Encapsulation of Disperse Dye by Phase Separation Technique Using Poly(styrene-maleic acid)

Shaohai Fu, Guifang Zhang, Lei Ding, Anli Tian, Chaoxia Wang

Key Laboratory for Eco-Textile of Ministry of Education, Jiangnan University, 1800 Lihu Road, Wuxi 214122, Jiangsu, People's Republic of China

ABSTRACT: C.I. disperse dye blue 60 was encapsulated by poly(styrene-maleic acid) using phase separation technique, followed by the preparation of the encapsulated disperse dye dispersion. The effects of process conditions on particle size of the dispersion were investigated. The results showed that the particle size of the encapsulated disperse dye dispersion was small, and the stability was excellent when mass ratio of poly(styrene-maleic acid) to disperse dye ($R_{p/d}$), dropping speed of phase separation agent (D_s), dis- perse dye content in dispersion (C_d), and dispersing time (D_t) were about 20%, 7 mL/min, 5–7.5%, and 1.5 h, respectively. Transmission electron microscope (TEM), zeta potentials, and contact angle indicated that C.I. disperse dye blue 60 was successfully encapsulated by poly(styrene-maleic acid). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3581–3586, 2011

Key words: phase separation technique; encapsulation; disperse dye; dispersion

INTRODUCTION

Disperse dye with high performance in hue, brilliant and color strength became the main colorants for polyester and acetate fiber in inkjet printing technology.[1] However, just as similar to the pigment, the disperse dye always existed in aggregation or coagulation and were hard to be dispersed in aqueous media.[2] To improve the stability, reduce the particle size, and particle size distribution of disperse dye dispersion, considerable works have been done by the researchers.

At present, varieties of methods have been developed and applied for disperse dye modification, such as spray drying,[3] emulsion polymerization,[4–6] homogenization by high pressure, grinding with aid of dispersant,[7–9] so on. Although there are so many methods for disperse dye modification, how to prepare the disperse dye dispersion with high stability and small particle size were still an obstacle for application in inkjet printing technology. Phase separation technique was an effective method for preparation of the core-shell colorant materials, For instance, Zhang et al.[10] encapsulated the pigment into polystyrene. In our previous research, the nanoscale organic pigment was encapsulated by poly(styrene-maleic acid).[11] Based on my knowledge, the phase separation technique was rarely used for preparation of the encapsulated disperse dye.

C.I. disperse dye blue 60 with high color strength and excellent light fastness were widely used as a colorant for inkjet printing ink.[2] In this article, we used poly(styrene-maleic acid) as shell and C.I. disperse dye blue 60 as core materials, and prepared the encapsulated disperse dye dispersion by phase separation method. The effects of process conditions on particle size were investigated.

EXPERIMENTAL

Materials

C.I. disperse blue 60 (press cake, water content 47%, its chemical structure was shown in Chart 1 Yabang Dyestuff, Changzhou, China) was dried before using NaOH, acetone (analytical grade; Lingfeng Chemical Reagent, Shanghai, China), and poly(styrene-maleic acid) (molar ratio of styrene to maleic acid was about 0.56, M_n = 9000, Nanocolorants and Digital Printing R&D Centre of Jiangnan University, Wuxi, China).

Preparation of encapsulated disperse dye

A certain amount of poly(styrene-maleic acid) was dissolved in 200 g acetone and then corresponding amount of C.I. disperse blue 60 was added into the above solution. The mixture was stirred for 30 min and then transferred to Ultra Turrax IKA T18 Basic (IKA Instruments, German) and dispersed at rate of 25,000 r/min for a desired time, after that 200 g ethanol was dropped into the above mixture. The mixture was centrifuged to get some slurry. The
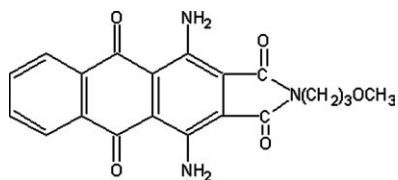
Chart 1 Chemical structure of C.I. disperse blue 60.

slurry was washed with ethanol for three times and then dried to obtain the encapsulated disperse dye.

Encapsulated disperse dye (10 g) was dispersed into 90 g of distilled water. The pH value of the mixture was adjusted to 9 using 0.1 mol/L sodium hydroxide solution. The mixture was treated with ultrasonic machine (Xinzhi instruments, Ningbo, China) for 10 min and then the encapsulated disperse dye dispersion was obtained.

