Preparation of polymer-encapsulated pigment for formulations of inkjet inks

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Abstract

In textile inkjet printing, pigment inks have become one of the main colorants because of its excellent light fastness and suitable to all sorts of fibers. Pigments are applied as aqueous dispersion due to their water insoluble. Encapsulation of pigments with polymer can protect them from agglomeration and unwanted environmental influences such as UV radiation or acid and alkali. The encapsulation leads to better storage stability, color stability and durability, and the film formation can be adjusted. In this paper, organic pigments (P.B.65, 73, 14, and 83) were encapsulated with polystyrene and polyacrylates via miniemulsion polymerization. The properties of pigment dispersions dispersed in water and monomers were evaluated. With ultrasonication time prolong, the particle size of pigment dispersions decreased. For 30 min ultrasonication, the particle size of P.Y. 14 and 83 dispersions in water was smaller than that of P.Y. 65 and 73. The particle size of pigment dispersion in styrene was smaller than that in acrylates. The stability of P.Y.83/monomer dispersion was the best. There was almost no separated monomer layer in P.Y.83 dispersions, but significant separated monomer layer can be seen in P.Y.65 dispersions. The encapsulation ratios and efficiency of P.Y.83 with polymers were larger than that of P.Y.65. Acrylates tend to adsorb better on the surface of pigment particles than methacrylates, while the encapsulation ratios of polyacrylates were higher.

Introduction

Textiles inkjet printing as a new printing method with higher resolution, lower pollution and shorter run length has attracted more and more people's attention. Pigmented and dyed water-based inks are two categories of inks in textile inkjet printing. Pigmented water-based ink has much more superiority than dyed ink due to higher light and wash fastness, suitable for all kinds of fibers and fabrics, shorter printing procedure. Pigments are applied as aqueous dispersion due to their water insoluble. Encapsulation of pigments with polymer can protect them from agglomeration and unwanted environmental influences such as UV radiation or acid and alkali. The encapsulation leads to better storage stability, color stability and durability, and the film formation can be adjusted[1].

In recently years, a variety of encapsulation techniques, e.g. emulsion, dispersion, and miniemulsion polymerization, have been developed to prepare nanocomposite particles for application in coatings, optics, and catalysis[2, 3]. One of the most common methods is emulsion polymerization. Successful encapsulations have been reported, for example, with inorganic titanium dioxide[4] and colloidal silica[5], using various polymeric materials. Because of the complexity of the particle nucleation mechanism in emulsion polymerization, it appears that it is difficult to achieve high encapsulation efficiencies by this technique.

In recent literature, miniemulsion polymerization was found to be attractive to obtain polymeric nanocomposites which can not be achieved by emulsion and dispersion polymerization. Miniemulsion polymerization offers some advantages compared to emulsion and dispersion polymerization. Miniemulsion is critically stabilized dispersion, which is consist of droplets in the range about 50-500 nm in diameter. Direct miniemulsions can be processed by shearing a mixture of oil, water, surfactant and a hydrophobe (costabilizer). The role of hydrophobe is to stabilize the small droplets against diffusion degradation, so-called Ostwald ripening. Contrary to emulsion polymerization, the monomer droplets are small and numerous so that the polymerization mainly occurs by radical entry into the existing miniemulsion droplets, called droplet nucleation, without nucleation of new particles.

Using the miniemulsion polymerization technique, the pigment can be encapsulated with polymers efficiently. Using the miniemulsion process, hydrophobic particles can be dispersed in the monomer phase without any former treatment, as for the polystyrene encapsulation of organic phthalocyanine blue pigment or carbon black particles[6]. However, for encapsulation of the hydrophilic particles such as titanium dioxide, magnetite or silica with hydrophobic polymers, hydrophobization is necessary prior to or during the introduction in the monomer phase.

In present work, organic pigments were encapsulated by polymers employing miniemulsion polymerization. The dispersibility of pigment in water and styrene and acrylates monomers was evaluated. The encapsulation ratios and efficiency pigment with different polymers were measured.

Experimental

Reagents

Water was distilled and deionized before use. The anionic surfactant sodium dodecyl sulfate (SDS) bought from Sinopharm Chemical Reagent Co., LtdS was used as received. The organic yellow pigments (P.Y.65, 73, 14, 83, Figure 1), gifts from Chang zhou North American Chemical Group, were used as supplied. The monomers styrene, methacrylate (MA), methyl methacylate (MMA), butyl acrylate (BA) and butyl methacylste (BMA) (Sinopharm Chemical Reagent Co., LtdS) were distilled under vacuum and kept refrigerated until use. The initiator 2, 2'-azobisisobutylo nitrile (AIBN) was purified by recrystallization from ethanol.

