

PREPARATION OF COMPOSITE MAGNETIC MICROSPHERES BY REACTIVE BLENDING*

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Abstract A novel method for preparation of polymer-based magnetic microspheres was proposed by utilizing melt reactive blending, which was based on selective location of Fe_3O_4 nanoparticles in PA6 domains of polystyrene (PS)/polyamide 6 (PA6) immiscible blends. The morphology of PA6/ Fe_3O_4 composite magnetic microspheres was studied by scanning electronic microscopy (SEM). The composite magnetic microspheres were spherical with a diameter range of 0.5–8 μm ; the diameter was sharply decreased with a very narrow distribution by adding terminal maleic anhydride functionalized polystyrenes (FPS) for reactive blending. Transmission electron microscopy (TEM) and thermogravimetry analysis (TGA) results showed that most of Fe_3O_4 was located in the PA6 microspheres. Magnetization data revealed the magnetite content of PA6/ Fe_3O_4 microspheres was about 32 wt% and the saturation magnetization could be up to 17.2 Am^2/kg .

Keywords: Composite magnetic microspheres; Fe_3O_4 ; Reactive blending; Selective location.

INTRODUCTION

Recently, polymer-based magnetic composite microspheres have attracted increasing attention in a wide range of industrial fields, such as coating for microwave absorption, cell labeling, cell separation, enzyme immunoassay and drug targeting, *etc*^[1–6]. Generally, the composite magnetic microspheres were prepared by either *in situ*^[7, 8] or *ex-situ* method^[9–14]. As for the first method, inorganic particles are directly precipitated into the inside of the polymer micelle or sphere; however it is restricted to the particles which only can be synthesized or formed by decomposition of corresponding compounds, and the magnetic particles are always prone to leak out outside of the polymer matrix that lead to low magnetic content. Different from the *in situ* method, magnetic particles are prefabricated first in the *ex-situ* method, and then combined with the polymer almost by a polymerization process, in which magnetic particles can be encapsulated based on two different principles. When the polymerization site is at the monomer droplets, which is classified as suspension polymerization^[9] and mini-emulsion polymerization^[10], magnetic particles are embedded in polymer micelles or spheres during the polymerization. The other category of polymerization is initiated in water phase or micelle, such as emulsion polymerization^[11], soap-free polymerization^[12], deposition polymerization^[13] and dispersion polymerization^[14]. In such kind of polymerization, the inorganic particles are dispersed into water phase and monomer, and the polymerization occurs around the particles. Although the *ex-situ* method seems to be more feasible than the *in situ* method, it still has many disadvantages. First, the complexity of the particle nucleation mechanism and the difficulties in controlling the dispersion stability of inorganic particles result in the major obstacles in

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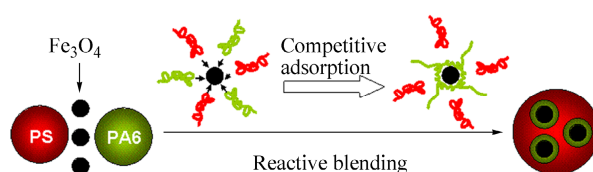
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preparing magnetic polymer microspheres with a high encapsulation efficiency and high magnetic response. According to previous reports, magnetite contents of these microspheres are relatively low (< 30 wt%)^[15]. Secondly, the *ex-situ* method is limited by the fact that many polymers can't be easily synthesized by radical polymerization. Finally, if the particles are too hydrophilic or too hydrophobic, they will segregate into the water or oil phases most often resulting in poor stability while it is difficult to design a suitable dispersant.

It is noticed that when nanoparticles are compounded with immiscible binary polymer blends, they always tend to selectively locate in one of the two phases^[16–19]. The uneven distribution depends on the balance of interfacial energies which is related to the interaction between the polymer chains and the filler surface^[20]. Our strategy to fabricate composite magnetic microspheres in this paper is by reactive blending Fe_3O_4 nanoparticles with two polymers, PA6 and PS. Due to the selective location of Fe_3O_4 in the more polar PA6 domains, the PA6-based composite magnetic microspheres could be obtained by selective extraction of PS. Moreover, the method to control the diameter of microspheres is the use of compatibilizer to tailor morphology. The sketch of the strategy is shown in Scheme 1.



