

Preparation of waterborne nanoscale pigment dispersions for formulations of inkjet inks

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Abstract

Textiles Inkjet printing as a new dyeing method with higher resolution, lower pollution and shorter run length has attracted more and more people's attention. Pigment inks have become one of the main colorant materials in this technology for its excellent light fastness and suitable to all sorts of textiles. However most of organic pigments with low polarity are hard to be wetted and dispersed in aqueous media, therefore the organic pigments should be modified before their application. In this paper, waterborne nanoscale pigment dispersion including Copper Phthalocyanine blue (P.B.15:3), Quinacridone red pigment (P.R.122), and Monoazo yellow pigment (P.Y.14) have been prepared by phase separation method and direct milling with dispersants method respectively. The properties (stability, particle size and apparent viscosity) of dispersion which prepared by different method were compared. The results show that the pigment dispersion has higher stability to alcohols, temperature and storage, and also lower viscosity; the phase separation method was more suitable to preparation of pigment dispersion for formulations of inkjet inks than direct milling with dispersants method; TEM photo indicated that the pigment particles were uniformly distributed in aqueous media and the XRD curves indicated that the pigment crystal was not changed after encapsulation by phase separation method.

Introduction

Textiles inkjet printing as a new dyeing method with higher resolution, lower pollution and shorter run length has attracted more and more people's attention. Pigment inks with excellent light fastness and suitable to all sorts of textiles have become one of the main colorant materials in this technology^[1]. However, most of organic pigments with low polarity always tend to be aggregation or coagulation and were hard to be wetted and dispersed in aqueous media, so the organic pigments should be modified before their application. The direct milling pigment with dispersants and the encapsulation pigment with polymer are the two common methods for pigment modification.

Polymeric dispersants have proven good properties in stabilizing pigments in aqueous media. These good properties include higher stability, smaller particles size, and less moisture sensitivity. Hydrophobic chain would attach to organic pigment surface by Van Der Waals force and hydrophilic chain would build a voluminous shell around particles and intensify the charges on the surface when dispersing in water^[2]. Unlike low molecular dispersants, the polymeric dispersants could always stay onto the pigment surface even if some parts of the chain are desorbed. In recent years, different structure of polymeric dispersants have been synthesized and applied in the pigment dispersion, especially for diblock polymers^[3] and graft polymers^[4]. Encapsulated pigments which use pigments as core and polymeric materials as shell could

also facilitate to improve pigments processing and its qualities. In the last decade, a variety of encapsulation techniques, such as emulsion polymerization and graft technique have been developed to modify pigments^[5-7]. Moreover, there also have been reported some others successful encapsulations for titanium dioxide, colloidal silica and carbon by polymeric materials, the methods include sedimentation, in situ polymerization, evaporation solvent, and so on^[8-11].

Although much research focuses on the pigment dispersion, it is still a big challenge to prepare stable waterborne nanoscale organic pigment dispersion for inkjet printing inks. In our research waterborne nanoscale pigment dispersion including Copper Phthalocyanine blue (P.B.15:1), Quinacridone red pigment (P.R.122), and Monoazo yellow pigment (P.Y.14), which utilized styrene-maleic acid copolymer as encapsulation layer, has been prepared by different methods. The stability, particle size and apparent viscosity of the dispersions were measured. Moreover, the shape of pigment particles was observed by TEM, and the pigment crystal was measured by XRD.

Experimental

Raw materials

Copolymer of styrene and maleic acid (PSMA, Molar ratio of maleic acid was about 0.56, Mn=9000, Nanocolorants and Digital Printing R&D Centre of Jiangnan University), Powder of P.R.122, P.B.15:3, P.Y.14 (Purity was 99.7%, 99.8%, 99.3% respectively, Wuxi Xinguang Chemical Industry Co., Ltd), Cotton textiles (120g/m², Dongguan Xinlong textile Industry Co., Ltd).

