

Colloidal Properties of Copolymer-Encapsulated and Surface-Modified Pigment Dispersion and Its Application in Inkjet Printing Inks

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ABSTRACT: A styrene–maleic acid copolymer (PSMA)-encapsulated 2-[(2-methoxy-4-nitrophenyl) azo]-N-(2-methoxyphenyl)-3-oxobutyramide (PY74) dispersion was prepared by the phase-separation technique. A surface-modified PY74 dispersion was prepared with PSMA sodium as a dispersant by the milling method. Furthermore, the two dispersions were applied to formulate pigment inks. The colloidal properties of these two dispersions were compared. The printing and color performance of the prepared inks were also investigated. The results show that the PSMA-encapsulated PY74 dispersion with a small particle size had higher stabilities of NaCl concentration, pH value,

and temperature than the surface-modified PY74 dispersion. The apparent viscosity of the PSMA-encapsulated PY74 dispersion changed little, while it changed greatly in the surface-modified PY74 dispersion with an increase of the shear rate from 10 to 100 s⁻¹. The ink printing and color performance of printed fabrics indicated that the PSMA-encapsulated PY74 dispersion was more suitable for the preparation of inkjet printing ink than the surface-modified PY74 dispersion. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 371–376, 2011

Key words: dispersions; dyes/pigments; nanoparticle

INTRODUCTION

Textile inkjet printing has attracted more and more attention for its high resolution, low pollution, and short run length. Pigment ink is suitable for all sorts of textiles and has become the main colorant in this technology.^{1,2} To prepare pigment inks with low viscosity, small particle size, and high stability, it is important to develop a method for the preparation of nanoscale pigment dispersion.

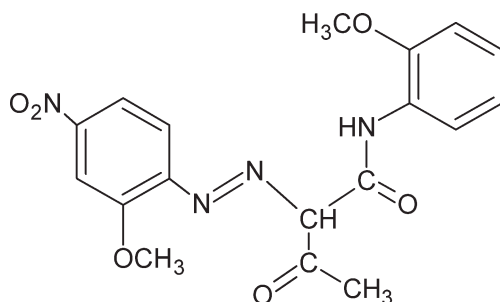
However, as we know, most organic pigments are hard to be wetted and dispersed in aqueous media for their low polarity, and need to be modified before application.³ The milling of organic pigments with the aid of a dispersant is a common modification method. Polymeric dispersants are a class of specially designed, structured materials and show good properties in the stabilization of organic pigments.^{4–8} In aqueous media, they build a

voluminous shell around organic pigment particles and intensify the charges on the pigment surface, which can greatly improve the stability of the pigment dispersion. Encapsulation of organic pigments into polymers is another important modification method.^{9–11} In the last decade, a variety of techniques has been developed, including miniemulsion polymerization,^{12,13} grafting,^{14,15} layer-by-layer assembly,^{16,17} and phase separation.¹⁸

Although there are so many methods for the preparation of nanoscale organic pigment dispersions, a method for the preparation of pigment dispersions with small particle sizes and excellent stability for inkjet printing ink is still a research hotspot. In our previous study, we used quinacridone and phthalocyanine as colorants and prepared styrene–maleic acid copolymer (PSMA)-encapsulated pigment dispersions by the phase-separation technique.¹⁸ In this study, we chose the azo pigment 2-[(2-methoxy-4-nitrophenyl) azo]-N-(2-methoxyphenyl)-3-oxobutyramide (PY74) as a colorant and prepared pigment dispersions by the phase-separation technique and milling method. The colloidal properties of the two dispersions were compared. Furthermore, the dispersions were used to formulate pigment inks; then, the printing and color performance of the pigment inks were also investigated.

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Scheme 1 Chemical structure of PY74.

EXPERIMENTAL

Materials

PSMA (made in our laboratory, number-average molecular weight = 9000, molar ratio of styrene to maleic acid = 1),¹⁹ hydrochloric acid (HCl; analytical grade) and sodium hydroxide (NaOH; analytical grade) were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). PY74 (purity = 99.8%, Scheme 1) was supplied by Wuxi Xinguang Co., Ltd. (Wuxi, China). Distilled water was used in all of the experiments.