Preparation of comparative dispersion

Poly(styrene-maleic acid) (9 g) was dissolved in 203.5 g of distilled water. After pH value of the solution was adjusted to 9.0 by adding 0.1 mol/L sodium hydroxide solution, 37.5 g C.I. disperse blue 60 was added. The comparative disperse dye dispersion was obtained when the mixture was dispersed by ultrasonic until the particle size did not change any more.

Characterization

Particle size and zeta potentials

The samples were diluted to 1000 times by distilled water. The Particle size and zeta potentials were measured by Nano-ZS90 (Malvern Instruments, England).

TEM photography

One drop of the dispersion was diluted to 2000 times by distilled water, and then placed on a 400-mesh carbon-coated copper grid and dried in air. The morphologies of comparative disperse dye and encapsulated disperse dye were characterized with a transmission electron microscope (TEM, JEM-100SX, Japan).

Contact angle

Encapsulated disperse dye and original disperse dye were uniformly put onto a glass slide and then pressed slightly with another glass slide to ensure a flat surface. The contact angle of the sample to distilled water was tested by Krüss DSA 100 (Krüss Co., Hamburg, Germany).

Stability

Centrifugal stability. The absorbance of the sample was measured using a UV/Vis spectrophotometer (UV-2000 and UV-2100 model, UNICO Instruments,

Shanghai, China). The wavelength of maximum absorbance was found at 630 nm. The samples were centrifuged at desired speed for 30 min and then its absorbance (630 nm) was measured.

Stability to temperature. The dispersion was stored and sealed in a container at a constant temperature for 24 h. The particle size of the dispersion was measured before and after storage. The stability to temperature (S) was evaluated using eq. (1),

$$S = \frac{|d_0 - d_T|}{d_0} \times 100\% \qquad (1)$$

where d_0 is the particle size of the original dispersion, and d_T is particle size of the dispersion stored at a desired temperature.

Stability to pH value. The dispersion was adjusted to a desired pH value using 1 mol/L HCl or 1 mol/L NaOH and stored at room temperature for 24 h. The stability to pH value (S) was evaluated using eq. (2),

$$S = \frac{|d_0 - d_{\mathrm{pH}}|}{d_0} \times 100\% \qquad (2)$$

where d_0 is the particle size of the original dispersion, and d_{pH} is particle size at the desired pH value.

RESULTS AND DISCUSSION

Preparation of the encapsulated disperse dye dispersion

Many factors such as amount of copolymer, dropping rate of phase separation agent, disperse dye content in dispersion, and dispersing time could greatly influence on the particle size of the encapsulated disperse dye dispersion. Figure 1 showed that
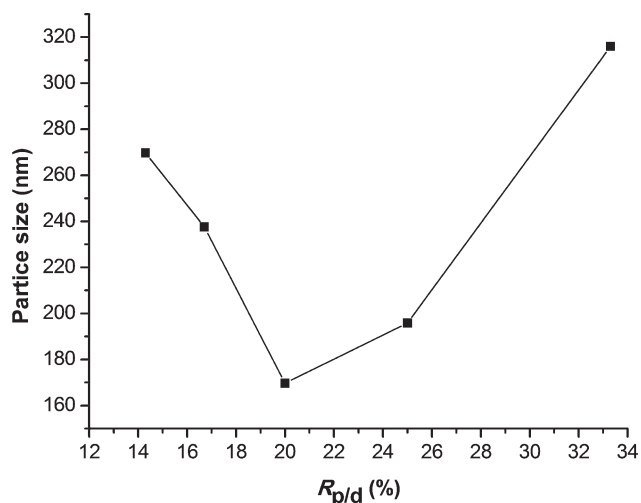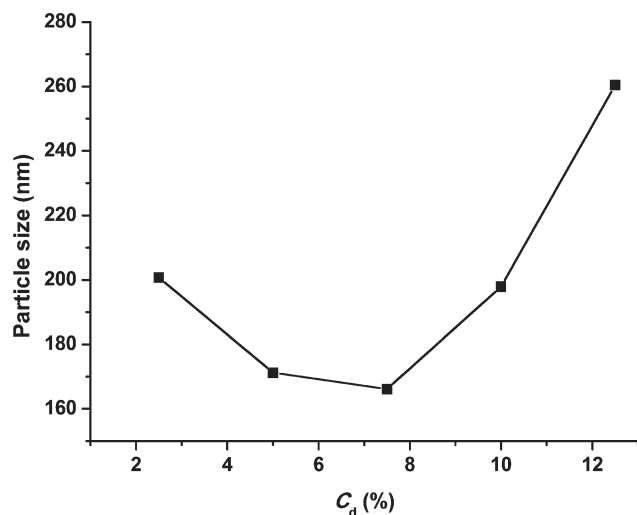

