

Polystyrene coating of Fe₃O₄ particles using dispersion polymerization

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Abstract

Polystyrene coating of Fe₃O₄ particles by dispersion polymerization was studied. The coating process was carried out in methanol with 2,2'-azobisisobutyronitrile as initiator, poly(*N*-vinylpyrrolidone) as stabilizer, and divinyl benzene as a cross-linking reagent. The cross-linking reagent played an important role in the dispersion polymerization. A continuous and dense polymer layer coating was formed on the Fe₃O₄ particles in the presence of the cross-linking reagent. The coating process was studied by sampling at fixed time intervals and the particle morphology of the samples was analyzed by TEM and the coating quantity by TG. In the presence of the cross-linking reagent, the layer coating on the Fe₃O₄ particles was formed by the adsorption of polymer sols that joined together to form a thick layer coating.

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1. Introduction

Inorganic core/organic shell hybrid composite particles with diameters of 0.2–10 μm have received interest in a wide range of industrial fields, e.g. medical diagnosis, electronics, toners, and paint application, because of their functional properties, high dispersibility and stability after a certain thickness of polymer coating [1]. Fe₃O₄ (iron black) particles, which have magnetic properties and a black color and are used in toner preparation, is a typical example. Iron black particles are naturally hydrophilic due to plentiful hydroxyls on the particle surface. The dispersion of iron black particles in an organic media is difficult. Therefore, the surface coating or modification of iron black particles is very important in many applications.

Several methods have been developed for the organic modification of particles, such as ball milling [2], mini-emulsion polymerization [3], two-step emulsion polymerization [4], *in situ* polymerization [5], surface-initiated graft polymerization [6], dispersion polymerization [7], etc. Dispersion polymerization is a very attractive method owing to the simplicity of the single-step process. A typical example is the dispersion polymerization of styrene in hydrocarbons, alcohols and various alcohol–ether or alcohol–water mixtures [7]. Many literature

reports have shown that inorganic oxide particles, such as titanium dioxide [1], silica nano-particles [8], etc., can be coated with a polymer shell by dispersion polymerization but there has been no report on the effect of a cross-linking reagent and the mechanism of the polymer coating in the presence of a cross-linking reagent in dispersion polymerization.

In the present study, the effect of a cross-linking reagent on coating using dispersion polymerization was studied. The coating process was analyzed by taking samples at different coating times and studying the morphology of the coated particles with TEM and SEM.

2. Experimental

2.1. Reagents

The purity and sources of the chemicals were: styrene (St, 99% purity, Tianjin Northern Tianyi Chemical Reagent Factory, China), divinylbenzene (DVB, 99% purity, Shanghai Chemical Reagent Factory, China), 2,2'-azobisisobutyronitrile (AIBN, Shanghai Fourth Reagent Factory, China), methanol (99% purity, Beijing Modern Eastern Fine Chemical Reagent Co., China), and polyvinylpyrrolidone (PVP, MW 30,000, chemically pure grade, Beijing Yili Chemicals Reagent Co., China). The iron black pigment particles (Tianjin Copy Technology Institute, China) had an average particle size about 300 nm.

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2.2. Dispersion polymerization

One-hundred twenty milliliters (95.0 g) PVP methanol solution with a concentration of 3.3 wt.% was put in a four-neck-flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet and outlet. Four milliliters (3.6 g) styrene monomer (and 2 ml (1.8 g) DVB) was poured into the 120 ml PVP methanol solution with agitation to form a composite solution. Two grams of iron black particles was added into the solution and dispersed by ultrasonic treatment for 5 min, and then 0.5 g AIBN was added into the suspension. The stirring speed of the agitator was fixed at 450 rpm. The flask was immersed in a water bath at 60 °C and kept under a nitrogen atmosphere. The polymerization was carried out at 60 °C for 8 h. After reaction, the polymerized particles were separated from the suspension by centrifugation at a speed of 4500 rpm for 5 min and washed with methanol five times, and then dried at 60 °C in a vacuum drier.

2.3. Characterization

Particle morphology was examined by a scanning electron microscope (SEM, JSM-6700, JEOL, Japan) and a transmis-

sion electron microscope (TEM, JEOL-2010, JEOL, Japan). Ten milligrams particle samples were used for the TG analysis, performed with a heating rate of 10 °C/min in a nitrogen atmosphere. The measurement temperature was 50–800 °C.

