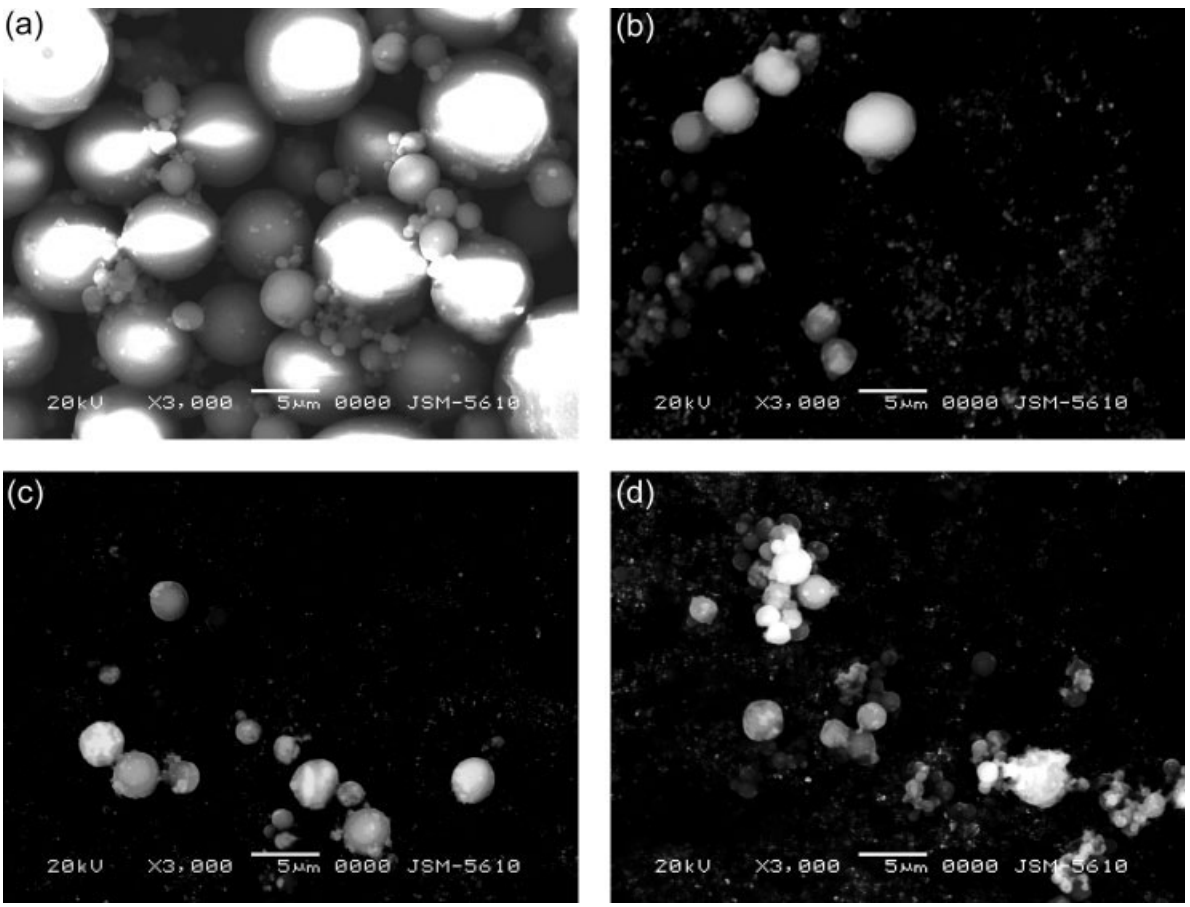

Figure 1 SEM images of magnetic PMMA microspheres (×3000) with various weight ratios of OMP/MMA of (a) 0.0526, (b) 0.105, (c) 0.158, and (d) 0.263.