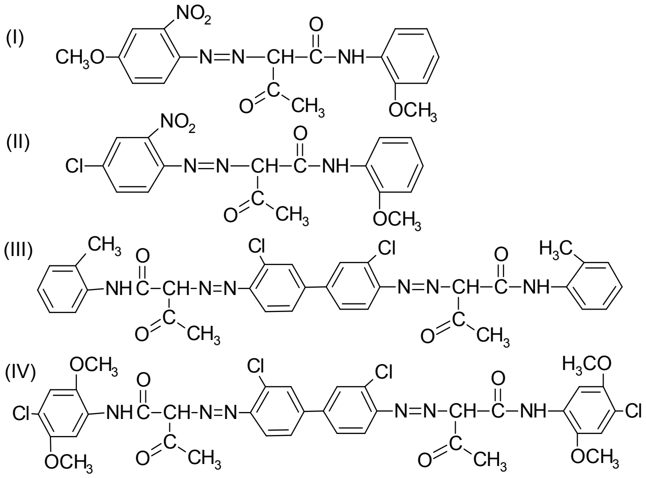

Figure 1. *Structures of yellow pigments (I) P.Y.65, (II) P.Y.73, (III) P.Y.14, (IV) P.Y.83*

Pigment dispersion

Pigment dispersion was normally carried out by mechanical milling or ultrasonication. The aim of these processes was to apply external force to break up pigment aggregates to small particles. During the dispersion process, dispersants adsorbed onto the surface of pigment particles to prevent particles agglomerating.

The SDS stabilized dispersion of pigment was prepared as follows: SDS (1g, 20% to pigment) was dissolved in water (44g). The pigment powder (5g) was added to the above solution slowly, stirring the mixture at 700 rpm for 1 h. The residual water (50g) was added, then the mixture was ultrasonicated in a JY98-3D Ultrasonic Pulverizer (Scientz company) at 800 W (1s pulse on/4s pulse off) for 10 min. During the ultrasonication process, the dispersion was cooled in a water bath.

Particle size and its distribution

The particle size was measured at 25°C using a Malvern Instrument NANO-ZS 90 at a fixed scattering angle of 90°. The dispersion was diluted with distilled water or monomer before measuring. Dynamic light scattering (DLS) measurements give a Z-average size, which is intensity mean of the particle diameter, and the polydispersity index (PDI), which provides information about the width of the particle size distribution.

Pigment encapsulation process

For prepare of monomer/pigment dispersion, two step emulsification procedures were produced. Firstly, the pigment was dispersed in SDS solution, and monomers were also emulsified with anionic surfactant SDS.

The monomer miniemulsion was prepared by ultrasonic emulsification. An oil phase including 10 g styrene, 0.4g hexadecane and 0.4 g AIBN was mixed with a surfactant solution of 0.1 g anionic SDS in 40 g water. After vigorously stirring the mixture at 1000 rpm for 1 h for pre-emulsification, the miniemul- sions were prepared by pulse ultrasonicating the mixture for 2 min. During the ultrasonication process, the emulsion was cooled in an ice-water bath.

The monomer miniemulsion was added into the SDS stabilized pigment dispersion drop by drop. The mixture was powerfully stirred at 800 rpm for 30 min, pulse ultrasonicated for 2 min (1s pulse on/4s pulse off). In order to prevent pre-polymerization of monomers during the ultrasonic process, the dispersion was kept in ice-water bath to maintain lower temperature. Finally, the reaction flask was heated to and maintained at 70°C for 4 h under slowly stirring.

Encapsulation ratio and efficiency

The free polymers were separated from emulsion by centrifugation. The emulsion was centrifugated at 13, 000 rpm in Centrifuge-5415 (Eppendorf, Germany) for 30min. The free polymers stayed at upper layer because of lower density. And, the pigments encapsulated with polymers were sedimentated at the bottom. The encapsulation ratio and efficiency were calculated as follows:

$$\text{Encapsulation ratio} = \frac{\text{encapsulated polymer(g)}}{\text{encapsulated polymer(g)+pigment(g)}} \times 100\% \quad (1)$$

$$\text{Encapsulation efficiency} = \frac{\text{free polymer (g)}}{\text{encapsulated + free polymer(g)}} \times 100\% \quad (2)$$

Results and Discussion

Pigment dispersions

Pigment dispersed in water

Pigment was not soluble in water and general organic solvents. Therefore, pigment must be dispersed in water or organic solvents. Pigment dispersion was normally carried out by mechanical milling or ultrasonication.

Ultrasonic waves of high intensity ultrasound generate cavitations in liquids. The cavitations can be used in liquids for many processes, e.g. for mixing and blending, deagglomeration, milling and cell disintegration. In ultrasonication process, pigment aggregates were broken up to small particles because of ultrasonic cavitations.

Table 1. Effect of ultrasonication time on particle size of pigment dispersions

Time (min)	Particle size (nm)			
	P.Y.65	P.Y.73	P.Y.14	P.Y.83
2	510.2	478.2	333.6	587.4
5	442.4	392.4	270.4	486.5
8	429.7	363.7	248.8	388.9
10	408.9	347.8	251.1	372.1
13	403.6	344.6	228.9	363.3
15	410.3	335.7	230.2	314.3
18	383.6	331.0	229.1	307.4
20	376.3	322.5	218.2	312.7
23	372.7	320.3	211.8	303.6
25	352.4	313.7	210.7	281.5
30	347.5	305.8	204.7	285.1

The yellow pigments were with azo chromophores, P.Y. 65 and 73 with mono-azo chromophore, P.Y. 14 and 83 with bis-azo chromophore (Shown in figure 1). It shown from table 1 that with prolong time of ultrasonication, the particle size of pigment dispersions declined. For 30 min ultrasonication, the particle size of P.Y. 14 and 83 was smaller than that of P.Y. 65 and 73. The reason was that there were much more carboxyl and methoxy groups in the molecule of P.Y. 14 and 83 than that of P.Y. 65 and 73. The pigments with more carboxyl and methoxy groups can be easily dispersed in water.