Preparation of pigment dispersion by phase separation method

Pigment dispersion of P.B.15:3, P.R.122 and P.Y.14 dispersion were prepared by the method described in our previous work^[12,13]. 10g PSMA and 440g media were mixed together, and then 50g pigment powder was added into the solution under stirring. The mixed slurry was dispersed by Ultra Turrax IKA T18 Basic (IKA Instruments Ltd) at 4000r/min for 1 hour, after that 250g distilled water were added into the slurry, PSMA slowly deposited and encapsulated onto the pigment surface. The mixture was filtered under vacuum, washed with distilled water and dried at 60 degree Celsius for 24 hours, and then encapsulation pigment powder was obtained.

The dispersion was prepared with 5g waterborne nanoscale pigment and 95 gram distilled water, adjusted pH value to 8 using sodium hydroxide solution (0.01M) and stirred by Ultra Turrax IKA T18 Basic for 30min.

Preparation of pigment dispersion by direct milling with dispersants

10g styrene-maleic acid sodium copolymers dissolved in 440g distilled water, adjusted pH value to 8, and then 50g pigment (WuXi XinGuang provided) was added into the solution under stirring. The slurry was transferred to Muller and dispersing for 6 hours.

Particle size

Pigment dispersions were diluted to 2000 times and balanced at 25 degree Celsius for 5 minutes, and then particle size was measured by Nano-ZS90 (Malvern Instruments Ltd, England).

Stability of pigment dispersion

Centrifuging stability^[12]: Pigment dispersion was centrifuged at 3000 r/min for 60 minutes, then 0.03g supernatant in the centrifugal tube was taken out and diluted to 2000 times with distilled water. Absorbency (A_{60}) of pigment dispersion was measured and the relativity absorbency r_{60} was calculated according to formula (1).

$$r_{60} = \frac{A_{60}}{A_0} \times 100 \% \quad (1)$$

Where A_0 is the absorbency of the dispersion before centrifuged, r_{60} can reveal the stability of dispersion which caused by weight, the larger r_{60} , the higher stability of dispersion is.

Freeze-thaw stability^[13]: the pigment dispersion was sealed and placed at -5 degree Celsius for 12 hours and then put into oven at 50 degree Celsius for another 12 hours, the changing rate of particle size (S_T) was calculated according to formula (2).

$$S_T = \frac{|d_0 - d_T|}{d_0} \times 100 \% \quad (2)$$

Where d_0 is the starting particle size of dispersion, d_T is particle size of pigment dispersion after freeze-thaw treatment, the smaller T_p , the higher stability to temperature of dispersion is.

Stability to alcohols: 20g glycerol and 80g pigment dispersion were mixed together to prepare the pigment mixture which alcohols content was reached to 20% and pigment content was about 4%. The mixture was diluted to 2000 times and then the changing rate of particle size to alcohols (S_A) was measured according to above method.

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

Where d_0 is the starting particle size of dispersion, d_T is particle size of pigment dispersion after adding alcohols. The smaller S_A , the higher stability to alcohols of dispersion is.

Apparent viscosity of pigment dispersion

Pigment dispersion was balanced at 20 degree Celsius for 5 minutes, and apparent viscosities were tested by DV- Ultra programmable rheometer (Brookfield, American).

Dyeing cotton textile and its K/S value

10 gram pigment dispersion (5% pigment weight content) and 90 gram deionized water were mixed and stirred for 30 minutes to prepare the dyeing bath. The cotton fabrics were dyeing with EHP 350 pad machine, the whole processes were done as follows:

Two-dip-two-pad (wet pickup, 70%)→dry (60 degree Celsius)→bake (120 degree Celsius, 3min). K/S values were measured with xrite-8400 colorimeter.

Particle shape of encapsulation pigment by phase separation method

The shape of pigment particles which prepared by phase separation method were observed by Transmission Electron Microscope (TEM, H-7000, Japan).

X-ray diffraction of encapsulation pigment by phase separation method

Effect diffraction angle on diffraction intensity of encapsulated pigments were determined by XRD (ARL-X ' TRA) using CuKa as radiation at a wavelength of $\lambda=1.54183\text{\AA}$ respectively. The generator settings were 40 kV and 35mA. Diffraction data were collected over a 15min range of 5°-45°, with a step width of 0.02° and a counting time of 5s per step. Sample preparation included spreading the powders into the holder (about 3 mm thick) and pressing slightly with a glass slide to ensure a flat surface.

