

Preparation and Characterization of Carbon Black-Polystyrene Composite Particles by High-Speed Homogenization Assisted Suspension Polymerization

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ABSTRACT: Composite particles of carbon black-polystyrene with controllable size were successfully prepared using high-speed homogenization-assisted suspension polymerization. The carbon black particles were modified by oleic acid to make it more hydrophobic and more compatible with polymers before the encapsulation process. The effects of homogenization speed, homogenization time, agitation speed, pigment concentration, and stabilizer concentration on the properties of complex spheres were investigated in detail. The results of orthog-

onal experiments proved that the stabilizer concentration plays the most important role in controlling the size of complex particles. The particles were also characterized by FTIR and SEM. SEM photographs proved that the complex particles had good spherical forms with smooth surfaces. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3255–3260, 2012

Key words: composite; suspension polymerization; carbon black; stabilizer concentration; orthogonal experiments

INTRODUCTION

It is well known that the aggregates of pigment are much easily formed just because the primary particle size of pigment particles is very small and the interparticular forces are very high. Due to its enormous technological importance,^{1–4} a lot of efforts have been made to avoid the pigment particles aggregating, such as using surfactants,^{2,5} milling the particles in the solid state with appropriate polymers including thermoset or thermoplastic polymers,⁶ or encapsulating the particles by polymerization methods.^{4,7–17} Although the pigment particles can disperse well by surfactants modification method, the surfactants can easily falling off from the particles limiting the application of pigment particles. Unfortunately, the milling method needs lots of time and energy, and particles prepared by milling method have irregular structure and different pig-

ment loading, which limited their application in high-quality toners. Compared with the previous two methods, the polymerization method has the following merits: First, the polymer used to encapsulate the pigment particles is cheap, second, the pigment can be well protected in the core-shell structure, pigment in the core while polymers in the shell, third, the obtained pigment-polymer particles can be directly used in the application.¹⁷

In polymerization methods, to protect pigment particles, the miniemulsion polymerization,^{7–11,17} emulsion polymerization,^{12,13} and suspension polymerization^{4,14–16} methods are widely used. Particles with sizes on a submicrometer scale or smaller are prepared by miniemulsion or emulsion polymerizations. Suspension polymerization has been usually used to prepare polymer beads with size ranging from 10 to 1000 μm . Interestingly, Widiyandari et al. reports the production of relatively small ($<10 \mu\text{m}$) nanopigment-polymer composites using high speed homogenization-assisted suspension polymerization.¹⁴ Suspension polymerization method are often used to prepare composite particle, because the particle prepared by suspension polymerization method has better spherical shape and contains less surfactant than that prepared by emulsion polymerization method.

Because of its excellent properties such as electroconductivity, chemical, and heat resistance; carbon black pigment has been used as toners in copier and laser printers. Most of the commercial products of

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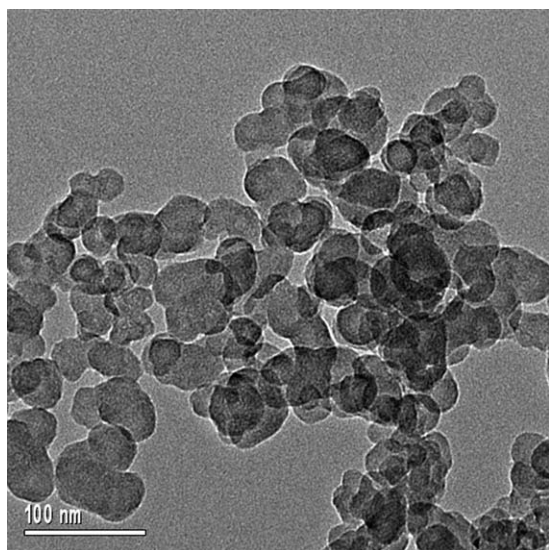


Figure 1 Transmission electron microscopy image of carbon black.

carbon black cannot well disperse in the monomer, which is unfavorable to prepare carbon back-polymer composite particles, especially in suspension polymerization method in which the pigment-monomer droplets are formed at first and then polymerized to composite particles. However, to our best knowledge, the carbon particles are never modified before encapsulation with polymers using suspension polymerization method.