3. Results & discussion

3.1. Particle morphology

TEM and SEM images of the uncoated and coated iron black particles are shown in Fig. 1. The morphology of the uncoated particles was polyhedron with a smooth surface. A continuous and dense polymer layer coating with a certain thickness was formed on the coated particles. Almost all the iron black particles were well coated, as shown in the SEM images in Fig. 1(d).

3.2. Particle coating process

Experiments showed that the particle coating could only be achieved in the presence of the cross-linking reagent DVB. Therefore, the particle coating process of dispersion polymerization with the cross-linking reagent (DVB) was analyzed. Samples were taken at 10 min intervals after the start of the

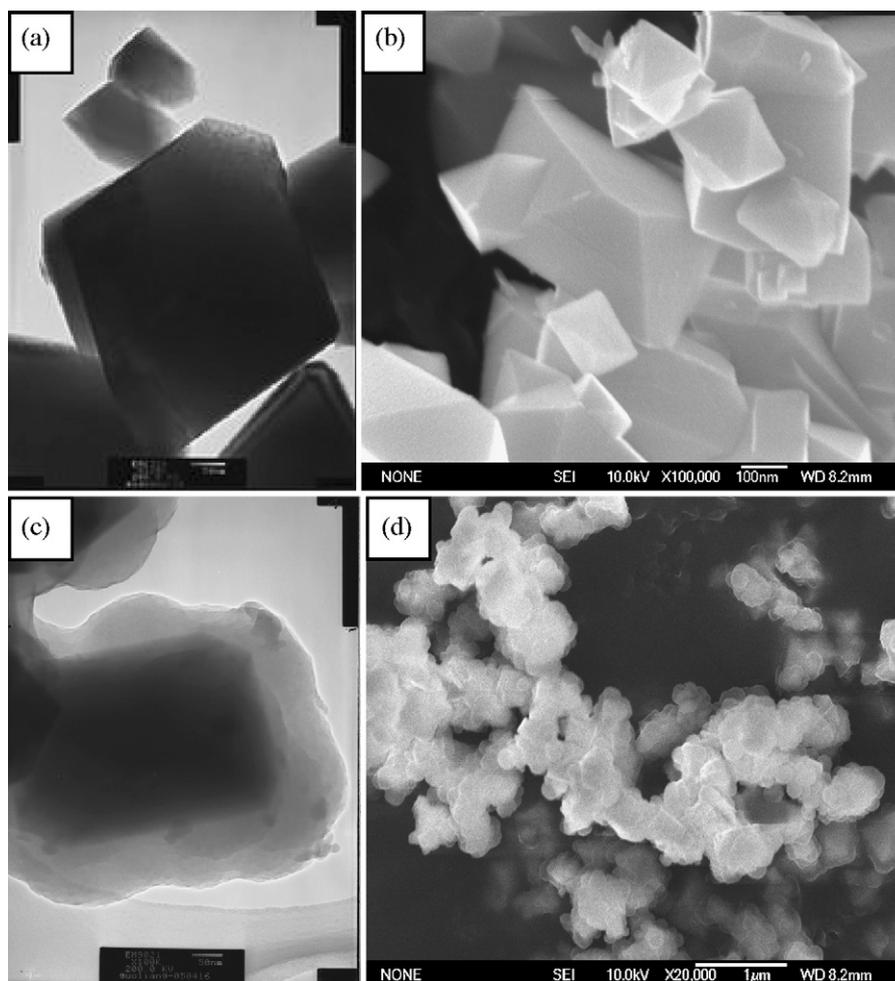


Fig. 1. TEM and SEM images of uncoated IB (a, b) and coated IB (c, d).