Results and discussions

Properties of pigment dispersion prepared by different method

Table 1 properties of pigment dispersion prepared by phase separation method^a

| Pigment dispersion | D (nm) | η (mpa.s) | Stability (%) | | |
|--------------------|--------|----------------|---------------|-------|-------|
| | | | r_{60} | S_T | S_A |
| P.R.122 | 104.6 | 3.25 | 100 | 0.38 | 0.49 |
| P.B.15:3 | 82.7 | 3.78 | 100 | 0.00 | 0.17 |
| P.Y.14 | 75.8 | 4.20 | 98 | 0.12 | 0.30 |

^aNote: the weight of pigment content was about 5%.

Table 2 properties of pigment dispersion prepared by direct milling with dispersant method^a

| Pigment dispersion | D (nm) | η (mpa.s) | Stability (%) | | |
|--------------------|--------|----------------|---------------|-------|-------|
| | | | r_{60} | S_T | S_A |
| P.R.122 | 166.7 | 7.25 | 96 | 0.60 | 0.61 |
| P.B.15:3 | 125.7 | 6.78 | 93 | 0.25 | 0.26 |
| P.Y.14 | 180.2 | 11.20 | 95 | 0.89 | 0.47 |

^aNote: the weight of pigment content was about 5%.

Properties of pigment dispersion are more close to modification method. Pigment dispersion was prepared by phase separation method and direct milling with dispersants method respectively; the properties of pigment dispersion were measured and listed in table 1 and table 2.

Compared with table 1 and table 2, it may be concluded that the phase separation method was superior to direct milling with dispersants method for preparation of pigment dispersion in our experimental. In phase separation method, the pigment aggregation or coagulation would be broken under shear forces at first, and then the dispersed pigments were encapsulated by PSMA. PSMA that encapsulated the pigment would greatly reduce the attraction forces among pigment particles and also improve the dispersing efficiency, thus led to smaller particle size and higher stability. In the direct milling with dispersants method, the chain of PSMA would be desorbed under certain conditions, thus led to poorer stability. In addition, not all PSMA could adsorb onto the pigment and some would dissolve into the media, resulting in increase the apparent viscosity and reducing the dispersing efficiency. This difference can be described by schematic 1.

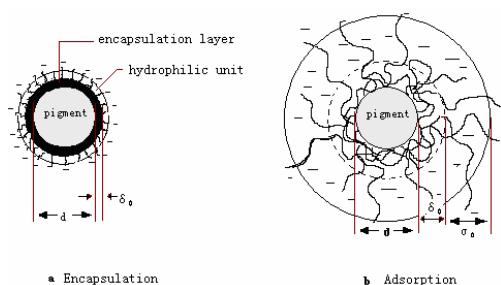


Fig.1 Schematic of interaction between pigment particles and polymeric dispersants. *d*: diameter of pigment particle, δ_0 : encapsulation layer, δ_a : Solvated layer.

Moreover, the color properties were also different when the pigment dispersions were prepared by different method.

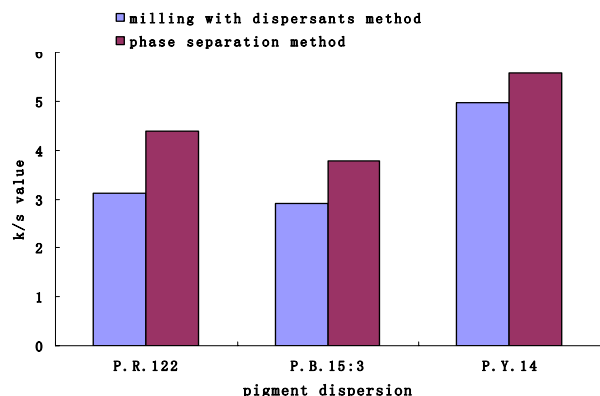


Fig.2 Effect of modification method on *k/s* value of dyeing cotton textile. The weight content of pigment was about 0.5%.

Fig.2 revealed that with the same dosage of pigment, the *K/S* value of dyed cotton fabrics was higher when the dispersions were prepared by phase separation method.