Styrene (St) is a conventional monomer for radical polymerizations and PSt has been widely used to encapsulate pigment particles^{4,7,14,15} because of its merits of cheap and anticorrosion. With its hydrophobic property, St is particularly suitable for suspension polymerization method. As a result, PSt was chosen to encapsulate carbon black particles in our research. In our previous work, Carbon black had been successfully modified by oleic acid,¹⁷ different from Han's method,⁷ to enhance the compatibility of the carbon black particles with hydrophobic polystyrene, and the carbon-polystyrene particles with good spherical forms had been successfully prepared using high speed homogenization-assisted suspension polymerization.

In this study, orthogonal experiments were carried out to investigate the influence of process parameters to the particle size of the prepared composite particles, the process parameters including speed of homogenizer agitation, time of homogenizer agitation, speed of reaction agitation, dispersion stabilizer concentration, and the amount of carbon black.

EXPERIMENTAL MATERIALS

St was reagent grade (Sinopharm Chemical Reagent, reagent grade), and was distilled before being used

to remove the inhibitor. 2,2'-azobisisobutyronitrile (AIBN; Shanghai Chemical Reagent) and benzoyl peroxide (BPO) initiators (all purchased from Shanghai Chemical Reagent) were recrystallized before use. Polyvinyl alcohol (PVA1788; Aladdin Reagent) was used as a suspension stabilizer. Carbon black (DEGUSSA) was used as inorganic paint. As shown in Figure 1, the particles had narrow size distribution with a size of ~ 50 nm. Oleic acid and ammonium hydroxide (Aladdin Reagent) were used to modify the carbon black particles before encapsulation process.

Methods

Modification of carbon black

The modification process of carbon black was the same as what was published in other article of the author.¹⁷ In a typical procedure, 20 g of carbon black and 100 g of H₂O were added into a 250 mL three-necked round-bottomed flask which was equipped with a Teflon blade mechanical stirrer. After the solution was heated to 60°C with mechanical stirring for 30 min, 6 g of oleic acid dissolved in 10 mL of acetone was added to the flask, and then 20 mL of ammonia solution (25–28 wt %) was added. After being heated for another 30 min, the particles were precipitated by dropwise addition of a 2M HCl solution and then washed with acetone five times to remove the excessive oleic acid. At last, the carbon black particles were separated by filtering method, dried in vacuum at room temperature, and stored for use.

Preparation of carbon black-polystyrene composite particles

The carbon black-polystyrene particles were prepared by high speed homogenization-assisted suspension polymerization method as shown in Figure 2. The formulation was listed in Table I. An

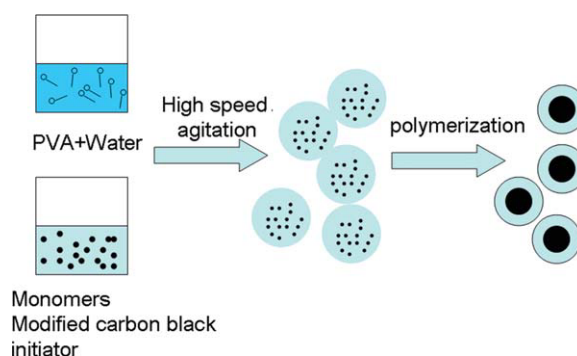


Figure 2 Schematic diagram of experimental steps. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Factor Level Chart of Orthogonal Table

Level	Modified carbon black (g); A	Homogenizer agitation speed (rpm); B	Time of homogenizer agitation (min); C	Speed of reaction agitation; D	PVA concentration (wt %); E
1	0.45	10,000	1	400	1
2	0.9	13,000	4	800	4
3	1.35	18,000	7	1,200	7
4	1.8	20,000	10	1,600	10

oil phase was obtained by mixing some contents of styrene monomers, modified carbon black and initiators, and then was mixed with a water phase (certain amount of the PVA solution). After being pre-mixed for some time at a high agitation speed using high-speed homogenizer (FLUKO, Fa25, and Germany), the suspension of monomer droplets was immediately introduced into a four-necked round flask that was equipped with a Teflon blade mechanical stirrer, a nitrogen inlet and a water-cooled reflux condenser. Polymerization of monomer droplets was carried out for 5 h at a polymerization temperature of 70°C under continuous agitation in the presence of nitrogen bubbling. After completion of the polymerization, the resultants were rinsed off with deionized water and methanol, then centrifugated repeatedly to remove the residual styrene and PVA. Finally, the centrifugal products were dried *in vacuo* at room temperature.

