

# Research on Nonmagnetic Single-component Toner(I)

## Preparation of P(St-BA)/CB Composite Microspheres by Dispersion Copolymerization

Haiguo Li Gang Wu Hong-Zheng Chen Mang Wang (Department of Polymer Science and Engineering, State Key Laboratory of Silicon Materials, Key Laboratory of Macromolecule Synthesis and Functionalization, Ministry of Education, Zhejiang University, Hangzhou 310027, China);

### Abstract

*Dispersion copolymerization of styrene (St) and n-butyl acrylate (BA) was carried out in the mixed solvent of alcohol-water in the present of carbon black (CB) using poly(N-vinylpyrrolidone) (PVP) as stabilizer, azobisisobutyronitrile (AIBN) as initiator. The obtained composite microspheres were characterized by optical microscope, particle size analyzer, scanning electron microscopy (SEM) and differential scanning calorimeter (DSC), and the results showed the particle size characteristics and heat performance ( $T_g \approx 65^\circ\text{C}$ ) of the microspheres can meet the requirements of toner in commercial use basically.*

### 1 Introduction

As the development of information technology and office automation, copiers and laser printers are widely used today, which make the demand of toners increase quickly. Conventionally, toners are produced by a pulverization method in which colorants, charge control agents (CCAs) and other additives are dispersed in a molten resin matrix, followed by cooling, crushing, pulverization and classification. Although this method has been widely used in commercial toners, a polymerization route has been proposed recently and attracted much attention. Compared with pulverized toners, polymerized ones usually have regular shape, small particle size, narrow size and charge distribution and better dispersion of colorants within the resin, which thus lead to better image quality.

Up to now, polymerized toners are mainly produced by suspension polymerization [1-3], emulsion aggregation [4] or encapsulation method [5]. Conventional suspension or emulsion polymerization usually produced microspheres with size larger than  $50\mu\text{m}$  or smaller than  $0.5\mu\text{m}$ , while the particle size of toners is usually in the range of  $5\mu\text{m}$  to  $15\mu\text{m}$ . So in order to get qualified toner, high-speed homogenizer or complicated multistep processing is necessary. In this study, composite microspheres with carbon black encapsulated had been synthesized by one-step in-situ dispersion polymerization, the size of which has met the requirement mentioned above. In order to improve the efficiency of encapsulation, carbon black was pretreated with silane coupling agent before polymerization.

### 2 Experimental

#### 2. 1 Materials

Carbon black pigment of industrial grade (Shanghai Coking & Chemical Development Co., China) with an average particle size of

22nm was used as colorant. Styrene (St, Sinopharm Group Chemical Reagent Co., China) and n-butyl acrylate (BA, Wulian Chemicals Factory, China) were used as comonomers after they were distilled at reduced pressure. Azobisisobutyronitrile (AIBN; Shanghai Fourth Reagent Factory, China) and poly(N-vinylpyrrolidone) (PVP; K30, Sinopharm Group Chemical Reagent Co., China) were used as initiator and stabilizer, respectively.  $\gamma$ -methacryloxypropyltrimethoxysilane (MPS), a silane coupling agent, was provided by Guotai-Huarong new chemical materials co. (Zhangjiagang, China).

#### 2. 2 Surface pretreatment of carbon black

Carbon black (1g) was first pretreated with concentrated acid and then dispersed in 100mL ethanol aided by ultrasonic. After that it was transferred to a flask, and 0.25g MPS, 5mL water, 3mL ammonia were added. The mixture was stirred at room temperature for more than 12 hours and finally filtered and dried.

#### 2. 3 Synthesis of composite microspheres by dispersion polymerization

Generally, 46ml of ethanol, 4ml of deionized water, 0.48g PVP and a certain amount of carbon black were charged into a flask and treated with ultrasonic for several minutes. Then the flask was heated to a setting temperature ( $70^\circ\text{C}$ ) and the monomers (6mL St and 2mL BA) in which AIBN had been dissolved were added. The polymerization reaction was carried out under  $\text{N}_2$  atmosphere for 22 hours. The final product was washed with ethanol, then filtered, and dried under vacuum.