Scheme 1 Strategy of preparing composite magnetic microspheres by reactive blending

EXPERIMENTAL

Raw Materials

PA6 ($M_n = 25000$) was kindly provided by Toray Industries, Inc. PS ($M_n = 100000$) was purchased from Shanghai SECCO Petrochemical Co. A terminal maleic anhydride functionalized polystyrenes (FPS, $M_n = 71000$) was used as a reactive compatibilizer for the PS/PA6 blends. Fe_3O_4 with an average diameter of 20 nm was provided by Shanghai Jingchun Co. Figure 1 shows the morphology of Fe_3O_4 .

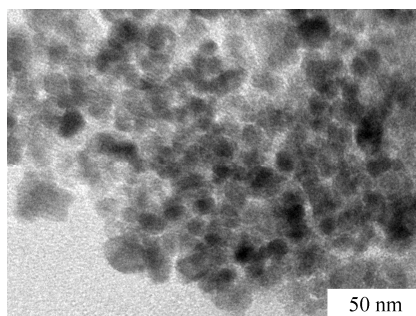


Fig. 1 TEM image of Fe_3O_4

Preparation of Composite Magnetic Microspheres

The blends were prepared in a Haake mixer (Rheocord 300P+Rheomin 600P, Thermo Electron Corp.) at 240°C under a rotational speed of 100 r/min. Before processing, all the raw materials were dried overnight at 80°C in a vacuum oven. The mixing procedure was as follows: PS and Fe_3O_4 were introduced into Haake for 4 min mixing, and then PA6 or PA6 and FPS mixture was added for another 6 min mixing. The mixtures were compressed into a 1 mm-thick sheet at 260°C for 15 min. Then, the PA6/ Fe_3O_4 composite magnetic microspheres were finally obtained by soxhlet extraction of the PS matrix in methylbenzene for 2 h. It should be pointed out that the sheet sample fell apart when it was immersed in methylbenzene, and the extracted microspheres were deposited in methylbenzene.

Characterization of Composite Magnetic Microspheres

The morphology of composite magnetic microspheres was investigated by scanning electron microscopy (SEM, JSM-6360LV, JEOL). In order to observe the morphology of Fe_3O_4 nanoparticles and the location of Fe_3O_4 in PA6 domains, transmission electron microscopy (TEM, JEM-2100, JEOL) was carried out for Fe_3O_4 particles and the blends at an accelerating voltage of 100 kV. Samples were cut into an ultra-thin section, approximately 80 nm in thickness, by using an ultra-microtome (Ultracut N, Reichert).

The size and size distribution of the composite magnetic microspheres were also determined from SEM micrographs by using Scion image software. Three to four micrographs were selected and each contains approximately 100–150 microspheres. The number-average (D_n) of mean particle size was calculated: ($D_n = \sum N_i D_i / \sum N_i$, where N_i is the number of particles having the diameter of D_i).

Thermogravimetry analysis (TGA) was performed for composite magnetic microspheres to determine the content of Fe_3O_4 in composite microspheres. The degree of magnetism of the composite magnetic microspheres was evaluated by the vibrating-sample magnetometer (VSM 7407, America Lake Shore Co.), calibrated against a cylindrical nickel standard at room temperature. A certain amount of magnetic composite microspheres were balanced and placed in the magnetometer. The degree of magnetism of the composite microspheres was then determined by applying an increasing magnetic field (0–200 A/m) at room temperature over the microspheres and the results were used to calculate the magnetic quality of the microspheres. Prior to these tests, the PA6-based microspheres were purified by a centrifugal separator to remove Fe_3O_4 particles separated from the PA6 domains.