Figure 1 Effects of amount of poly(styrene-maleic acid) on particle size, D_s : 7 mL/min, C_d : 5%, D_t : 1.5 h.
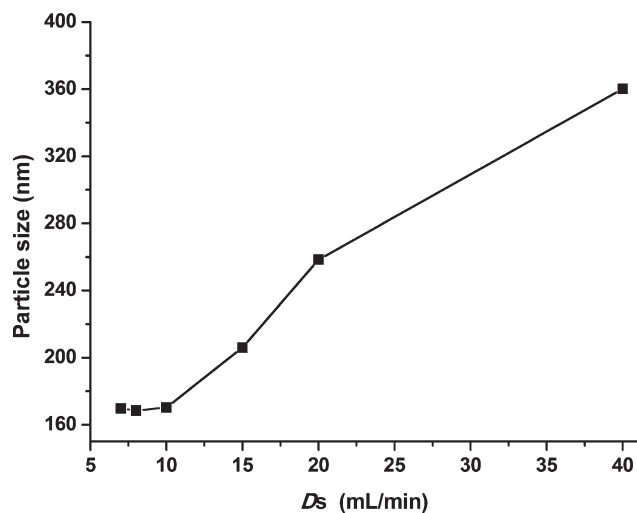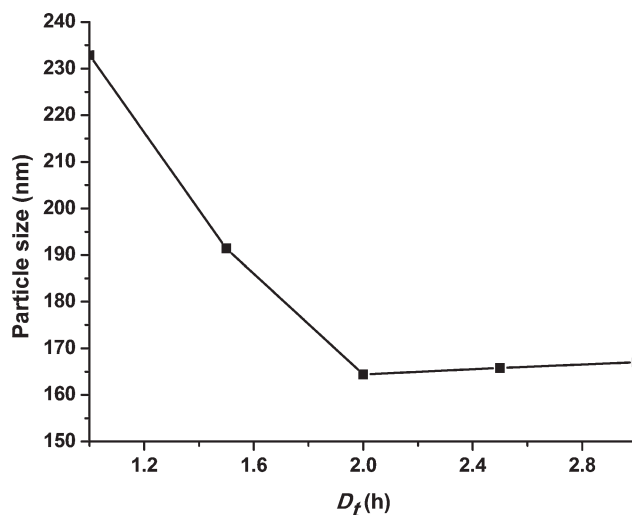
Figure 2 Effects of dropping speed of phase separation agent on particle size, $R_{P/D}$: 20%, C_d :5%, D_t : 1.5 h.

Figure 4 Effects of dispersion time on particle size, D_s : 7 mL/min, $R_{P/D}$: 20%, C_d :5%.

the particle size reached to minimum, when the mass ratio of poly(styrene-maleic acid) to disperse dye was about 20%. The disperse dye surface could not be completely encapsulated when amount of poly(styrene-maleic acid) was small; therefore, the dispersed particles would combine again via Van der Waals force, thus, leading to a large particle size. On the other hand, when amount of poly(styrene-maleic acid) was large enough, the excessive poly(styrene-maleic acid), which was not coated on disperse dye surface, would dissolve in aqueous media and then the viscosity of dispersing media increased greatly, which resulted in a poor wettability and low dispersing efficiency, thus also leading to a large particle size.

Figure 2 showed that the particle size increased little, when dropping rate of phase separation agent was less than 10 mL/min. The poly(styrene-maleic acid) would

be precipitated on disperse dye surface, when phase separation agent was added. It was known that the precipitation speed of poly(styrene-maleic acid) was slow at low dropping rate of phase separation agent, which led to a uniform and complete coated layer on the disperse dye surface. On the contrary, an uneven and incomplete coated layer would be formed when dropping rate of phase separation agent was fast enough. In addition, some poly(styrene-maleic acid) molecules might tangle with each other under these conditions, which also lead to a large particle size.