Characterizations

The composite polymer particles were sonicated to disperse them in water and the particle sizes were investigated using Laser Particle Size Analyzer (Microtrac, S3500). The morphology of particles was recorded using Scanning Electron Microscope (HITACHI, S-3400N) and Transmission electron microscopy (JEM2011).

A Fourier transform infrared spectrometer (FTIR, Thermo Nicolet Nexus 470) was used to investigate the resin functions of modified carbon black and complex polymer particles. The spectra were obtained by KBr pellets method.

Thermal analysis was acquired using Thermogravimetric analysis apparatus (TGA, linseis STA PT-1000C) under a flowing nitrogen atmosphere, with the heating rate at 20°C/min and temperature ranging from 100 to 600°C.

RESULTS AND DISCUSSION

For high-quality toner, composite particles with smaller particle size, narrow size distribution, and spherical morphology were required. Nanoblue pigment-polymer composite particles with size below

10 μm had been successfully prepared by Widiyandari et al. using high-speed homogenization-assisted suspension polymerization.¹⁴ In this study, the similar method was used to prepare carbon black-PSt particles.

Characterization of modified carbon black

Oleic acid was selected to modify the carbon black particles to make it well dispersed in oil monomers. Although the methods had been introduced in our other article,¹⁷ the modified carbon black particles were never investigated in detail.

FTIR spectrum results afforded analysis of resin functions in the prepared composite carbon black-PSt microspheres. As shown in Figure 3, the FTIR spectrum of oleic acid-modified carbon particles is significantly different from unmodified carbon black particles. Compared with unmodified carbon black, oleic acid modified carbon black displays remarkably strong absorption at 1739 cm⁻¹ caused by carboxylic acid groups. The intensity of absorption bands at 3436 cm⁻¹ (hydroxyl group of carbon black particles) significantly decreased, which showed that the carbon black particle was more hydrophobic after modification by oleic acid.

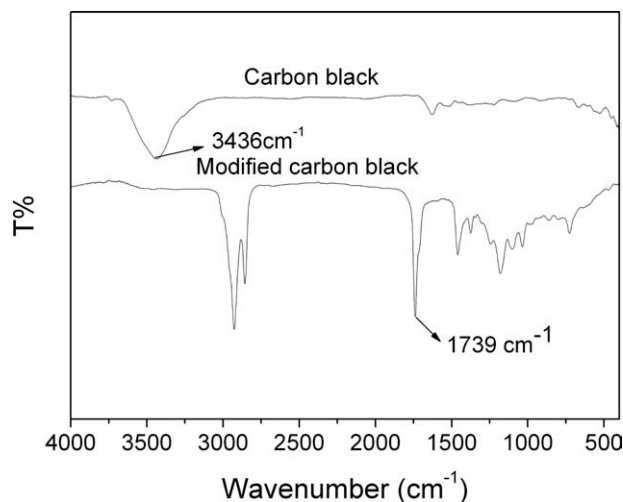


Figure 3 FTIR spectra of carbon black particles modified by oleic acid.

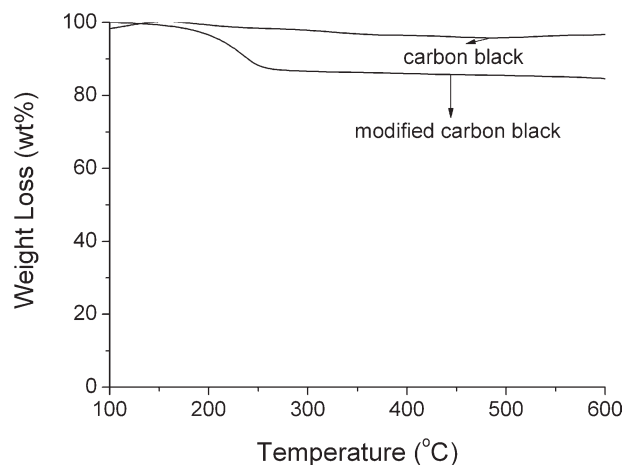


Figure 4 TGA curves of carbon black particles modified by oleic acid.