RESULTS AND DISCUSSION

Figure 2(a) is the SEM image of the PS/PA6/ Fe_3O_4 blends (90/10/5, weight ratio). It can be observed that PS/PA6 form sea-island structure where PA6 is the dispersed domain. Figure 2(b) displays the composite magnetic microspheres extracted from PS/PA6/ Fe_3O_4 blends (90/10/5, weight ratio). As shown in Fig. 2(b), it can be seen that the composite magnetic microspheres are well shaped. Figure 2(c) is the TEM image of the PS/PA6/ Fe_3O_4 blends (90/10/5, weight ratio). From Fig. 2(c), one can find that most of Fe_3O_4 nanoparticles are selectively located in PA6 domain but few are aggregated at the PS/PA6 interface. Although hydrophilic Fe_3O_4 nanoparticles are preferred to locate in the more polar PA6 domain, the mixing sequence may drive some particles to the interface by transferring themselves from PS to PA6.

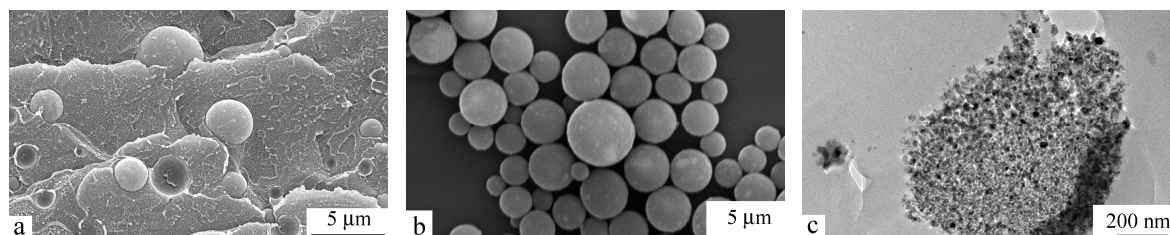


Fig. 2 Electron microscopy images: (a) SEM image of PS/PA6/ Fe_3O_4 (90/10/5) blend, (b) SEM image of the extracted magnetic composite microspheres and (c) TEM image of ultra-thin section of PS/PA6/ Fe_3O_4 blend (90/10/5)

In order to decrease the size and size distribution of PA6/ Fe_3O_4 magnetic microspheres, FPS was added for reactive blending to improve the compatibility of PA6 and PS. Figures 3(a) and 3(b) are the SEM images of the composite magnetic microspheres extracted from PS/PA6/ Fe_3O_4 /FPS blends with the weight ratio of 70/30/15/0 and 70/30/15/2 respectively. When 2 phr FPS was added, the mean diameter of composite magnetic microspheres decreases from 7.7 μm to 1.7 μm and the distribution becomes more uniform, as can be seen from Figs. 3(a) and 3(b). In order to further verify the location of Fe_3O_4 in PA6 domain, TGA was carried out for the composite magnetic microspheres extracted from PS/PA6/ Fe_3O_4 /FPS blends (70/30/15/2) (Fig. 4). As shown in Fig. 4, when the temperature is about 450°C, the PA6 is completely decomposed and the residual weight is

about 30%. The value is well correlated to the concentration of Fe_3O_4 in PA6, indicating that most of Fe_3O_4 is preferentially dispersed in PA6 domains. However, small amount of Fe_3O_4 nanoparticles is dispersed at the surface of PA6 microspheres (Fig. 3b). This may be attributed to the transfer of Fe_3O_4 nanoparticles from PS to PA6 or the reaction between anhydride of FPS and the hydroxyl groups on the Fe_3O_4 surface which results in the “pull-out” of Fe_3O_4 from PA6 domain^[21].

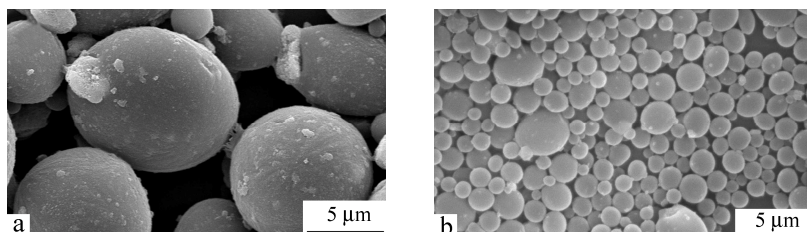


Fig. 3 SEM images of the magnetic composite microspheres extracted from PS/PA6/ Fe_3O_4 /FPS blends with the weight ratio of (a) 70/30/15/0 and (b) 70/30/15/2