Figure 3 indicated that the particle size reduced to minimum when the disperse dye content was about 5–7.5%. When the disperse dye content was low, the poor dispersing efficiency would be obtained for small collisions among disperse dye particles. On the contrary, when the disperse dye content was high enough, the viscosity of dispersing media

Figure 3 Effects of disperse dye content on particle size, D_s : 7 mL/min, $R_{P/D}$: 20%, D_t : 1.5 h.
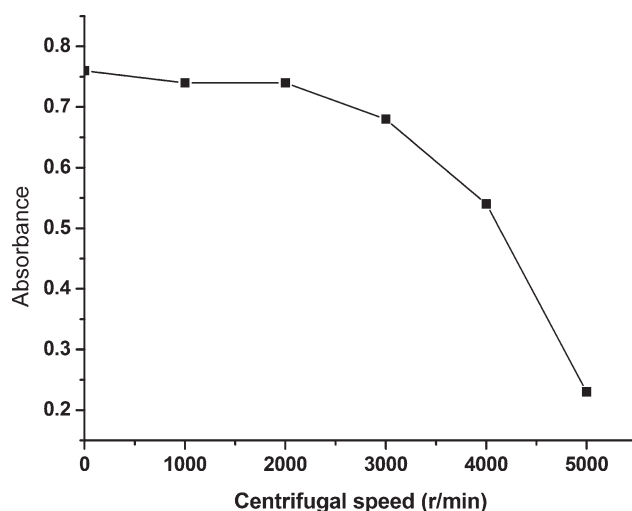
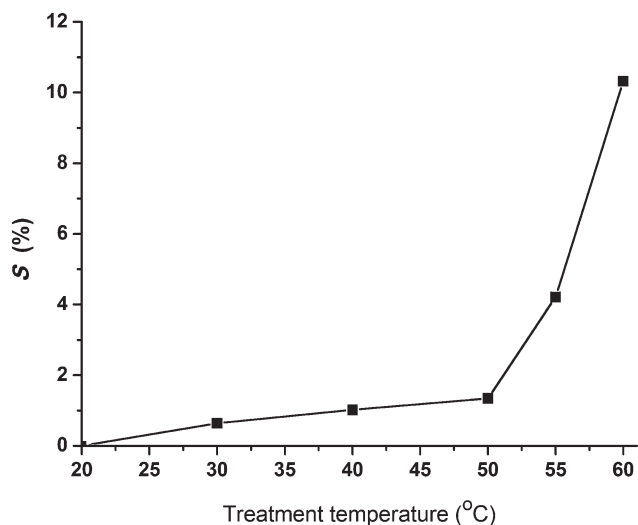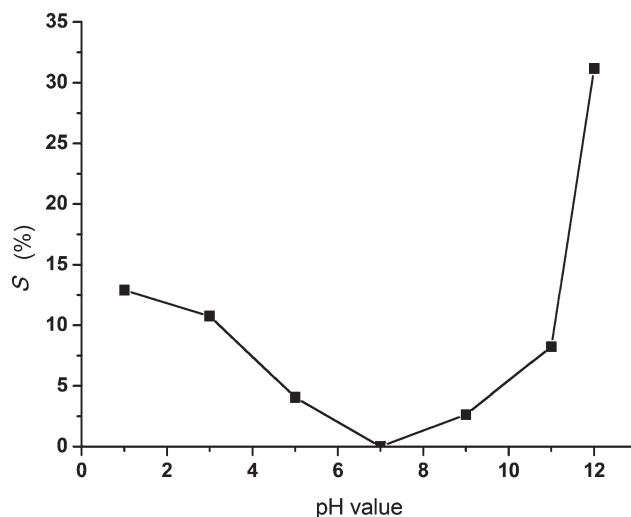**Figure 5** Effect of centrifugal speed on absorbance of encapsulated disperse dye dispersion.

Figure 6 Stability to treatment temperature of encapsulated disperse dye dispersion.

Figure 7 Stability to pH value of encapsulated disperse dye dispersion.

would increase greatly, thus leading to the low dispersing efficiency for its poor wettability, which also resulted in large particle size.