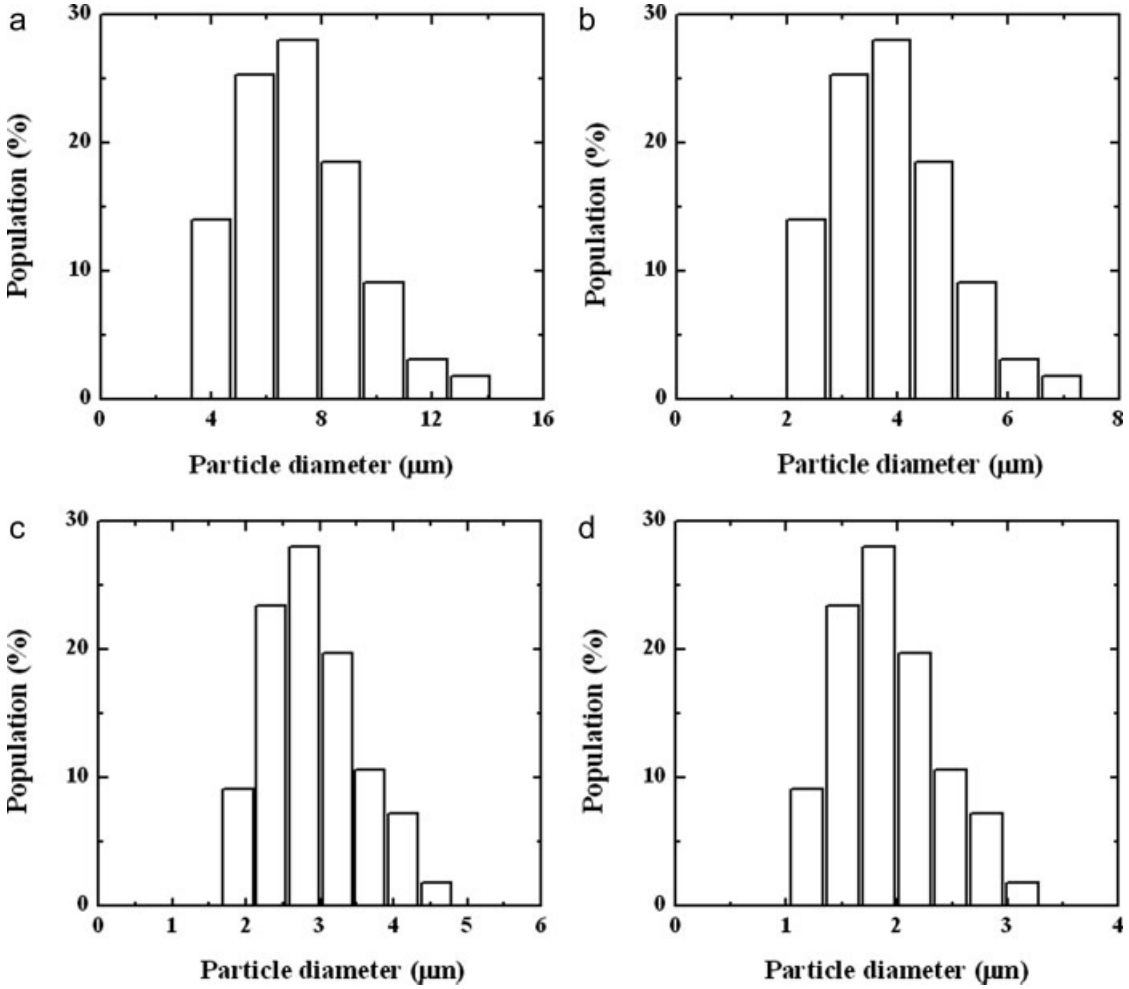

Figure 2 Histograms of particle size distributions of magnetic PMMA microspheres with various weight ratios of OMP/MMA of (a) 0.0526, (b) 0.105, (c) 0.158, and (d) 0.263.

standard deviations of 30.6, 27.6, 22.2, and 24.4% in the cases with the weight ratios of OMP to MMA of 0.0526, 0.105, 0.158, and 0.263, respectively.