Preparation of the PSMA-encapsulated PY74 dispersion

PSMA (10 g) was dissolved in 200 g of acetone, and then, 50 g of PY74 was added to the solution. The mixture was dispersed by an Ultra Turrax IKA T18 Basic instrument (IKA Instruments, Ltd., Staufen, Germany) at 4000 rpm for 1 h, and then, 250 mL of water (pH < 5) was dropped into the mixture at a rate of 10 mL/min. The mixture was centrifuged to obtain a slurry. The slurry was washed three times with distilled water and then dried at 60°C to obtain a PSMA-encapsulated PY74 powder.¹⁸ The PSMA-encapsulated PY74 powder (10 g) was added to 90 g of distilled water. Then, the pH value of the mixture was adjusted to 8 by an NaOH solution (0.01 mol/L), and last, the mixture was stirred at a rate of 4000 rpm for 30 min at 60°C.

Preparation of the surface-modified PY74 dispersion

PSMA (10 g), distilled water (440 g), and a corresponding amount of NaOH was mixed at 60°C for some time to obtain a uniform solution. Then, the pH value of the solution was adjusted to 8. Finally, 50 g of PY74 was added to the solution and milled on a bead miller (with 0.8 mm ZrO₂ beads as a milling medium, stirring speed = 2000 rpm) for 3 h.

Preparation of the inkjet printing inks

The inkjet printing inks were prepared by PSMA-encapsulated and surface-modified PY74 dispersions. The formulation in a weight basic was as follows: 50% PY74 dispersion, 15% glycerol, 10% ethylene glycol monomethyl ether, 2% urea, 1.5% Tween-80, and 21.5% distilled water. These components were mixed under stirring at 300 rpm until a homogeneous dispersion was obtained. After they were through a 0.5- μ m pore filtering sieve, the inks were prepared and loaded on an inkjet printing machine (Mimaki JV4-180 piezoelectric inkjet printer, Japan, Shinagawa, Tokyo).

Measurement

Particle size and ζ potential

The dispersion was diluted 2000 times. The particle size, size distribution, and ζ potentials were measured by a dynamic light-scattering method in a Malvern laser-scattering analyzer (Nano-ZS90, Malvern Instruments Co., Ltd., Worcestershire, England).

Contact angle

The samples were pressed with a pressing machine to form slices. A drop shape analysis system (DSA100, Krüss Co., Hamburg, Germany) recorded the contact angles of the sample with distilled water.

Stability

Stability to NaCl. The dispersion (0.1 g) was added to an NaCl concentrated solution and mixed for 5 min and then stored at room temperature for 6 h. The change rate of particle size (d) of the dispersion was calculated by eq. (1):

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

where D_2 is the particle size before treatment and D_1 is the particle size after treatment.

Stability to pH value. HCl solution (1 wt %) and NaOH solution (1 wt %) were used to adjust the pH value of the dispersion; then, the dispersions were stored at room temperature for 6 h, and d was calculated according to eq. (1).

Stability to temperature. The dispersion was sealed and stored at different temperature for 6 h, and then, d was calculated according to eq. (1).

Apparent viscosity

The viscosity of the dispersion was measured with a spindle-type viscometer (Brookfield DV-III, Massachusetts) at 25°C with shear rates from 10 to 100 s⁻¹.

