Properties of Copper Phthalocyanine Blue Encapsulated with a Copolymer of Styrene and Maleic Acid

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ABSTRACT: Copper phthalocyanine blue was encapsulated with a copolymer of styrene and maleic acid (PSMA) via a phase-separation technique, and a PSMA-encapsulated pigment dispersion was prepared. The effects of the additive on the stability of the dispersion were studied. Scanning electron microscopy photographs revealed that the particles in the PSMA-encapsulated pigment dispersion were more uniform than those in a PSMA-dispersed pigment dispersion. X-ray photoelectron spectroscopy provided evidence that the PSMA-encapsulated pigment acquired abundant carboxylic groups that could improve its wettability to water. Moreover, the results also indicated that the PSMA-encapsulated pigment dispersion had improved color strength, its stability could be greatly influenced by the pH value and ion strength, and its apparent viscosity changed little with an increase in the shear rate. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 211–215, 2010

Key words: dispersions; dyes/pigments; particle size distribution

INTRODUCTION

Organic pigments are widely used in coatings, inks, plastics, and some other industrial products for their superior performance with respect to hue, brilliance, color strength, transparence, and so on.[1] However, organic pigment dispersions prepared by conventional methods have poor stability in aqueous media because of their large particle sizes and broad size distributions.[2] To improve the quality of organic pigment dispersions, some dispersants have been developed. Polymeric dispersants are a class of specially designed and structured materials with good properties for stabilizing organic pigments.[3–7] In aqueous media, polymeric dispersants build voluminous shells and intensify the charges on the surface of an organic pigment; this can effectively prevent the flocculation and coagulation of the organic pigment in a dispersion.[3] At present, many polymeric dispersants with different structures have been synthesized and applied to organic pigment modification; these include, among others, AB diblock acrylic polymers[8] and graft polymeric dispersants.[9]

Encapsulating organic pigments with polymeric materials is another way of improving their quality.[10–13] In the last decade, varieties of techniques have been developed to encapsulate organic pigments with polymers. For instance, miniemulsion polymerization was used to encapsulate the pigment phthalocyanine blue in polystyrene latex particles.[14] A graft method was applied to pigment encapsulation through the introduction of active groups into a pigment on which several functional monomers were grafted via a diazotization reaction.[15,16] A layer-by-layer assembly technique was used for the encapsulation of organic pigments with nanosilica.[17,18] When a copolymer of styrene and maleic acid (PSMA), which consisted of hydrophilic and hydrophobic chains, was used as a shell material, the stability of an organic pigment dispersion was greatly improved. The effect of PSMA on the stability of the organic pigment dispersion was mainly reflected in the following two ways. First, the hydrophobic chain of PSMA was tightly encapsulated onto the organic pigment surface via van der Waals forces, and this greatly reduced its desorption; second, the hydrophilic chain was stretched into aqueous media, and this provided enough repulsive force among the organic pigment particles.[19]

To prepare a nanoscale organic pigment dispersion with high stability, in this study, the pigment
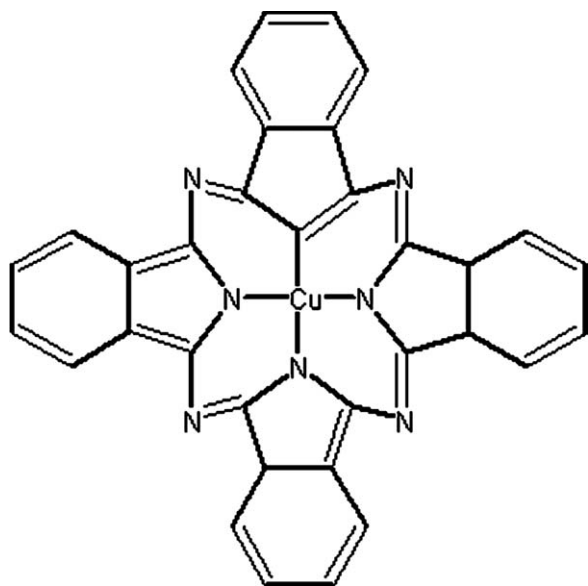
Figure 1 Chemical structure of copper phthalocyanine blue.

copper phthalocyanine blue was encapsulated with PSMA by a phase-separation technique, and the properties of the PSMA-encapsulated pigment dispersion were investigated.