Furthermore, the relationship between the particle diameter and the weight ratio of OMP to MMA for the magnetic PMMA microspheres is shown in Figure 3. Obviously, the particle size of the magnetic PMMA microspheres significantly decreases with the higher weight ratio of OMP to MMA. It may be due to that the presence of the OMP improves the stabilization of the modified suspension polymerization system. Certainly, the further investigation would be helpful to explain the phenomenon. In addition, the nonmagnetic PMMA microspheres with the larger particle diameter of 8.4 μm and relative standard deviation of 30.5% are also obtained as a control group. Compared with the magnetic polystyrene[14] and nonmagnetic PMMA[25] microspheres by the suspension polymerization with the particle diameters of 100–300 and 150–370 μm, respectively, the particle

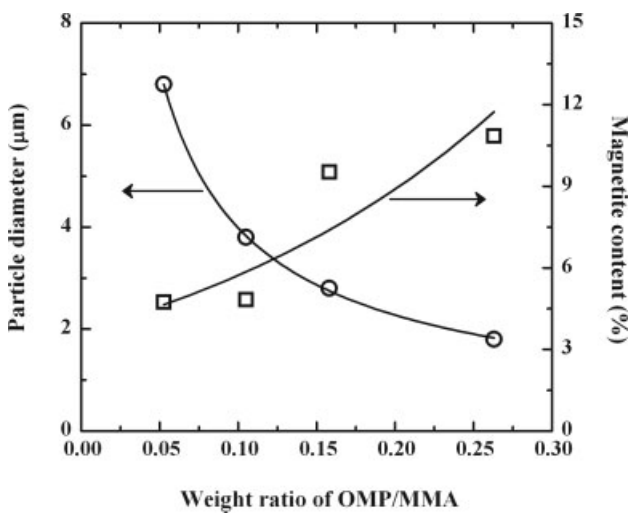

Figure 3 Variations of particles diameter and magnetite content of magnetic PMMA microspheres with weight ratio of OMP/MMA. (○), particle diameter; (□), magnetite content.

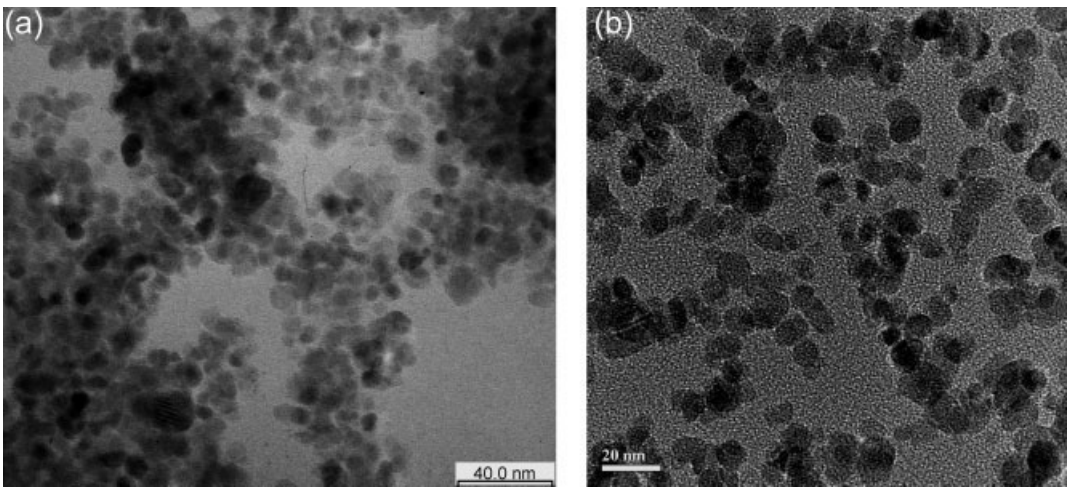

Figure 4 TEM images of OMP and microtomed magnetic PMMA microspheres (dark regions represent the OMP). (a) OMP in hexane (×250 K) and (b) Microtomed magnetic PMMA microspheres with weight ratio of OMP/MMA of 0.158 (×100 K).

size of the PMMA microspheres prepared by the modified suspension polymerization in this work is smaller and with narrower size distribution.