#### 2. 4 Characterization

The size and size distribution of particles were measured with optical microscopy (BX51, OLYMPUS, Japan) and LS230 particle size analyzer (BECKMAN COULTER). The morphological properties of the microspheres were observed by field emission scanning electron microscopy (JEOL, Japan). The thermal behavior of the microspheres was measured with a differential scanning calorimeter (DSC Q100, TA). Measurements were carried out over a temperature range of  $25\text{--}120^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

### 3 Results and discussion

#### 3. 1 Surface pretreatment of carbon black

As shown in figure 1, carbon black was first treated with MPS before polymerization according to the method described by

Philipse, et.al [6]. This step was proved to be necessary for the subsequent polymerization. Without pretreatment, it was difficult to retain carbon black inside each particle and serious coalescence usually occurred. However, treating carbon black with MPS can effectively overcome these problems. This is because the vinyl group of MPS can react with monomers to produce grafted polymer chain on the carbon black surface, which can effectively enhance the affinity of monomers or polymer chains to the carbon black. In addition, bare carbon black was proved to be a strong radical scavenger [1], which can retard or even completely inhibit the polymerization reaction. Surface pretreatment with MPS may also weaken this effect to some extent.

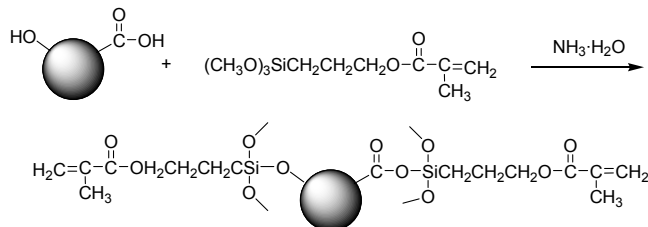


Figure 1. Schematic drawing of grafting carbon black with MPS.

### 3. 2 Particle size characteristics of the composite microspheres

As shown in Figure 2(a), microspheres with particle size of about 10 $\mu$ m were successfully obtained when 1 wt% (based on monomers) treated carbon black and 2 wt% (based on monomers) initiator were added. A bimodal distribution of the particle size can be seen more clearly in Figure 3(a) ( $D_{0.75}$  presented in the figure means particle size corresponding to 75% accumulated volume, while  $\text{span}=(D_{0.9}-D_{0.1})/D_{0.5}$  is used to characterize the size distribution). Except the sharp peak at 10.3 $\mu$ m, another one around 1 $\mu$ m should be ascribed to pure polymer microspheres without carbon black encapsulated. Because in the process of polymerization, there must be a part of polymer nucleated by absorbing stabilizer after the chain length had reached a critical value. So the amount of stabilizer has an important effect on the proportion of such particles in the final products. As shown in Figure 2(b) and Figure 3(b), when more stabilizer was added, the particle size turned smaller and the distribution turned broader. This is because more particles without carbon black encapsulated were stabilized, which lead to more pure polymer particles. In order to improve the proportion of composite microspheres, we can lower the amount of stabilizer, but too less stabilizer may destroy the homogeneity of the reaction system.

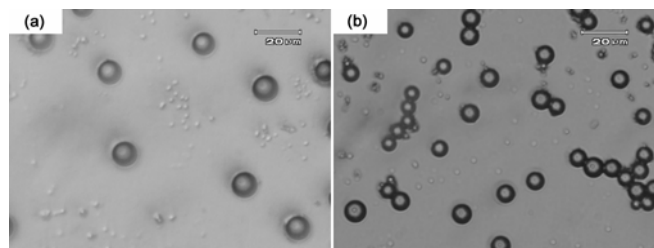


Figure 2. Optical micrographs of microspheres prepared with (a) 0. 48g (b) 0. 54g PVP.

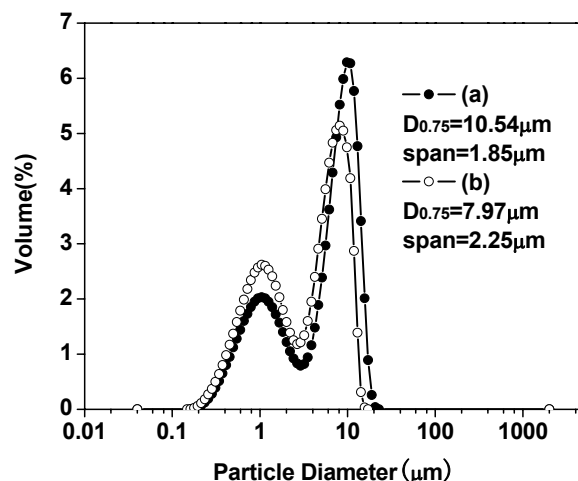


Figure 3. Particle size distribution of sample shown in Figure 2.