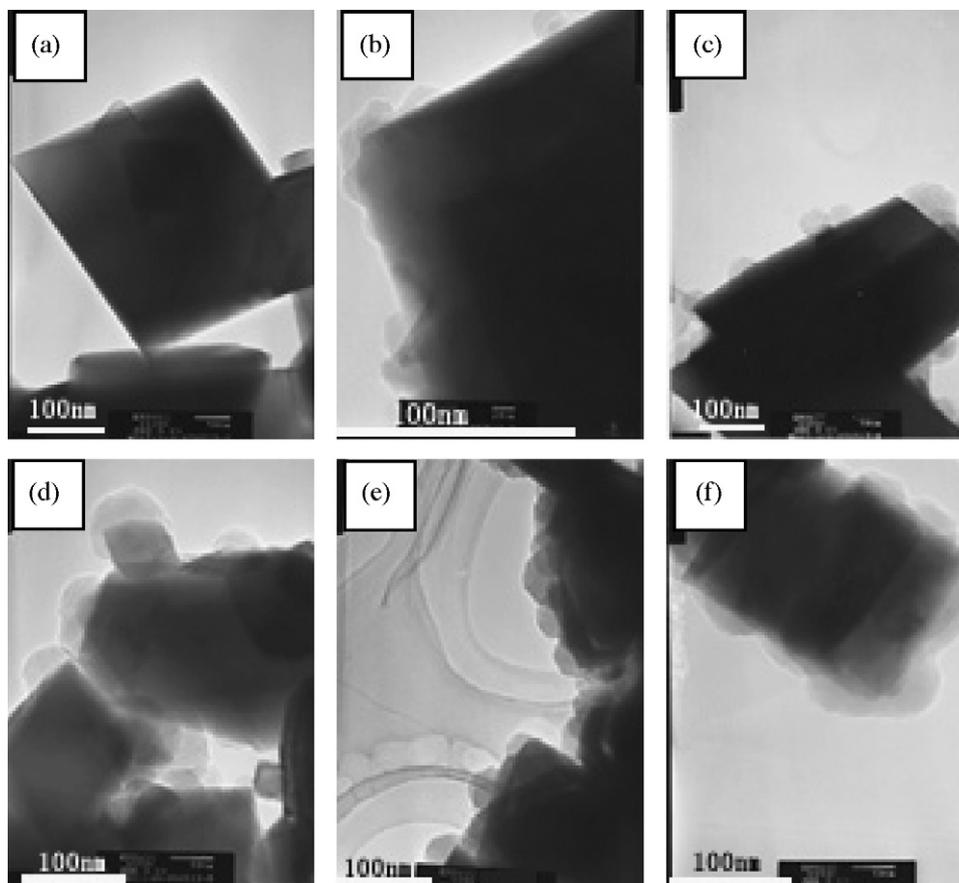


Fig. 2. TEM images of the iron black particles in the coating process in presence of the cross-linking reagent DVB at different reaction times. (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min; (e) 50 min; (f) 60 min.

reaction. The particle morphology of the samples was examined with TEM. The TEM images of the particle samples at different reaction time are shown in Fig. 2.

In the initial 10 min of reaction, there was almost no polymer sol adsorbed on the particle surface, as shown in Fig. 2(a). When the reaction was performed for 20 min, some polymer sols with diameters about 20 nm adsorbed on the particle surface can be seen, as shown in Fig. 2(b). After 30 min reaction, the sol diameters became larger and were about 30 nm, and more sols were

adsorbed on the particle surface, as shown in Fig. 2(c). After 40 min reaction, even more sols were adsorbed on the particle surface and the sol had grown up to 50 nm, as shown in Fig. 2(d). When the reaction time was 50 min and 60 min, the coated layer became thicker, and the layer became more continuous after 60 min coating. After 1 h reaction, the polymer quantity on the particles was about 8.3%. The coating quantity versus reaction time is shown in Fig. 3.

Thereafter, more and more sols of polymer micro-sphere were adsorbed on the particle surface. These sols grew with time and joined together to form a continuous and dense polymer layer on the particle surface. This shows that the particle coating was produced by the adsorption and growth of polymer sols on the surface.

3.3. Effect of the cross-linking reagent

Experiments were carried out in the absence of the cross-linking reagent DVB. TEM and SEM images showed that the iron black particles were not coated with the polymer, as shown in Fig. 4. In these images, it is seen that there was hardly any polymer sol on the iron black particles, even after 8 h coating reaction. Only a few polymer micro-spheres were attached on the surface of iron black particles, and these polymer micro-spheres diameters were about 100 nm. Most of the micro-spheres were stably dispersed in the solution.