Characterization of OMP and magnetic PMMA microspheres

As for the magnetite particles, the dispersity of the OMP in hexane and the morphology of the microtomed magnetic PMMA microspheres were observed by TEM as shown in Figure 4. It is seen that the nano-sized OMP would apparently aggregate in hexane [Fig. 4(a)]. On the other hand, the distribution of the magnetite nanoparticles encapsulated inside the PMMA microspheres is comparatively uniform. The shape of the OMP is close to a sphere with the particle diameter of about 8 nm, which is consistent with the observations of Ma et al.[17,20] and Zheng et al.[24] To confirm the structure of the synthesized magnetite particles, the XRD patterns of the dried OMP and magnetic PMMA microspheres are illustrated in Figure 5(a,b). Compared with the standard XRD pattern of the crystalline Fe_3O_4 as shown in Figure 5(c), from Joint Committee on Powder Diffraction Standards, the peaks of the two samples match the five diffraction peaks at (220), (311), (400), (511), and (440). The results demonstrate that the PMMA microspheres contain the expected component of the crystalline magnetite.

The magnetite contents of the dehydrated OMP and magnetic PMMA microspheres were measured through the TGA runs in the condition of air atmosphere at the heating rate of 20°C/min. Figure 6 illustrates the TGA curves, depicting the variations of the residual masses of the samples with temperature. The organic materials and magnetite of the samples are completely burned to generate gas products and converted into iron oxides at the elevated temperature (say higher than 500°C), respectively.[24,26] The magnetite amounts of the samples can be estimated from the residual mass percentages. In Figure 6(a), it shows that the oleic acid would completely decompose when the temperature reaches about 470°C. The TGA curve of the magnetite shows the slight

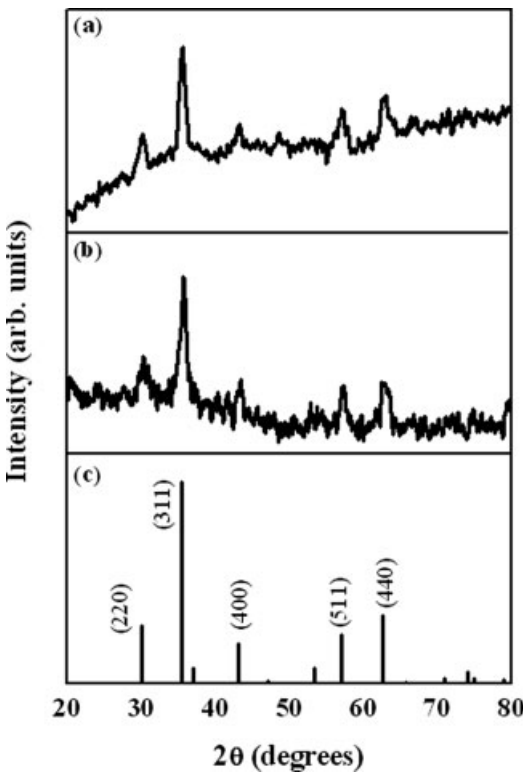

Figure 5 XRD patterns of OMP and magnetic PMMA microspheres. (a) OMP. (b) Magnetic PMMA microspheres with weight ratio of OMP/MMA of 0.158. (c) Standard XRD pattern of Fe_3O_4.