TGA measurement was performed to determine the amount of oleic acid that attached to the surfaces of the carbon black particles. Figure 4 showed the TGA curves of carbon black particles and oleic acid modified carbon black particles. There was not any obvious weight loss for carbon black particles at a temperature of 600 °C; however, the mass profile of oleic acid modified carbon black particles exhibits a well-defined decrease step with 16.2 wt % of weight loss at temperature ranging from 100 to 600°C. The inflection temperature was 233°C while the mass loss rate was a maximum, which can prove that 16.2 wt % of the modified carbon black was attributed to grafted oleic acid.

The size analysis of complex particles

To investigate the effects of process parameters such as speed of homogenizer agitation, time of homogenizer agitation, speed of reaction agitation, PVA concentration, and the amount of carbon black to the particle size of the prepared composite particles, as shown in Table I, Orthogonal experiments were conducted. Orthogonal chart with five factors and four levels was chosen. The factors and levels were listed in Table I. In all Samples, the weight of modified carbon black and styrene was 8 g, and the weight of water phase and oil phase was 100 g, the initiators used was 1 wt % of BPO and 2 wt % of AIBN to the monomers, and the reaction temperature was 70°C. For factor A, the amount of carbon black (or modified carbon black) was set as 4.8, 9.6, 14.4, and 19.2 wt % to the monomer. In our experiments, the homogenizer agitation speed were 10,000, 13,000, 18,000, and 20,000 rpm, the time of homogenizer agitation time was 1, 4, 7, and 10 min, the speed of reaction agitation was 400, 800, 1200, and 1600 rpm. The PVA concentration was ranging from 1 to 10 wt % to total reaction medium according to previous

report. The complex particles were sonicated to disperse them in water and their sizes were measured by a Laser Particle Size Analyzer.

The reaction conditions and results of orthogonal experiments were listed in Table II. The influences of the speed of homogenizer agitation, time of homogenizer agitation, speed of reaction agitation, PVA concentration, and the amount of carbon black on the M_v size (mean volume diameter) of complex particles were acquired with range analysis of the experimental results in Table II. Range means the difference between the maximum and minimum.

It could be found from range analysis that the influence of PVA concentration was most obvious and the time of homogenizer agitation had the least influence on the M_v of complex particles. It could also be seen from Table II that the M_v of the complex particles decreased drastically with the increase of PVA concentration from 1 wt % to 10 wt %.

In suspension polymerization process, the oil phase was broken into droplets in the water phase by high shear stress, then the polymerization of monomers proceed in the oil droplets after being heated to a certain temperature, at last microspheres were achieved with the monomers converting to polymers. In our system, at first, the oil phase was broke into tiny oil droplets under high shear stress afforded by high speed homogenizer, then the suspension solutions were transferred to the three-necked round bottom flask to initiate the polymerization under much lower speed agitation. Because the shear stress in the polymerization process was much, lower than that in the homogenization process, the tiny droplets coalescent into bigger droplets

TABLE II
The Recipes of the Orthogonal Experiments

Sample	A	B	C	D	E	M_v
1	1	1	1	1	1	11.89
2	1	2	2	2	2	1.553
3	1	3	3	3	3	1.429
4	1	4	4	4	4	0.38
5	2	1	2	3	4	0.705
6	2	2	1	4	3	0.908
7	2	3	4	1	2	4.09
8	2	4	3	2	1	1.279
9	3	1	3	4	2	4.69
10	3	2	4	3	1	17.4
11	3	3	1	2	4	0.63
12	3	4	2	1	3	1.768
13	4	1	4	2	3	1.379
14	4	2	3	1	4	2.178
15	4	3	2	4	1	7.29
16	4	4	1	3	2	1.253
K1	3.813	4.666	3.670	4.982	9.465	
K2	1.745	5.51	2.829	1.21	2.897	
K3	6.122	3.36	2.394	5.197	1.371	
K4	3.025	1.17	5.812	3.317	0.973	
R	4.377	4.34	3.418	3.987	8.492	