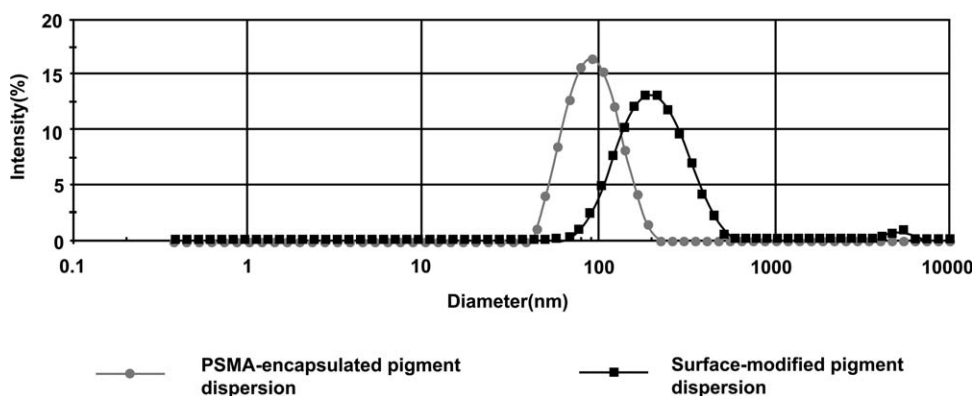


Figure 1 Particle size distribution of the dispersion.

Physical properties of the PY74 inks

The PY74 ink was evaluated for its properties in terms of viscosity, surface tension, particle size, and stability. The viscosity of the inkjet inks was measured with a spindle-type viscometer at 25°C with shear rate 30 s⁻¹. The surface tensions of the inks were measured with a ring method in the drop shape analysis system (DSA100). The particle size was measured by a dynamic light-scattering method. The centrifugal stability and freeze-thaw stability of the PY74 inks were measured according to ref. 18.

Centrifugal stability

After the dispersion was centrifuged at 3000 rpm for 30 min, the super dispersion in the centrifugal tube was taken out and diluted by distilled water 2000 times. The wavelength of maximum absorbance was found at 420 nm by a spectrophotometer, and the absorbance was recorded as A_{30} . The relative absorbance (r_{30}) was calculated according to eq. (2):

$$r_{30} = \frac{A_{30}}{A_0} \times 100\% \quad (2)$$

where A_0 is the absorbance (420 nm) of the dispersion before centrifugation. r_{30} could reveal the stability of the dispersion against weight.

Freeze-thaw stability

The dispersion was sealed and kept at -5°C for 24 h and then put into an oven at 50°C for another 24 h. The change rate of particle size (S_d) was calculated according to eq. (3):

$$S_d = \frac{|d_0 - d_T|}{d_0} \times 100\% \quad (3)$$

where d_0 is the starting particle size of the dispersion and d_T is particle size of the dispersion after the freeze-thaw treatment.

Printing performance of the inks and color performance of the printed fabrics

The printing performance of the inks was tested on the Mimaki JV4-180. The clogging nozzle rate (B) was calculated according to eq. (4):

$$B = \frac{C_1}{S} \times 100\% \quad (4)$$

where C_1 is the amount of clogged nozzle and S is the sum of the nozzle on the print head. The cotton fabrics (24 × 24 cm²) was printed by the Mimaki JV4-180. The color strength (K/S values) of printed fabrics was determined using the Kubelka-Munk equation and measured by a colorimeter (Xrite-8400, Granville) under illuminant D65 with the 10 standard observer. The rubbing fastness and washing fastness were tested according to AATCC standard 8-2001, 61.

RESULTS AND DISCUSSION

Particle size distribution

Figure 1 shows that the particle size of the PSMA-encapsulated PY74 dispersion was smaller, and the size distribution was narrower than that of the surface-modified PY74 dispersion. The PY74 could be wetted and dispersed more easily in acetone than in water because of its low polarity.³ After encapsulation, the PSMA layer hindered the PY74 to combine with each other; this led to a small particle size and a narrow particle size distribution.

Contact angle and ζ potentials

Table I shows that the absolute ζ potential of the PSMA-encapsulated PY74 was smaller than that of the surface-modified PY74. Unlike the surface-modified PY74 dispersion, in the PSMA-encapsulated PY74 dispersion, some -COOH that was absorbed on the PY74 surface would not react with OH⁻; this led to small charges on the PY74 surface.