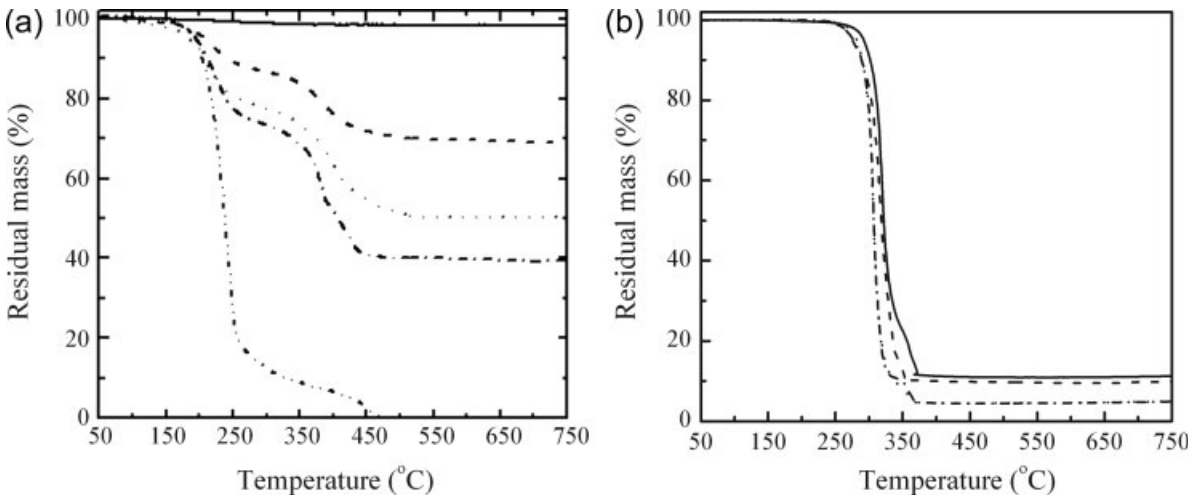

Figure 6 TGA curves of OMP and magnetic PMMA microspheres. (a) OMP with various weight ratios of oleic acid/magnetite of 0.443 (– – –), 0.886 (. . .), and 1.33 (– · –). ——: magnetite; – ·· –: oleic acid. (b) Magnetic PMMA microspheres with various weight ratios of OMP/MMA of 0.0526 (– · –), 0.105 (. . .), 0.158 (– – –), and 0.263 (——).

decrease of 1.59% in weight that may be caused from the impurities.[27] The weight of the OMP starts to lose from 180°C and continuously decreases with temperature. Accordingly, the magnetite contents of the OMP are measured as 66.7, 48.8, and 38.0 wt % for the cases with the weight ratios of oleic acid to magnetite of 0.443, 0.886, and 1.33, respectively.

On the other hand, the magnetic PMMA microspheres remarkably degrade from 270°C and reach the final values of the residual mass when the temperature is raised above 400°C [Fig. 6(b)]. The magnetic PMMA microspheres with higher weight ratio of OMP to MMA would have the higher percentage of the residual mass. The corresponding magnetite contents of the magnetic PMMA microspheres can be measured as 4.74, 4.82, 9.52, and 10.85 wt % for the cases with the weight ratios of OMP to MMA of 0.0526, 0.105, 0.158, and 0.263, respectively. Note that the actual magnetite content of the PMMA particles is greater than the value calculated from the applied weight ratio of OMP to MMA. It is because that the MMA with the solubility of 15 g/L (20°C) would partially dissolve in the water phase. Thus some nonmagnetic PMMA particles are generated simultaneously.

The yields of the magnetic PMMA microspheres are 28.0, 40.3, 43.1, and 79.6% for the cases with the weight ratios of OMP to MMA of 0.0526, 0.105, 0.158, and 0.263, respectively. The yield is defined as the weight ratio of the obtained magnetic PMMA microspheres to the employed materials including MMA, OMP, and DVB. Further, the magnetite con-