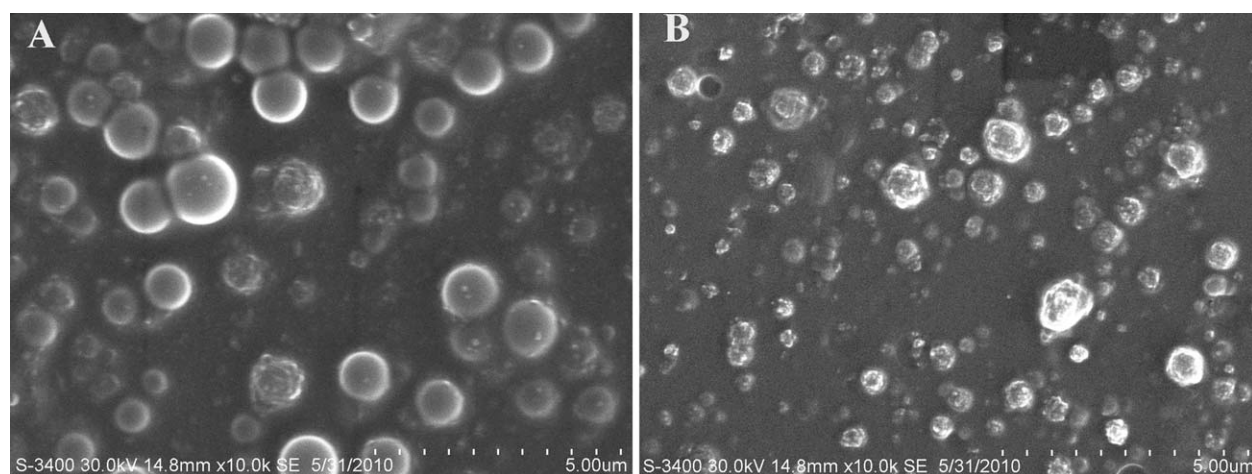


Figure 5 SEM photos of samples, A-sample 6; B-sample 13.

during the polymerization process. Meanwhile, droplet coalesce was prevented by the presence of surface-active agents. There exists a balance between the droplet breakage and coalescence. The higher concentration of PVA is in the solution, the fewer amounts of tiny droplets will coalescent and relatively smaller size of oil droplets will form after the polymerization process. Therefore, the concentration of surface-active agent PVA plays the most important role in controlling the size of microspheres in our system. However, particles with size below 10 μm cannot achieve even with PVA concentration of 10 wt % that prove that the high-speed homogenization process was necessary for preparation of particles with small size. Without high-speed homogenization process, the monomer droplet size exceeds 10 μm under the low shear force afforded by low-speed mechanical stirring, so the particle size prepared is large. It can be explained by Winslow and Matreyek's results,¹⁸ they suggested that particle size of bead suspension polymerization was mainly determined by the droplet size in the lower conversion stage and by the stability of the monomer/polymer droplets in the high-conversion stage.

As shown in Figure 5(A), the SEM photos of Samples 6 and 13, the complex particles of Sample 6 had good spherical forms with smooth surfaces which were necessary for application in high quality toners. Unfortunately, the complex particles of Sample 13 had irregular structure with rough surfaces as shown in Figure 5(B), which may be caused by the large amount (19.2 wt %) of carbon black being designed to the complex particles. Kiatkamjornwong and Pomsanam¹⁵ had found similar result in the synthesis of carbon-Polystyrene complex spheres using BPO as a initiator. They claimed that when the carbon black loading was about 7 wt %, an irregular particles' shape (aggregated form) was obtained, and the percentage of conversion could

not be completely determined because of a strong inhibitory effect on the radical polymerization. It was also found that carbon black particles had inhibitory effect on the radical polymerization in our previous work, when 16 wt % of BPO to the total monomers was used, only 80% of conversion could be achieved with 10 wt % of carbon black loaded. Luckily, we found that AIBN had higher initiating efficiencies than BPO in the polymerization process with the existence of carbon black particles. When the amount of AIBN was 2 wt % to the total monomers, the fractional conversion was 90% with 10 wt % of carbon black loaded. Although the inhibiting problems were conquered by using composite initiators of AIBN and BPO, the composite particles with rough surface occurs when the content of carbon black particles was up to 20 wt % as shown in Figure 5(B). We speculated the rough surface was caused by some carbon black particles diffusing to the surface of the complex particles during the encapsulation process.