TABLE I
Contact Angle and ζ Potentials

Sample	ζ potential (mV)	Contact angle ($^{\circ}$)
PSMA-encapsulated pigment	-30.4	67.4
Surface-modified pigment	-37.9	—
Original pigment	—	143.7

Table I also shows that the contact angle with distilled water of the PSMA-encapsulated PY74 was smaller than that of the original PY74, which indicates that the wettability of PY74 to distilled water was improved when $-\text{COOH}$ was introduced onto the PY74 surface.

Stability and rheological behavior

Figure 2 shows that the change rate of particle size increased with increasing NaCl concentration, especially in the surface-modified PY74 dispersion. Na^+ compressed the double-electric layer of PY74, and the compressing effect increased with an increase in Na^+ concentration, which resulted in a poor stability to NaCl concentration. Moreover, the action mode between PSMA and PY74 was different in these two dispersions.¹⁸ The desorption of PSMA from PY74 was small for complete absorption in the PSMA-encapsulated PY74 dispersion and large for partial absorption in the surface-modified pigment dispersion. Therefore, the double-electric layer of the surface-modified PY74 was more affected by the NaCl concentration; this led to a poor stability.

Figure 3 indicates that the change rate of particle size in the two dispersions increased first and then decreased with increasing pH value, and the change

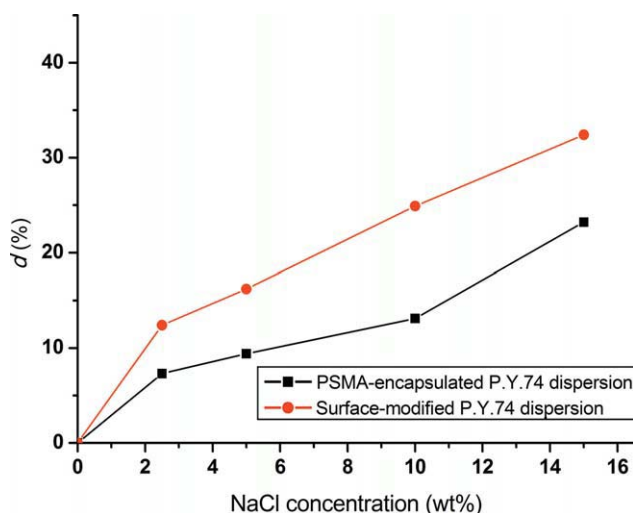


Figure 2 Effect of the NaCl concentration on the stability of the dispersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

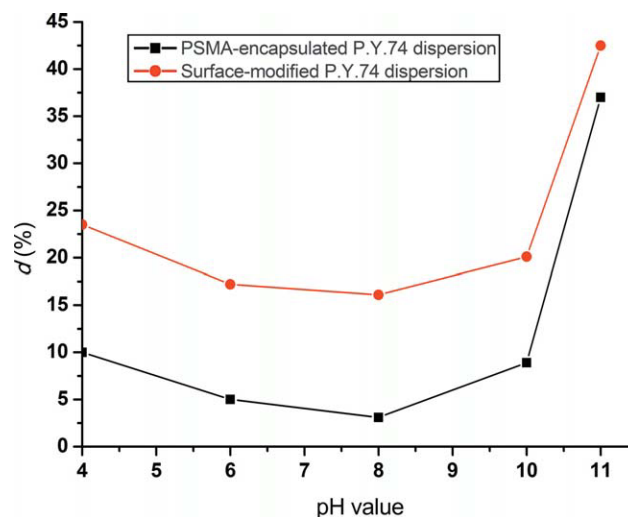


Figure 3 Effect of the pH value on the stability of the dispersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate of particle size in the PSMA-encapsulated PY74 dispersion was smaller than that in the surface-modified PY74 dispersion. The higher the pH value of the dispersion was, the greater was the amount of $-\text{COOH}$ that would react with OH^- and the more charges were produced on the PY74 surface. Therefore, the repulsive forces among the PY74 increased, and this led to an excellent stability to pH value. On the contrary, when the pH value was high enough, the neutralization of $-\text{COOH}$ and OH^- reached its maximum; thus, the solubility of PSMA increased, and the desorption of PSMA from PY74 also increased, which resulted in a poorer stability.