In order to get desired particle size, the agitation rate during the polymerization is also very important because it directly correlate with the dispersion of reaction stuff and the produced particles in the medium. When the agitation rate was increased from 200rpm to 250rpm, larger particles ( $D_{0.75}=16.78\mu\text{m}$ ) with more narrow size distribution ( $\text{span}=1.43\mu\text{m}$ ) was obtained. In order to further understand the mechanism, the reaction mixture was sucked out during the polymerization process and observed with microscope directly, without diluted or treated with ultrasonic. As shown in Figure 4, when the agitation rate was set as 250rpm, microspheres had a relative better dispersion. So the above result may be explained as follow: when the agitation rate was low, the coalescence between particles made the opportunity of capturing oligomers in the medium for different particles not equal, which lead to a broader size distribution finally. On the other hand, too larger agitation rate will do no good to the reaction as well, because it will destroy the steric stabilization function of PVP.

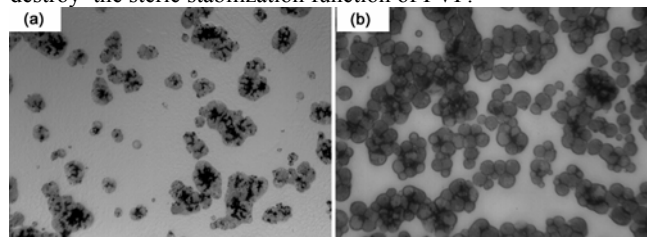


Figure 4. Dispersion state of microspheres at different agitation rate:(a) 200rpm (b) 250rpm.

As for dispersion polymerization, the polarity of the reaction medium also has an important effect on the size and size distribution

of particles. We can tune the polarity and thus the size of particles by choosing different solvents. The reaction medium used in above experiments was a mixture of ethanol and water. Here, we replaced ethanol with n-propanol, a solvent with lower polarity. As a result, the initiator and monomers become more compatible with the medium, while its affinity to polymerized microspheres lowered relatively. So the growth rate of particles slowed down and the stability of the reaction system was improved. Finally we got more uniform microspheres, as shown in Figure 5(a). As we reincreased the polarity of medium by increasing the proportion of water, this size uniformity disappeared again, as shown in Figure 5(b). Although we could get more uniform microspheres in propanol-water system, it should be pointed out that the monomer conversion was relative low for the reason metioned above and it's not beneficial for the production of polymerized toner because washing with large amount of water after polymerization is a very important factor that increases the cost.

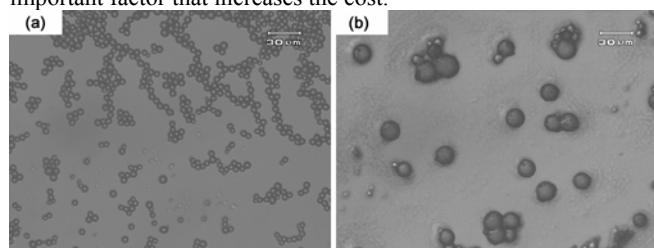


Figure 5. Optical micrographs of microspheres prepared in the medium of (a) 46mL n-propanol and 4mL water (b) 42mL n-propanol and 8mL water.

For toners, the amount of colorant in the resin must reach a certain value, so we investigated situations when more carbon black was added. As shown in Figure 6(a) and 6(b), the particle size decreased with more carbon black added. This is because carbon black acted as “seed” in the polymerization, which means the number of particles increased with carbon black feed level. As a result, the opportunity of capturing oligomers in the solvent for individual particle lowered relatively and the size decreased. We could get composite microspheres with size of 4-5µm by adjusting recipe such as the initiator concentration.