EXPERIMENTAL

Materials

PSMA (weight-average molecular weight = 59,000, molar ratio of styrene to maleic acid = 1 : 1) was prepared and characterized in our previous work.[20] Hydrochloric acid (HCl; analytical-grade), sodium hydroxide (NaOH; analytical-grade), potassium chlo-

ride (KCl; analytical-grade), aluminum chloride (AlCl$_3$; analytical-grade), ethanol (analytical-grade), and glycerol (analytical-grade) were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Copper phthalocyanine blue (CI Pigment Blue, 15 : 3, purity = 99.8%; Fig. 1) was supplied by Wuxi Xinguang Co., Ltd. (Wuxi, China).

Preparation of the PSMA-encapsulated pigment dispersion

PSMA (10 g) was dissolved in acetone, and then 50 g of copper phthalocyanine blue was added to the solution under stirring. The mixture was dispersed at 4000 rpm for 1 h with an Ultra Turrax IKA T18 Basic instrument (IKA Instruments, Ltd., Staufen, Germany). Ethanol (250 mL) was dropped into the mixture at the rate of 10 mL/min. The mixture was centrifuged to produce a slurry. After the slurry was washed three times with distilled water, it was dried at 60°C to yield a PSMA-encapsulated pigment powder.

The dispersion was prepared with 10 g of the PSMA-encapsulated pigment powder and 90 g of distilled water. The pH value was adjusted to 8 with a NaOH solution (0.01 mol/L). The mixture was kept at 60°C for 30 min under stirring at the rate of 4000 rpm to yield the dispersion.

Preparation of the PSMA-dispersed pigment dispersion

PSMA (10 g) was hydrolyzed in 440 g of water; the pH value of the PSMA solution was adjusted to 8; and then 50 g of copper phthalocyanine blue was added to the solution, which was milled on a bead
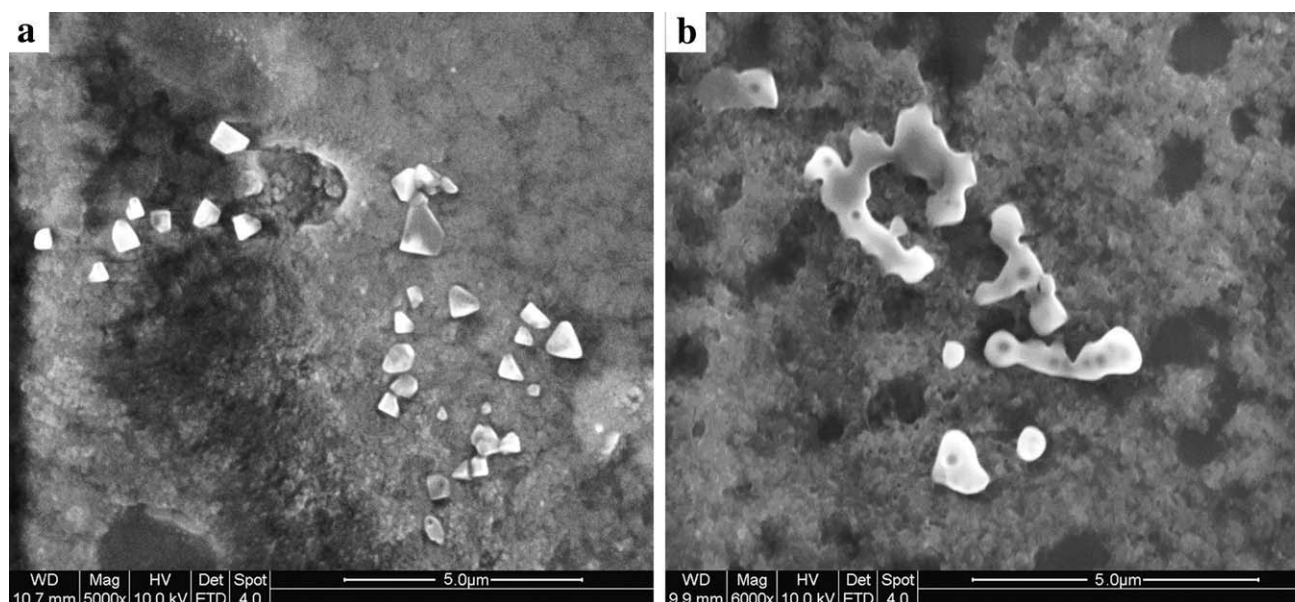

Figure 2 Scanning electron microscopy images of the particles in (a) the PSMA-encapsulated pigment dispersion and (b) the PSMA-dispersed pigment dispersion.

miller (with a 0.8-mm ZrO bead as the milling medium and a stirring speed of 2000 rpm) for 3 h.