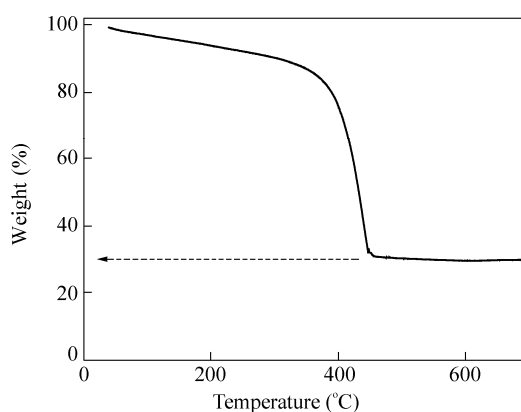


Fig. 4 TGA curve of PA6/ Fe_3O_4 microspheres extracted from PS/PA6/ Fe_3O_4 /FPS (70/30/15/2) blends

The influence of PA6 content on the number-average diameters of composite magnetic microspheres is shown in Fig. 5. Note that the weight ratio of PA6 and Fe_3O_4 was set at 2:1 for all of the mixtures. It can be seen that whether an addition of FPS or not, the diameter of composite magnetic microspheres increases with increasing PA6 content. For mixtures without FPS, the mean diameter of the magnetic microspheres extracted from PS/PA6/ Fe_3O_4 blends with a composition of 90/10/5, 80/20/10 and 70/30/15 is 2.2 μm , 2.6 μm and 7.7 μm , respectively. This is because collision frequency of the dispersed PA6 drops increases significantly with the PA6 content increasing during the molten compounding, and this leads to a sharply increased diameter. Experimental results showed that further increase of the PA6 content results in a remark change in morphology of PS/PA6/ Fe_3O_4 blends from the matrix-dispersed structure to a co-continuous type, which means the PA6 domains become continuous.

Adding 2 wt% FPS can not only decrease the diameter of composite magnetic microspheres (from 7.7 μm to about 1.0 μm for the blends with 30 wt% PA6), but also broaden the maximum PA6 content for maintaining the matrix-dispersed type morphology from 30 wt% to more than 50 wt% (Fig. 5a). This is because FPS acts as a reactive compatibilizer which significantly reduces the interfacial energy between PS and PA6. The compatibilization mechanism was due to the reaction of the maleic anhydride group with the terminal amine group of the PA6 chains *in situ*; this led to the formation of PS-*b*-PA6 copolymers at the PS/PA6 interface, as shown in Scheme 2.

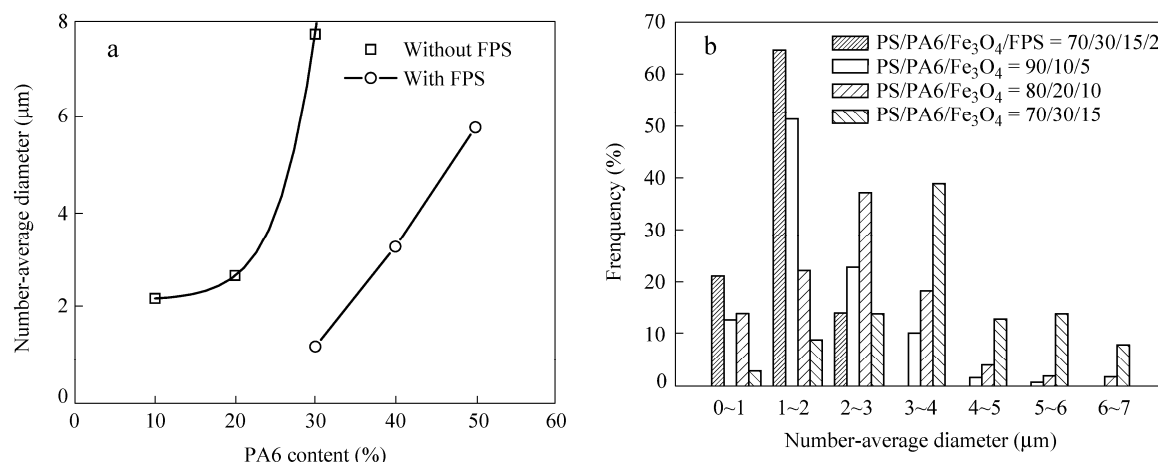
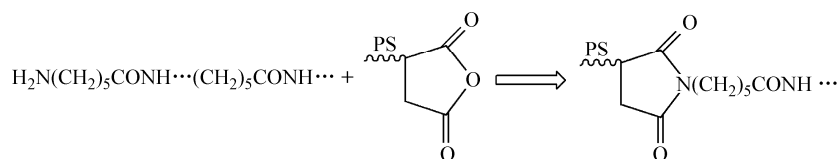