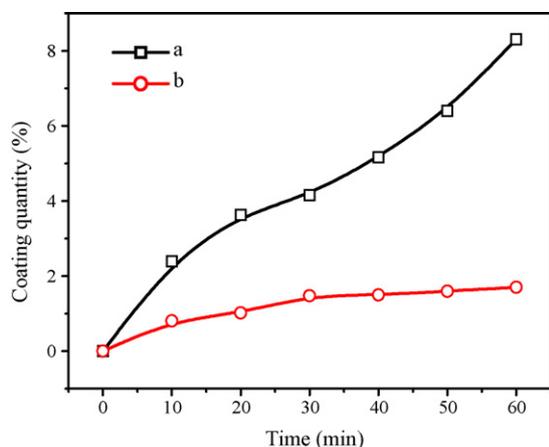


Fig. 3. Particle coating quantity vs. reaction time (a) in the presence of DVB; (b) in the absence of DVB.

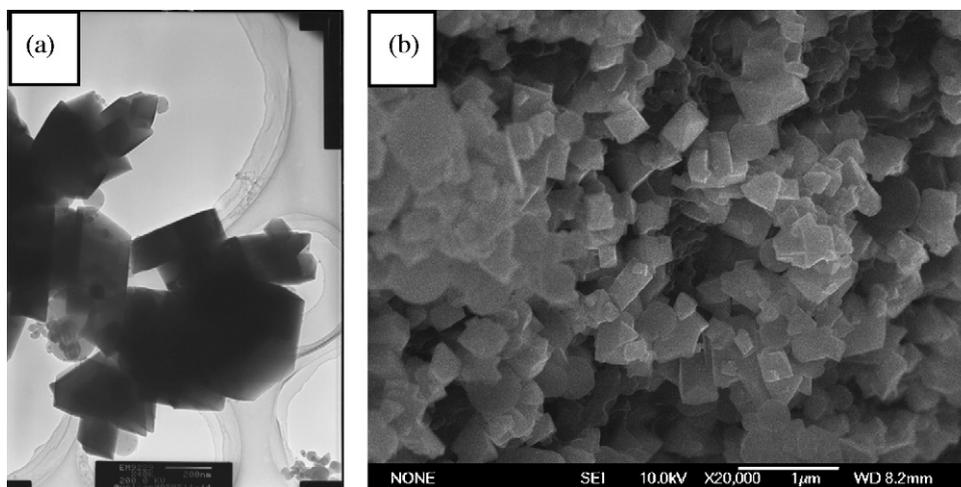


Fig. 4. Images of iron black particle after 8 h reaction in the absence of DVB. (a) TEM, (b) SEM.

Samples in the coating process were also taken out for TG measurement. The coating quantities were very small and hardly changed with reaction time, as shown in Fig. 3. The polymer quantity on the iron black particles surface was less than 1.8% in the absence of cross-linking reagent DVB even after 8 h coating.

3.4. Coating mechanism analysis

Polyvinylpyrrolidone (PVP) is a typical stabilizer in polar solvents in polymerization processes. The carbonyl group in PVP can form a hydrogen bonding with the hydroxyl group on the particle surface and the hydrophobic carbon chains are dispersed in the continuous phase, which enables the particles to be well dispersed [9,10]. In addition, PVP can stabilize the polymer sols, and improve the dispersion of the polymer coated particles due to steric hindrance effect from PVP adsorption on sol/particle surface.

The iron black particles were stably dispersed in methanol in the present of PVP stabilizer. In the absence of the cross-

linking reagent DVB, only homo-polymerization of the styrene through the vinyl groups occurred, the polymer sol was in long chain and was twisted together, forming micro-spheres at large size. The micro-spheres were mainly dispersed in the continuous phase, and were difficult to be adsorbed on the particle surface of iron black, which caused that the iron black particles were not coated with polymer even after 8 h reaction. This process is simply shown in Fig. 5(a).

However, the cross-linking reagent DVB played an important role in the dispersion polymerization. In the presence of DVB, the copolymerization rate of styrene and DVB was increased, and the polymer sols were easily separated out from the continuous phase, forming a high concentration of polymer sols in smaller size in the continuous phase [11]. A large number of polymer sols in steric structure with a small size were apt to be adsorbed on the particle surface. The adsorbed sols on the particle surface promote the continue polymerization of styrene monomer and oligomer. The continuous adsorption and the polymer sol growth led to a dense layer coating. This process is simply shown in Fig. 5(b).