Figure 4 showed that particle size reduced with an increase of dispersing time, and decreased when dispersing time was more than 2 h. The disperse dye became smaller and smaller under shear force as dispersing time increased. Meanwhile, the aggregation speeds of small disperse dye increased for high surface energy. When the aggregation speed and dispersing speed reached to balance, the particle size reduced to minimum and would not decrease with further increasing the milling time.
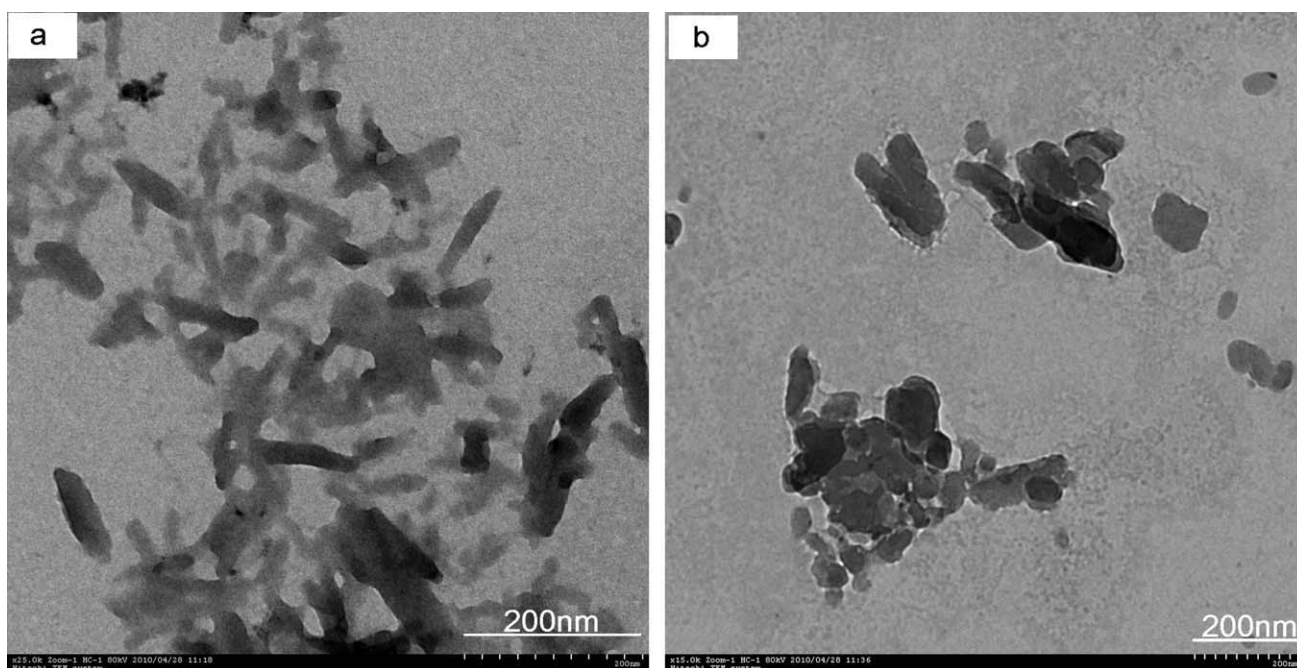
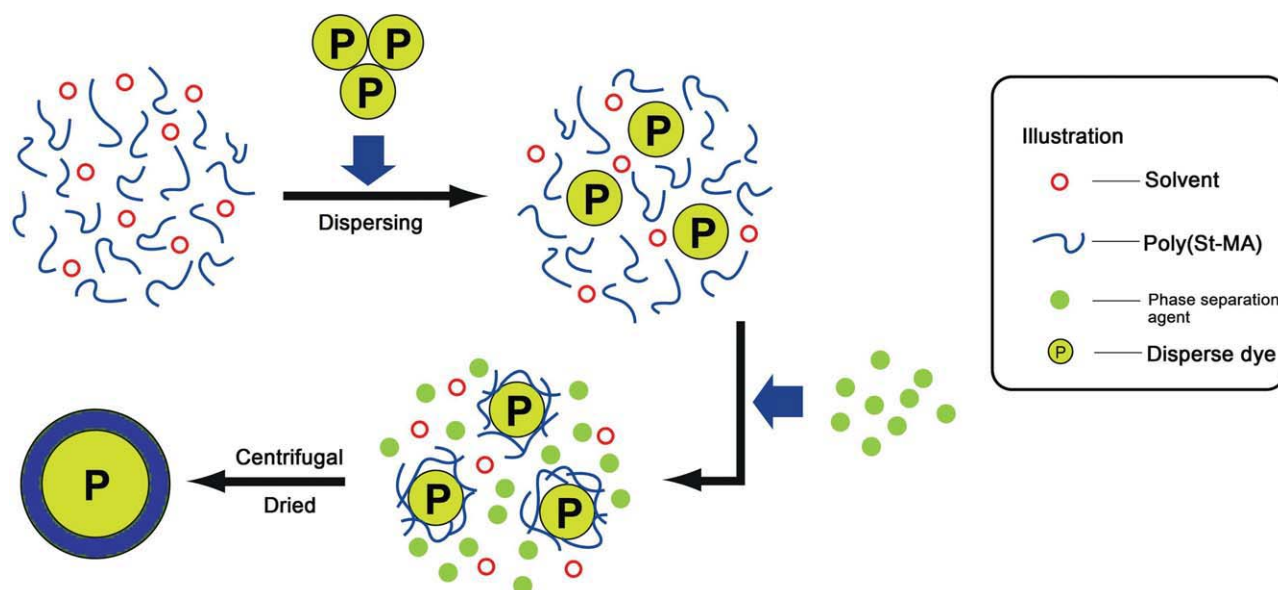## Stability of encapsulated disperse dye dispersion