Fig. 5 Influence of PA6 content on (a) number-average of magnetic composite microspheres and (b) the size distribution of magnetic composite microspheres for PS/PA6/Fe₃O₄/FPS blends with constant weight ratio of PA6 and Fe₃O₄ set at 2:1

Figure 5(b) shows the size distribution of composite magnetic microspheres in various PS/PA6/Fe₃O₄ blends. It can be seen that the increase of PA6 content results in a broader distribution of the composite microspheres. A quite narrow distribution of the magnetic composite microspheres can be obtained by adding of 2 wt% FPS.



Scheme 2 Compatibilization mechanism: reaction between the amine end group of PA6 and the anhydride group of FPS leading to the formation of imide linkages

The magnetization curves of Fe₃O₄ and PA6/Fe₃O₄ microspheres extracted from PS/PA6/Fe₃O₄/FPS (70/30/15/2, weight ratio) are shown in Fig. 6. As shown in Fig. 6, the saturation magnetization of PA6/Fe₃O₄ microsphere is about 17.2 Am²/kg. Compared to the value of Fe₃O₄ nanoparticles (52.7 Am²/kg), it is sure that

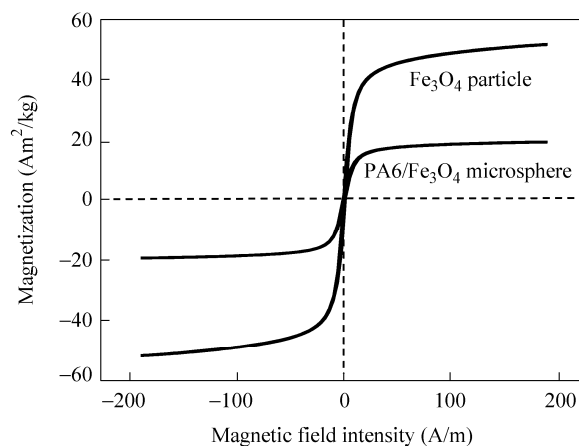


Fig. 6 Magnetic curves of Fe₃O₄ and PA6/Fe₃O₄ microspheres

the magnetic content of the microspheres is about 32 wt%, which was a slight lower than the actual content of Fe_3O_4 in the PA6 domain (33.3%). That may be attributed to that few Fe_3O_4 located at the surface of PA6 domain is separated from the microspheres by centrifugation. The magnetic content can be up to 32%.

CONCLUSIONS

In this study, we proposed a novel method based on the selective location of Fe_3O_4 particles in PA6 domains of immiscible PS/PA6 blends to prepare composite magnetic microspheres by reactive blending. The obtained microspheres are well shaped and most of Fe_3O_4 was dispersed in the interior of the microspheres. Composite magnetic microspheres were characterized based on morphology, size/size distribution and magnetic properties. The results showed the magnetic composite microspheres can be produced in the size range of 0.5–8.0 μm . Adding FPS as compatibilizer can reduce the diameter of microspheres while achieve a more uniform distribution. The weight content of Fe_3O_4 in microspheres can be up to 32% and the degree of magnetism of the magnetic composite microspheres is 17.2 Am^2/kg .

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