Measurements

The dispersion was diluted with deionized water, then dried on a cover glass, and finally sputter-coated with gold. The pigment particle morphology was observed with an XL30 scanning electron microscope (Philips, Eindhoven, the Netherlands). The dispersion was diluted 2000 times, and its particle size distribution was measured with a Nano-ZS90 instrument (Malvern Instruments, Ltd., Worcestershire, England).

Samples were pressed with a pressing machine to form a slice. A DSA100 drop shape analysis system (Krüss Co., Hamburg, Germany) recorded the contact angles of the PSMA-encapsulated pigment and original pigment with respect to water at different pH values. Three replicates of each sample were made to obtain an average value.

Elemental analysis of the samples was determined with PHI-5702 and PE-2400 instruments (Perkin-Elmer Co., USA).

Different doses of KCl, $AlCl_3$, HCl, NaOH, ethanol, and glycerol were added to the PSMA-encapsulated pigment dispersion. After the mixture was stirred at 600 rpm for 20 min, it was sealed and stored at $-5°C$ for 24 h; then, it was moved into an oven at $60°C$ for another 24 h. The stability of the dispersion was measured by the change rate of the particle size (d) as follows:

$$d = \left(1 - \frac{|D_2 - D_1|}{D_1}\right) \times 100\% \qquad (1)$$

where D_1 and D_2 are the average particle sizes before and after the treatment of the dispersion, respectively. D_1 and D_2 were measured with a Nano-ZS90 instrument (Malvern Instruments). The dispersion was equilibrated at 25°C for 10 min, and its apparent viscosity was determined with a DV-III instrument (Brookfield Co., USA).

The dispersion was diluted 2000 times; its absorbance was measured with a UV-2100 spectrophotometer (Beckman Co., USA).
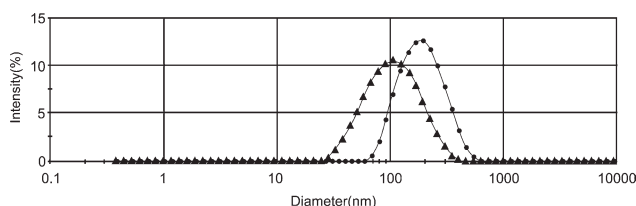

Figure 3 Particle size distribution of (▲) the PSMA-encapsulated pigment dispersion and (●) the PSMA-dispersed pigment dispersion.
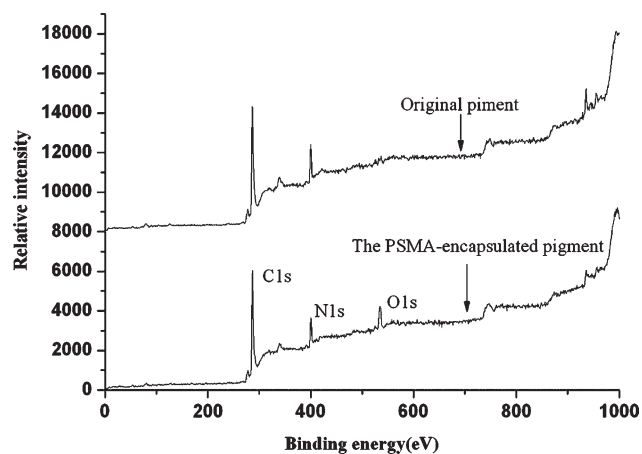

Figure 4 X-ray photoelectron spectroscopy of the PSMA-encapsulated pigment and original pigment.

RESULTS AND DISCUSSION

Morphology

Figure 2 shows that the particles of the PSMA-encapsulated pigment were distributed in aqueous media more uniformly than those of the PSMA-dispersed pigment in the dispersion. It was thought that the differences in the two dispersions might have been caused by a variety of interaction forces between PSMA and the pigment. In the PSMA-dispersed pigment dispersion, some PSMA was adsorbed onto the pigment by point adsorption; the stretched chain of PMSA was so long that it could easily bridge two or more particles, as shown in Figure 2(b). In the PSMA-modified pigment dispersion, however, PSMA was completely absorbed onto the pigment, so PSMA was hardly desorbed.