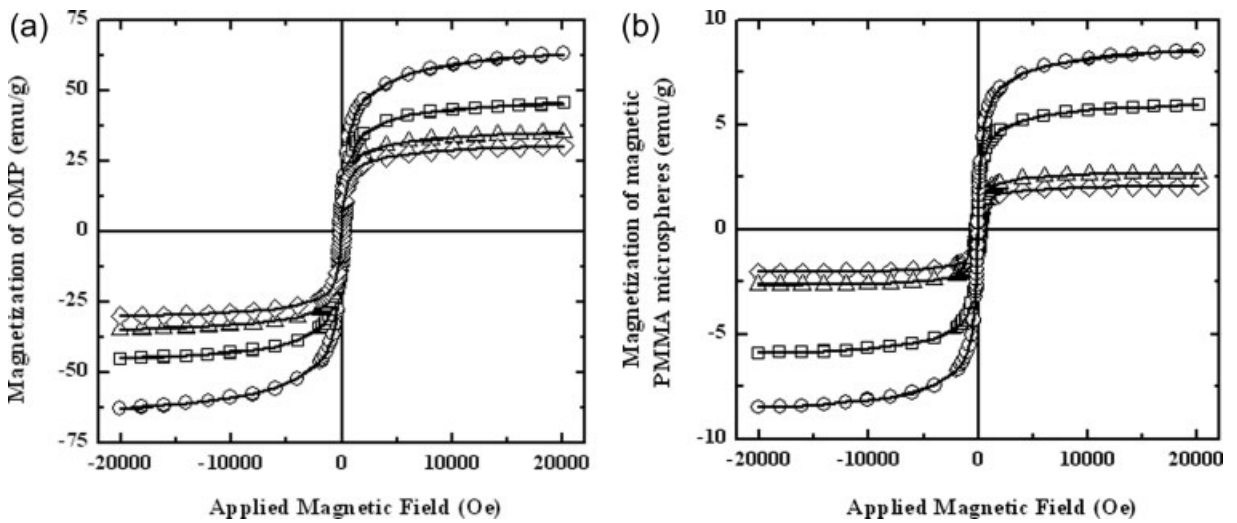

Figure 7 Magnetization curves of OMP and magnetic PMMA microspheres measured by SQUID. (a) OMP with various weight ratios of oleic acid/magnetite of 0.443 (□), 0.886 (△), and 1.33 (◇). ○: magnetite. (b) Magnetic PMMA microspheres with various weight ratios of OMP/MMA of 0.0526 (◇), 0.105 (△), 0.158 (□), and 0.263 (○).

TABLE I
Magnetic Properties of OMP and Magnetic PMMA Microspheres

Samples		Ms (emu/g)	Mr (emu/g)	Mr/Ms (−)	Hc (Oe)
Magnetite		63.0	1.14	0.0181	10.7
	0.443[a]	45.3	0.925	0.0204	11.1
OMP	0.886[a]	35.0	1.30	0.0371	10.6
	1.33[a]	30.2	1.31	0.0433	12.1
Magnetic PMMA	0.0526[b]	2.04	0.089	0.0436	12.4
microspheres	0.105[b]	2.66	0.117	0.0440	12.0
	0.158[b]	5.92	0.253	0.0427	12.7
	0.263[b]	8.51	0.336	0.0395	12.0

[a] Weight ratio of oleic acid to magnetite in preparation of OMP.
[b] Weight ratio of OMP to MMA in preparation of magnetic PMMA microspheres.

tent of the magnetic PMMA microspheres calculated from the yields has the range of 6.56–11.7 wt% close to the measured values (4.74–10.85 wt%). As shown in Figure 3, the magnetite content of the magnetic PMMA microspheres increases with the higher weight ratio of OMP to MMA, indicating the exponential relationship.

In addition, the magnetic properties of the magnetite, OMP and magnetic PMMA microspheres were characterized by a SQUID magnetometer at the room temperature as shown in Figure 7. The magnetization of the samples would approach the saturation values when the applied magnetic field increases to 14000 Oe. All the magnetization curves show the typical superparamagnetic behavior without the hysteresis loop. Furthermore, the values of the saturation magnetization (Ms), residual magnetization (Mr) per gram, remanence/saturation magnetization ratio (Mr/Ms) and coercivity (Hc) of the samples are listed in Table I. It is obvious that the magnetite has the greatest Ms value of 63.0 emu/g. The Ms of OMP and magnetic PMMA microspheres would significantly decrease and increase with the higher weight ratios of oleic acid to magnetite and OMP to MMA, respectively, from the variation of the magnetite content. The superparamagnetic properties of the magnetite, OMP and magnetic PMMA microspheres are also reflected in the small Mr/Ms and Hc values (Table I).