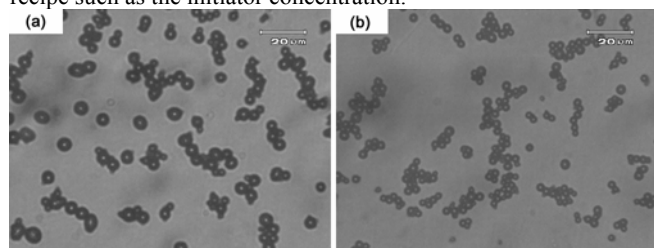


Figure 6. Optical micrographs of microspheres prepared with (a) 3% (b) 5% carbon black.

### 3. 3 Surface morphology of the composite microspheres

The in situ dispersion polymerized microspheres is spherical in shape as shown in Figure 7. For the reason that part of the carbon black relatively near the surface is not completely encapsulated by the polymers, the surface of individual particle shown in the inset of

Figure 7 is relative rough. This also proves that the particle obtained contains carbon black, because if not, the surface should be absolutely smooth.

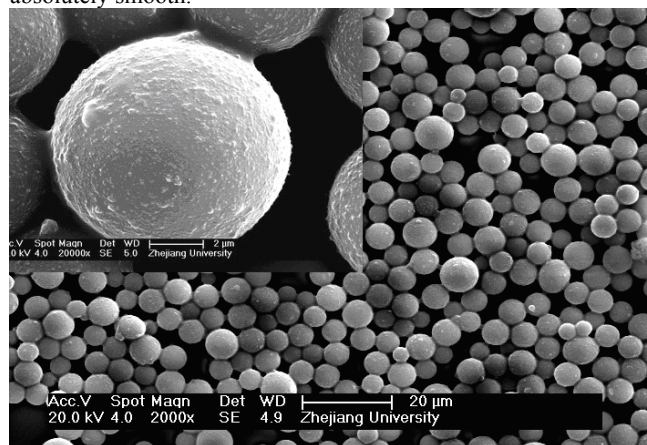


Figure 7. SEM photograph of as-prepared microspheres. The inset shows an enlarged microsphere.

### 3. 4 Thermoanalysis of the composite microspheres

Styrene (St) and n-butyl acrylate (BA) were choosen as comonomer in this study, because the glass transition temperature (Tg) of polystyrene is relative high (100 °C), while that of poly(n-butyl acrylate) is relative low (-56 °C). So we can easily adjusting the Tg of copolymer by changing the ratio of these two monomers.

In order to meet the requirement of toner, the volume ratio of St to BA was set at 3 in the study, so the molar ratio was 3.74. The resulting microspheres were investigated by differential scanning calorimetry to identify the Tg value. As shown in Figure 8, the Tg of pure copolymer microspheres was 68.5 °C. When carbon black was added, Tg lowered a little. This is because Tg usually correlated with the molecular weight of the resin. As mentioned above, carbon black acts as “seed” in the polymerization, which make the critical chain length of polymer decrease and thus the molecular weight is lowered. In addition, the surface groups of the carbon black may also inhibit the rate of polymerization and decreased the molecular weight of the resulting polymerized microspheres [1].

*Haiguo Li received his B. S. in polymer science and engineering from Zhejiang University (2002) and is presently a Ph. D. student in the Organic Semiconductor Laboratory. His research focuses on the organic-inorganic hybrid materials for optoelectronic applications.*

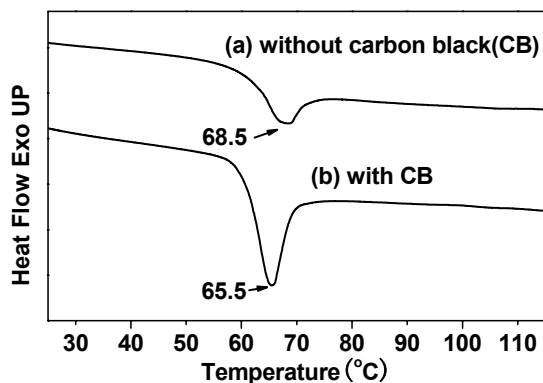


Figure 8. DSC heating scanning curves of microspheres (a) without and (b) with carbon black.

## 4 Conclusions

Composite microspheres with carbon black encapsulated had been synthesized by one-step in-situ dispersion polymerization. The particle size showed a bimodal distribution with the main peak located in the range of several microns to more than ten microns. The composite microspheres possessed a spherical shape but relative rough surface and the  $T_g$  was about 65 °C, which could meet the requirements of toner in commercial use basically.

## 5 Acknowledgements

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## Author Biography