Figure 3 also shows that the particle size changed sharply when the pH value was higher than 10,

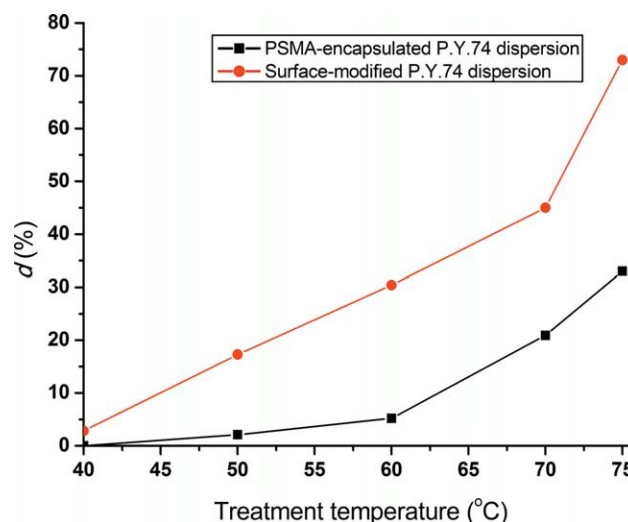


Figure 4 Effect of the treatment temperature on the stability of the dispersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

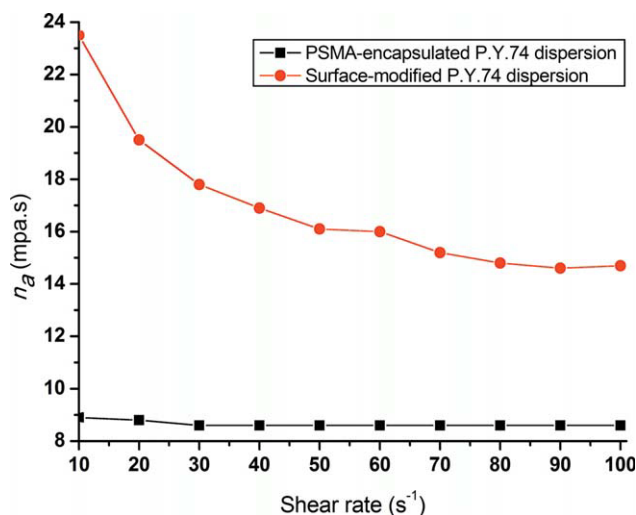


Figure 5 Effect of the shear rate on the apparent viscosity of the dispersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which indicated that the stability of the dispersion was destroyed and the particles combined with each other. In addition, the attractive forces between PSMA and PY74 in the surface-modified PY74 dispersion was smaller than in the PSMA-encapsulated PY74 dispersion; therefore, the desorption of PSMA from PY74 in the surface-modified PY74 dispersion occurred more easily at the same pH value. This led to a poorer stability.

Figure 4 indicates that the change rate of particle size in the two dispersions was small when the treatment temperature was in the range 40–60°C and great when the treatment temperature was higher than 60°C. Moreover, the change rate of particle size in the PSMA-encapsulated PY74 dispersion was smaller than that in the surface-modified PY74 dispersion when they were treated at the same temperature. The desorption of PSMA from PY74 increased with increasing temperature; this led to a large change rate of particle size in the dispersion. Moreover, as analyzed previously, the attractive forces among PSMA and PY74 were larger in the PSMA-encapsulated PY74 dispersion than that in the surface-modified PY74 dispersion; this led to the small change rate of particle size in the former dispersion.