Particle size distribution

Figure 3 shows that the particle size of the PSMA-encapsulated pigment dispersion was mainly in the range of
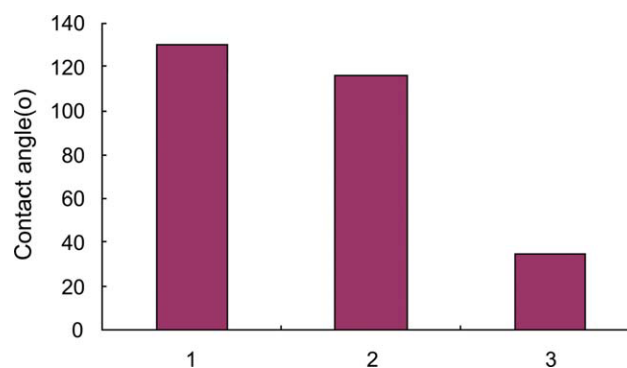

Figure 5 Water contact angles of (1) the original pigment, (2) the PSMA-encapsulated pigment with a pH value of 7, and (3) the PSMA-encapsulated pigment with a pH value of 10. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Electrolyte concentration (mmol/L)	KCl			AlCl$_3$		
	D_1 (nm)	D_2 (nm)	d (%)	D_1 (nm)	D_2 (nm)	d (%)
0.0	89.7	93.0	96	89.7	93.0	96
2.5	82.1	88.2	93	79.3	86.3	91
5.0	78.3	85.4	91	95.3	123.4	71
10.0	77.5	88.0	87	149.8	260.9	26
15.0	77.8	95.4	77	179.0	334.2	13

TABLE II
Effect of Alcohols on the Stability of the PSMA-Encapsulated Pigment Dispersion

Alcohol concentration (wt %)	Ethanol			Glycerol		
	D_1 (nm)	D_2 (nm)	d (%)	D_1 (nm)	D_2 (nm)	d (%)
0	89.7	93.0	96	89.7	93.0	96
5	86.5	88.7	98	89.3	85.81	96
10	88.4	91.7	96	90.3	93.0	97
15	89.6	86.5	97	91.7	88.4	96
20	90.5	93.1	97	88.5	85.7	96

40–130 nm, and its average particle size was about 89.7 nm; however, the particle size of the PSMA-dispersed pigment dispersion was mainly in the range of 60–190 nm, and its average particle size was about 200.7 nm.

Surface characterization and wettability

Figure 4 shows that the PSMA-encapsulated pigment was composed of carbon, nitrogen, and oxygen elements in addition to hydrogen (this was analyzed with an elemental analyzer). In comparison with the original pigment, the molar content of oxygen increased, and the amount of nitrogen was reduced in the PSMA-encapsulated pigment. These results implied that PSMA was encapsulated onto the pigment.

Figure 5 shows that the contact angle of the PSMA-encapsulated pigment with respect to water was smaller than that of the original pigment, especially at a higher pH value. The reason was that some —COOH on the PSMA-encapsulated pigment surface was hydrolyzed and turned into —COO— at a high pH value;[21] this could improve the wettability by water of the organic pigment.

Stability

Stability with respect to electrolytes

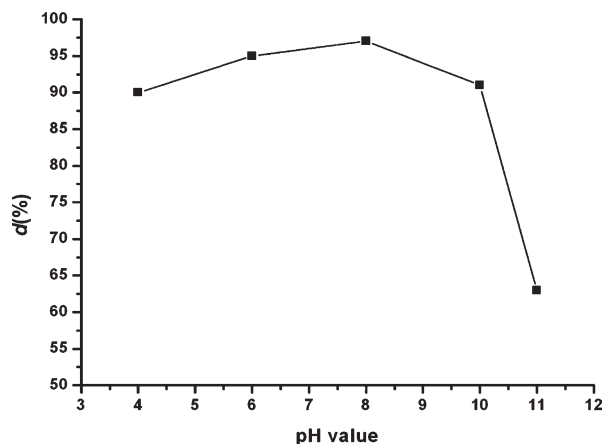Table I indicates that the particle size decreased with the NaCl concentration increasing, whereas it

decreased first and then increased sharply with an increase in the AlCl$_3$ concentration. In the case of electrolytes, ionization of electrolytes in the media played an important role in the stability of the dispersion, in which the produced counterions could compress the electric double layer so that the repulsive forces among the particles were reduced. As the electrolyte concentration increased, the counterion interaction became remarkable and thus led to decreased particle size and poor stability. In addition, Al^{3+} could react with —COO$^-$ to form an insoluble salt; as a result, a large particle size and poor stability resulted when the Al^{3+} concentration was higher than 2.5 mmol/L.

Stability with respect to the pH value

Figure 6 indicates that the stability of the dispersion increased with an increase in the pH value, but when the pH value was higher than 11, the stability decreased sharply. The hydrolysis degree of PSMA increased as the pH value increased, and so more —COO$^-$ was produced on the particle surface. The increased number of —COO$^-$ ions enhanced the repulsive forces among the particles, and this led to higher stability. However, when the pH value was high enough, most —COOH of PSMA reacted with OH$^-$, and then some PSMA dissolved into the water; this led to poor stability.