The reason for this may be attributed to the pigment dispersion with different particle size. Particles with smaller size were easier to adsorb onto the cotton textiles. In addition, the smaller particles, and the more surface area would create, which results in improving the cover area.

The shape of particle and its distribution of encapsulated pigment

In order to acquire the shape information of pigment particles which prepared by phase separation method, the pigment particles were observed by TEM and its distribution were tested by DLS method.

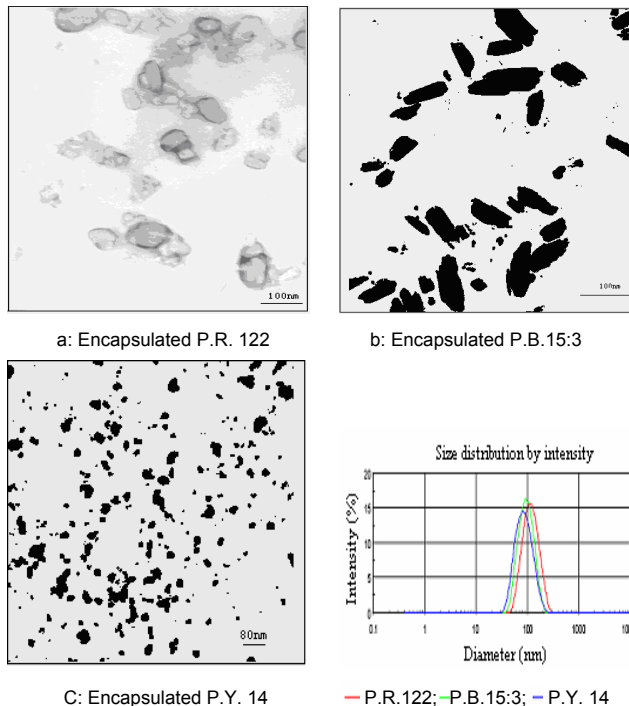


Fig.3 TEM photo of pigment **Fig.4** Size distribution of encapsulated pigment.

Fig.3 and Fig.4 indicates that pigment particle sizes were uniformly dispersed in aqueous media, the particle shape of P.R.122, P.B.15:3, P.Y.14 was ellipse, club-shaped and roundness respectively. In aqueous media, hydrophilic chain of PSMA would build a voluminous shell and intensify the charges of particles, which could effectively hinder its attraction each other, thus the pigments could stably and uniformly be dispersed in aqueous media.

XRD of encapsulated pigment

The diffraction is a special behavior when the X-ray is scattered by the crystal. The direction of diffraction will be different when pigment crystal was changed. It is well known that the color performances of pigment dispersion were mainly determined by the molecular structure, and were also affected by crystal structure.

Fig.5 revealed that the curves shapes of encapsulation pigments were similar to that of starting materials, and the peaks appear almost at the same position, which told us that the crystal structure was not changed after encapsulation. That is to say the pigment crystal was not changed during pigment processing.

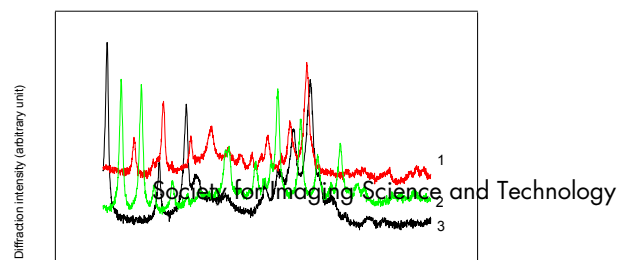


Fig.5 XRD of encapsulated pigment; 1-P.Y. 14, 2-P.B.15:3, 3-P.R. 122

Conclusions

The pigment dispersion prepared in our experimental has higher stability to alcohols, temperature and centrifugal force, and also lower viscosity. The phase separation method was superior to preparation waterborne nanoscale pigment dispersion than direct milling with dispersants method. The pigment particles were uniformly dispersed in aqueous media and the pigment crystal was not changed by phase separation method. Pigment dispersion which prepared by phase separation method can be applied in inkjet printing inks.

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Author Biography

Associate professor Shaohai Fu received his PhD in textiles from Jiangnan University (2006). Since then he has worked southern yangtze University. His work has focused on the development of inkjet printing pigmented inks.