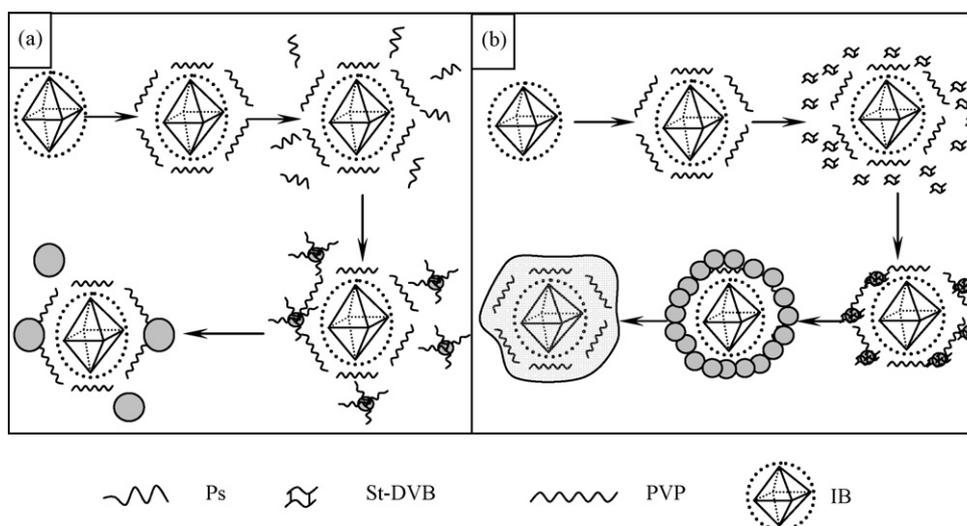


Fig. 5. A sketch of the dispersion polymerization process: (a) in the absence of DVB; (b) in the presence of DVB.

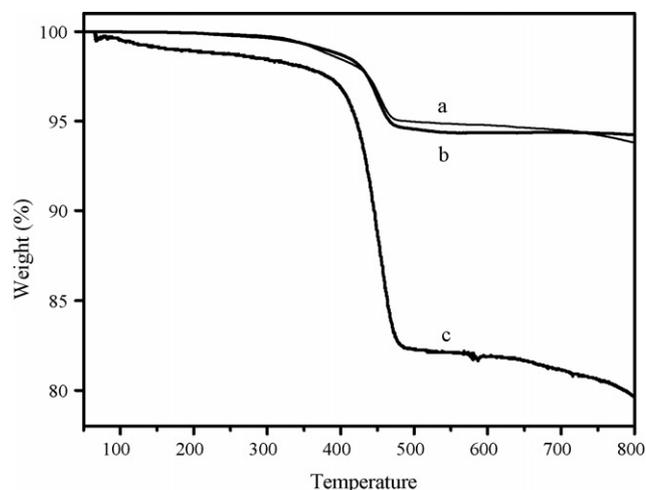


Fig. 6. Coating quantities at different reaction condition St/DVB(ml): (a) 4/2; (b) 6/2; (c) 6/2 (with pre-dispersion).

3.5. Effects of particle pre-dispersion

The effect of the styrene quantity on the coating quantity was investigated. The coating quantities at 4 ml (3.6 g) and 6 ml (5.4 g) styrene with 2 ml DVB were compared. The coating quantities after reaction for 8 h are compared in Fig. 6. It can be seen that the amount of styrene has no effect on the coating quantity because styrene was in excess compared to the coated quantities on the surface of the iron black particles.

The effect of particle pre-dispersion in the monomer was also investigated. Fe_3O_4 particles were first dispersed in the mixture of St and DVB, and treated with an ultrasonic treatment at room temperature for 5 min, and then the suspension was poured into a 3.3 wt.% of the PVP methanol solution and with ultrasonic treatment for 5 min. Then 0.5 g AIBN was added into the reactor. It was found that the quantity of polymer coated on the iron black particles was about 20% through TG measurements, as shown in Fig. 6. The apparent density of the iron black particles decreased from 4.1 g/cm^3 to 2.7 g/cm^3 . It can be inferred that the pre-treatment enhanced adsorption of the monomer and cross linking reagent on the iron black particles. The polymer sol adsorption on the particle surface became easier and the coating quantities became larger.

4. Conclusion

Iron black particles were well coated by dispersion polymerization in the presence of divinyl benzene as the cross-linking

reagent. The cross-linking reagent was necessary in the coating process. A continuous and dense polymer coating layer was achieved. In the absence of the cross-linking reagent, the particles could not be coated, and only a few polymer micro-spheres of about 100 nm were attached on the particle surface. The particle surface was changed from hydrophilic to hydrophobic after coating.

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