For the further investigation, the variation of the Ms with the magnetite content for the magnetite, OMP and magnetic PMMA microspheres is depicted in Figure 8. The Ms value is approximately proportional to the magnetite content within the experimental range. It implies that the Ms of the polymer microspheres is related to the amount of the encapsulated magnetite per unit mass. One may address that the Ms value of the prepared magnetic PMMA microspheres is in the same order as those of the magnetic poly(methyl methacrylate-DVB-glycidyl methacrylate) and poly(styrene-DVB-glycidyl methacrylate) microspheres by the modified suspension polymerization of about 7.3 emu/g[18,28] as well as the magnetic polystyrene microspheres by the suspension polymerization of 3.6 emu/g.[14] Moreover, the dissolution percentage of the encapsulated OMP of the magnetic PMMA microspheres carried out at different pH values is shown in Figure 9. It is found

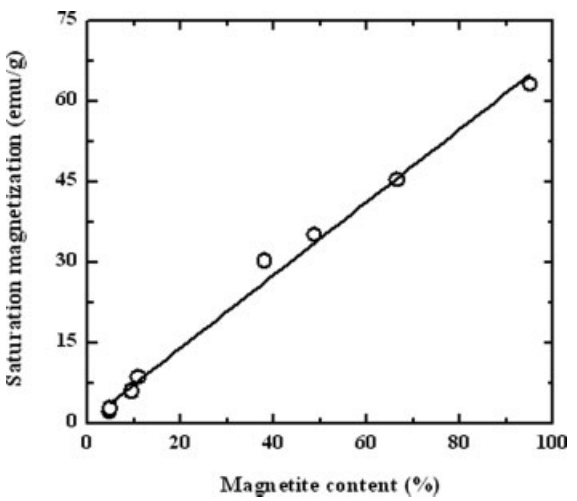

Figure 8 Variation of Ms with magnetite content for OMP and magnetic PMMA microspheres.

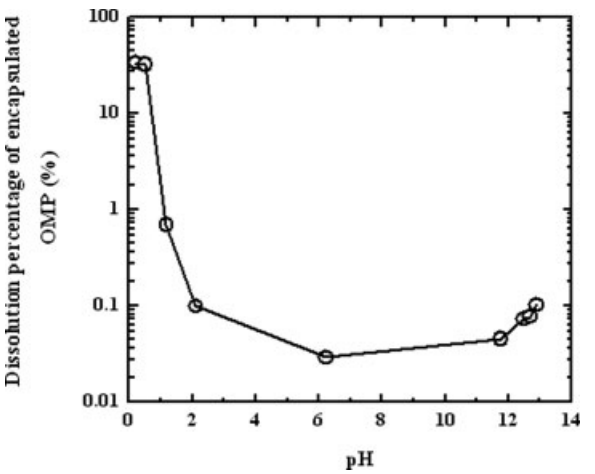

Figure 9 Dissolution percentage of encapsulated OMP of magnetic PMMA microspheres with pH. Magnetic PMMA microspheres with weight ratio of OMP/MMA of 0.158.

that the magnetic PMMA microspheres have good stability in the pH region of 2.1–12.9, while the dissolution percentage of the encapsulated OMP is less than 0.1%. However, the dissolution of the encapsulated OMP becomes remarkable when the immersing solution is more acid. As a result, the study can provide the useful information for the preparation of polydisperse and magnetic polymer microspheres by the modified suspension polymerization.

CONCLUSION

The magnetic PMMA microspheres were successfully prepared by the modified suspension polymerization with the various weight ratios of OMP to MMA. The magnetic PMMA microspheres with the polydispersity have the average particle diameter of 1.8–6.8 μm, decreasing with the higher weight ratio of OMP to MMA. The encapsulated OMP of 8 nm diameter contribute the magnetite content of 4.74–10.85 wt % for the PMMA microspheres. The OMP and magnetic PMMA microspheres are superparamagnetic with the saturation magnetization of 30.2–45.3 and 2.04–8.51 emu/g, respectively, which is proportional to the magnetite content. The magnetic PMMA microspheres show the good stability in the aqueous solution in the pH region of 2.1–12.9. Note that the magnetite content and yield of the magnetic PMMA microspheres increase with the higher weight ratio of OMP to MMA. As a result, the weight ratio of OMP to monomers plays an important role in controlling the properties of the magnetic polymer microspheres by the modified suspension polymerization.

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