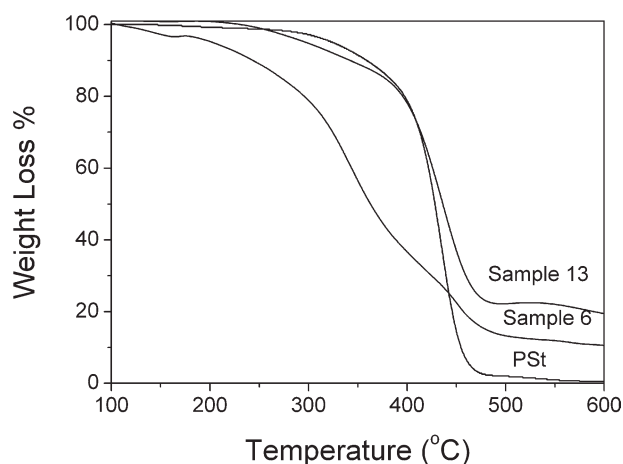


Figure 6 TGA curves of complex particles, A-sample 13; B-sample 6.

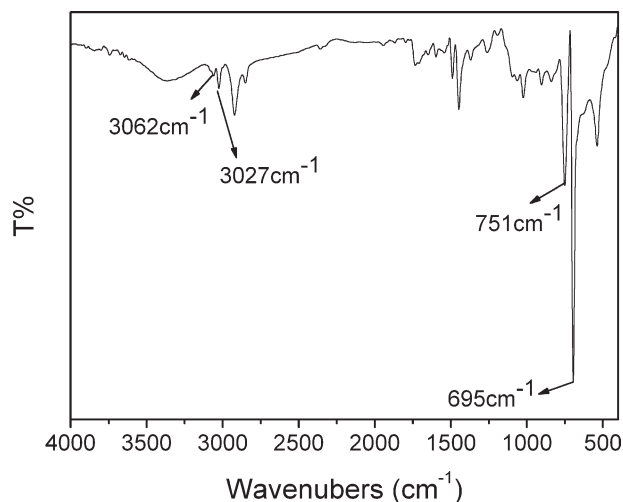


Figure 7 FTIR spectrum of sample 6.

The amount of carbon black in the complex particles was characterized by TGA measurement. As shown in the heat curve of PSt in Figure 6, there is a well-defined decrease step with nearly 100 wt % of weigh loss at temperature ranging from 100 to 600°C. However, 10.3 and 19.4 wt % of residual are remained at 600°C for Samples 6 and 13, which proved the amount of carbon black particles was 10.3 and 19.4 wt % in the complex particles, respectively. The amount of carbon black, which was encapsulated in the complex particles, was close to the feeding amount of 9.6 and 19.2 wt % for Samples 6 and 13. It can be concluded that all the carbon feeding was nearly encapsulated in the complex particles.

FTIR spectrum results provide analysis of resin functions in the prepared composite carbon black-PSt particles. As shown in Figure 7, there exists absorption at 3062 and 3027 cm^{-1} (aromatic C-H stretching); 751 and 695 cm^{-1} (bending vibration of monosubstituted benzene ring) in the FTIR spectrum of Sample 6. The FTIR spectrum result proved the formation of composite particles.

CONCLUSIONS

Carbon black particles with size of around 50 nm had been successfully modified by oleic acid with 16.2 wt % of oleic acid attached to the surface of carbon black. Composite particles of carbon black and polystyrene with smooth surfaces can be obtained even when the carbon black loading was 10 wt %. The results of Orthogonal experiments prove that the stabilizer concentration plays a more important role in controlling the size of complex particles than other factors such as homogenization speed, homogenization time, agitation speed, and pigment concentration.

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