The encapsulated disperse dye was prepared under the optimal conditions as follows: mass ratio of poly(-styrene-maleic acid) to disperse dye ($R_{p/d}$), 20%; dropping speed of phase separation agent (D_s), 7 mL/min; disperse dye content in dispersion (C_d), 5%; and dispersing time (D_t), 1.5 h. The dispersion was prepared using above encapsulated disperse dye. To wide its application, the stability to centrifugal force, temperature, and pH value of the dispersion was investigated.

Figure 5 showed that the absorbance of the encapsulated disperse dye dispersion reduced small when

Figure 8 TEM photography of (a) comparative dispersion and (b) encapsulated disperse dye dispersion, D_s : 7 mL/min, $R_{P/D}$: 20%, C_d :5%, D_t : 1.5 h.

Figure 9 Process for preparation of encapsulated disperse dye by phase separation technique. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

centrifugal speed was lower than 3000 r/min. The sedimentation speed of the disperse dye particles would be offset by the Brownian motion at low centrifugal speed, thus the absorbance reduced small. However, when centrifugal speed was higher than 3000 r/min, some large particles were deposited for high centrifugal forces, thus leading to a large change of absorbance.

Figure 6 showed that the particle size changed small at low treatment temperature, whereas greatly when treatment temperature was higher than 50°C. The fact was that the poly(styrene-maleic acid) completely encapsulated onto the disperse dye surface in encapsulated disperse dye dispersion, the attractive forces between poly(styrene-maleic acid) and disperse dye was large, and it was hard to be peeled off at low treatment temperature.

Figure 7 indicated that the change rate of particle size first decreased and then increased with an increase of pH value. When pH value was low, the electric repulsive forces among particles were small for few $-COO^-$ on disperse dye surface, thus leading to large change rate of particle size. Moreover, when pH value was high enough, some poly(styrene-maleic acid) would be desorbed from disperse dye surface for its high solubility in dispersing media, which also resulted in large change rate of particle size.

### Surface characterization of encapsulated disperse dye

The morphology of encapsulated disperse dye and original disperse dye was shown in Figure 8. It could be seen that particles of the former [Fig. 8(a)] was larger and more uniform than that of the latter [Fig. 8(b)], which indicated that some

poly(styrene-maleic acid) were encapsulated onto disperse dye surface. The encapsulation process might be divided into two steps (Fig. 9); first, the poly(styrene-maleic acid) were dissolved and absorbed onto the disperse dye surface in actone; second, poly(styrene-maleic acid) were precipitated and encapsulated onto the disperse dye surface after adding some phase separation agent and drying.