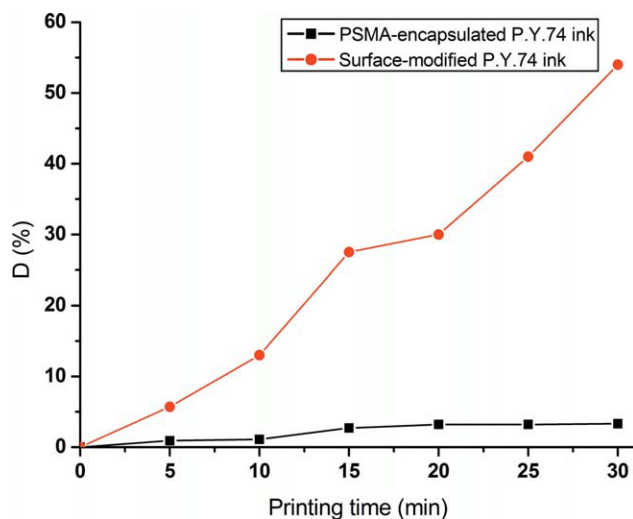


Figure 6 Printing performances of the pigment ink. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows that apparent viscosity of the PSMA-encapsulated PY74 dispersion was lower than surface-modified PY74 dispersion and was quite stable, regardless of the change of shear rate from 10 to 100 s⁻¹. In the latter, some PSMA dissolved in aqueous media; thus, the viscosity increased greatly. Moreover, the chain of PSMA was uniformly aligned under increasing shear rate; this led to an obvious decrease in the viscosity under shear rate.

Printing and color performance of the pigment ink

The physical properties of the inks made from the PSMA-encapsulated and surface-modified PY74 dispersion are shown in Table II. The stability of the two pigment inks was excellent, which indicated that the additives had good compatibility with the dispersion.

Figure 6 indicates that the nozzle-clogging rate of the ink made from the PSMA-encapsulated PY74 dispersion was lower than that of the surface-modified PY74 dispersion. These differences might have been due to the larger particle size and the easier clogging the nozzle of the printhead. Moreover, the long stretched chain and poor stability of the surface-modified PY74 ink might have also caused poor printing performance.

TABLE II
Physical Properties of the Pigment Inks

Pigment ink	Particle size, <i>D</i> (nm)	Apparent viscosity, η_a (mPa s)	Surface tension, σ (mN/m)	Stability (%)	
				Centrifugal	Freeze-thaw
Surface-modified pigment ink	226.0	6.24	28.9	83	26
PSMA-encapsulated pigment ink	110.8	4.72	29.7	91	4

TABLE III
Color Performance of the PSMA-Encapsulated PY74 Ink and Surface-Modified PY74 Ink

Sample	K/S value	Washing fastness (grade)	Rubbing fastness (grade)	
			Dry	Wet
PSMA-encapsulated pigment ink	4.2	2	2–3	2
Surface-modified pigment ink	3.9	1	1–2	1

Table III shows that the color strength, rubbing fastness, and washing fastness of the printed fabrics with the PSMA-encapsulated PY74 ink were superior to those of the surface-modified PY74 ink. The smaller the PY74 particle was, the more surface area was produced; this greatly improved the color strength of the ink.²⁰ The fabrics that were printed by the PSMA-encapsulated PY74 ink had better fastness; this might have been due to the smaller particle size and better penetrability; as a consequence, lots of PY74 particles could move and enter the inner fabrics. Second, the PSMA that encapsulated the PY74 surface formed a layer at high temperature, which greatly improved the fastness of the printed fabrics. Third, a smaller particle size and a smoother coating layer formed on the fabrics.

CONCLUSIONS

The phase-separation method was suitable for the preparation of nanoscale PY74 dispersions. The stability to NaCl concentration, pH value, and temperature of the PSMA-encapsulated PY74 dispersion were superior to those of the surface-modified PY74 dispersion. The rheological behavior of the PSMA-encapsulated PY74 dispersion was closer to Newton fluidity than that of the surface-modified PY74

dispersion. The nozzle-clogging rate of the PSMA-encapsulated PY74 ink was lower than that of the surface-modified PY74 ink when the Mimaki JV4-180 printer was used. The color strength, rubbing fastness, and washing fastness of the fabrics were better when they were printed with the PSMA-encapsulated PY74 ink.

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