Stability with respect to alcohols

Table II shows that the alcohols had little effect on the stability of the dispersion, no matter how much ethanol or glycerol there was. These results indicated that the dispersion had good stability with respect to alcohols.

Fluidity

Figure 7 shows that the apparent viscosity of the PSMA-encapsulated pigment dispersion was lower than that of the PSMA-dispersed pigment dispersion and did not change at different shear rates. In the former, PSMA was completely encapsulated onto the pigment, and the stretched chain was short, so
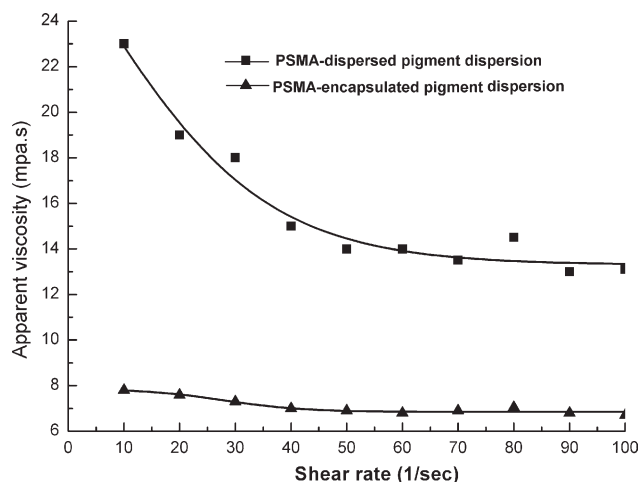

Figure 6   Effect of the pH value on d.

Figure 7 Effect of the shear rate on the apparent viscosity of the PSMA-encapsulated pigment dispersion and PSMA-dispersed pigment dispersion (pigment weight content = 10%).

there was no obvious fluctuation in the apparent viscosity as the shear rate increased. In the latter, PSMA was adsorbed onto the pigment by point adsorption; the stretched chain of PMSA was so long that the apparent viscosity was greatly increased. With the shear rate rising, the stretched chain of PSMA was uniformly aligned, and this resulted in the decrease in the apparent viscosity; when the shear rate was high enough that all PSMA was aligned, the apparent viscosity did not change anymore.

Absorbency of the dispersion

Figure 8 reveals that the PSMA-encapsulated pigment dispersion exhibited enhanced absorbency in comparison with the PSMA-dispersed pigment dis-
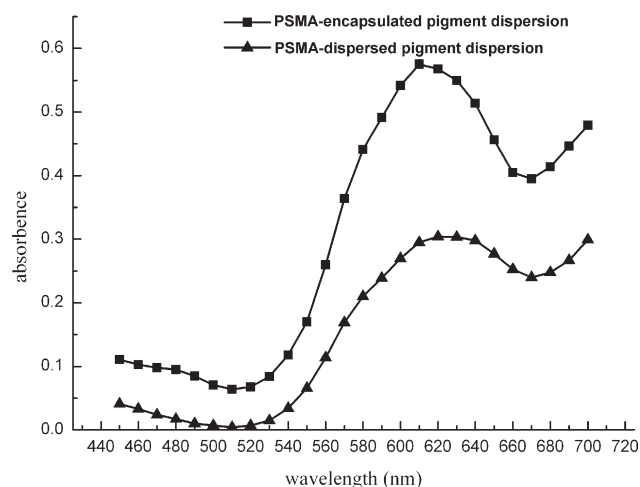

Figure 8 Absorbency of the PSMA-encapsulated pigment dispersion and PSMA-dispersed pigment dispersion.

persion. It is known that the smaller the particle size is, the more light a dispersion will absorb.[22] The experimental results showed that the average particle sizes of the PSMA-encapsulated pigment dispersion and PSMA-dispersed pigment dispersion were 89.7 and 200.7 nm, respectively, so improved color depth was supplied to the dispersion. In addition, λ_{max} of the PSMA-encapsulated pigment dispersion was lower than that of the PSMA-dispersed pigment dispersion, and this indicated that the color of the former was purer than that of the latter.

CONCLUSIONS

The PSMA-encapsulated pigment dispersion was prepared via a phase-separation technique. The wettability of the PSMA-encapsulated pigment with respect to water was improved, especially at a high pH value. The apparent viscosity of the PSMA-encapsulated pigment dispersion was lower than that of the PSMA-dispersed pigment dispersion. The stability of the PSMA-encapsulated pigment dispersion was greatly influenced by electrolytes and pH values. The PSMA-encapsulated pigment dispersion could provide superior color strength for substrates.

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