Zeta potential was an important parameter that determines the long-term stability of the dispersion. Generally, the particles in dispersions with high zeta potentials were electrically stable, whereas with low zeta potentials tended to coagulate or flocculate.[12,13] Figure 10 showed that the zeta potentials of encapsulated disperse dye were -53.27 mV, whereas the original disperse dye were -10.67 mV. In the former, $-COOH$ in poly(styrene-maleic acid) that encapsulated onto disperse dye surface would react with OH^- and then turned to $-COO^-$, thus leading to an increase of zeta potentials. These results also indicated
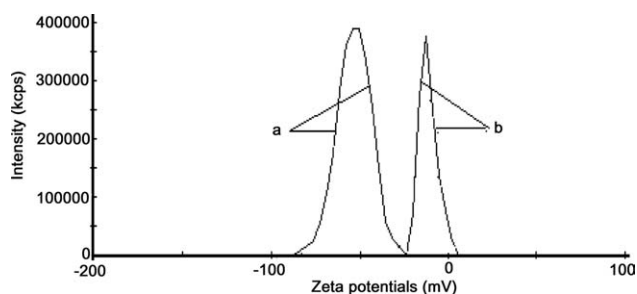
Figure 10 Zeta potntials distribution of (a) encapsulated disperse dye (b) original disperse dye, D_s : 7 mL/min, $R_{P/D}$: 20%, C_d : 5%, D_t : 1.5 h.
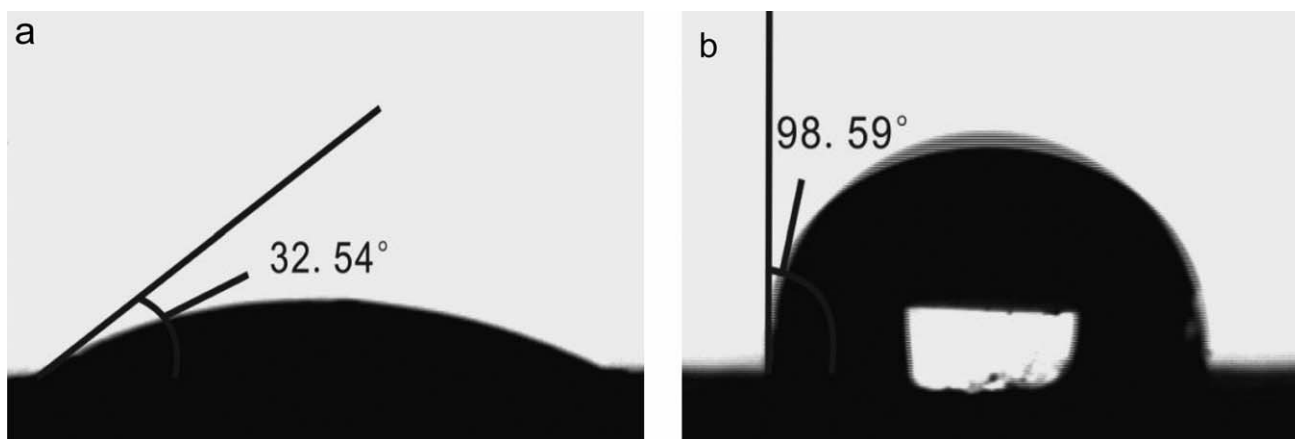
Figure 11 Contact angle of (a) encapsulated disperse dye and (b) original disperse dye, D_s : 7 mL/min, $R_{P/D}$: 20%, C_d : 5%, D_t : 1.5 h.

that some poly(styrene-maleic acid) were encapsulated onto disperse dye surface.

The polymer encapsulation improved the wettability of C.I. disperse dye 60 because of introducing water soluble groups (—COOH) as shown in Figure 11. Compared with the water contact angle of 98.59° for the original disperse dye, the encapsulated disperse dye had a water contact angle of 32.54°. The changing of contact angles further confirmed that the poly(styrene-maleic acid) was successfully encapsulated onto disperse dye.

CONCLUSIONS

C.I. disperse dye blue 60 was successfully encapsulated with poly(styrene-maleic acid) by phase separation technique. The particle size of encapsulated disperse dye dispersion could greatly influence by the amount of poly(styrene-maleic acid), dropping speed of phase separation agent, disperse dye content in dispersion, and dispersing time. The optimal process conditions were that the mass ratio of poly(styrene-maleic acid) to disperse dyes was 20%, the dropping speed of phase separation agents was 7 mL/min, the content of dyes was 5–7.5%, and the dispersing time was 1.5 h. The encapsulated disperse dye dispersion prepared under above conditions had high stability to pH value, temperature, and centrifugal forces.

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