Pigment dispersed in monomers

Table 2. Particle size of pigment dispersions.

Monomer	Particle size (nm)			
	P.Y.65	P.Y.73	P.Y.14	P.Y.83
St	689	518	1423	1386
MA	—[a]	745	1702	—
MMA	—	3425	1403	1766
BA	1247	623	1449	1995
BMA	—	763	1313	1343

[a] The pigment was aggregated to large particles when diluted with monomer.

Table 2 showed that the particle size of pigment dispersed in styrene was smaller than that dispersed in acrylates. There were benzene rings in pigment, which can interact with styrene that also had benzene ring. But for acrylate monomers, the interaction between acrylates and pigment was small; pigment can not be well dispersed in acylate monomers.

Table 3. Stability of pigment dispersions in monomers (12h[a])

Monomer	Upper layer ratios of pigment dispersion			
	P.Y.65	P.Y.73	P.Y.14	P.Y.83
St	0.10	0.20	0.00	0.10
MA	0.30	0.10	0.10	0.05
MMA	0.20	0.10	0.05	0.05
BA	0.28	0.11	0.10	0.05
BMA	0.10	0.10	0.10	0.05

[a] The pigment dispersions were placed still for 12 hours after ultrasonication.

Table 4. Stability of pigment dispersions in monomers (6d[a])

Monomer	Upper layer ratios of pigment dispersion			
	P.Y. 65	P.Y. 73	P.Y. 14	P.Y. 83
St	0.80	0.50	0.20	0.10
MA	0.80	0.28	0.20	0.05
MMA	0.75	0.25	0.25	0.05
BA	0.50	0.28	0.20	0.05
BMA	0.60	0.40	0.25	0.05

[a] The pigment dispersions were placed still for 6 days after ultrasonication.

The pigment/monomers dispersions were produced by ultrasonicating the mixture of pigment and monomers. But due to no emulsifier adding, the dispersions would be separated to two layers, which the upper one was transparent monomers and the under one was pigment/monomer dispersion. The lager ratio of upper layer indicated that this pigment dispersion was unstable; there was less interaction between pigment particles and monomers.

Table3 and 4 showed the upper layer ratios of pigment dispersions in different monomers, kept still for 12 hours and 6 days, respectively. The upper layer ratios of P.Y. 65 dispersions in all monomers were the largest, and these of P.Y. 83 dispersions were the smallest, especially in acrylate monomers there almost no monomer layer separated. The stability difference was related to the structures of pigments and monomers. There were benzene ring, carboxyl and methoxyl groups in yellow pigments, and the numbers of these groups increased with the pigment structure increasing. The structure of P.Y.65 and 73 with mono-azo chromophore have two benzene rings and two carboxyl groups, but for P.Y.14 and 83 with bis-azo chromophore there were four benzene ring and four carboxyl groups. There were some interactions between pigments and monomers which also have benzene ring or carboxyl groups. The interaction enhanced with the numbers of benzene and carboxyl groups in pigment increasing. Therefore, P.Y.83 dispersions in all monomers were very stable and almost no separated monomers layer.

Pigment encapsulation with polymers

Pigments P.Y.65 and 83 were encapsulated with polystyrene or polyacrylates via miniemulsion polymerization. The encapsulation ratios and efficiency were shown in table 5, 6.

According to mechanism of miniemulsion polymerization, radicals of initiators entered into the monomer droplets to initiation polymerization. Therefore, in order to acquire good encapsulation efficiency, all monomers must adsorb on the surface on pigment particles. Free monomer droplets (without pigment) would polymerize to hollow polymer micro spheres, which can not encapsulate pigment particles.

It is shown from table 5 and 6 that the encapsulation ratios and efficiency of P.Y.83 was higher than that of P.Y.65. The reason of that was that there were much more benzene ring and carboxyl groups in P.Y.83; the hydrophobic interaction between pigment and monomers was higher, so the monomers tend to adsorb on the surface of pigment particles. However, for P.Y.65 with smaller structure, the hydrophobic interaction was smaller, some monomer droplets entered into the micells of surfactant to form free polymers.

Table 5. P.Y.65 encapsulation with polymers [a]

Monomer	Encapsulation Ratio (%)	Encapsulation Efficiency (%)
St	34.15	57.16
MA	31.98	41.38
MMA	33.44	71.73
BA	34.48	39.19
BMA	33.44	71.73

[a] The weight ratios of pigment to monomer were 1:1.

Table 6. P.Y.83 encapsulation with polymers[a]

Monomer	Encapsulation Ratio (%)	Encapsulation Efficiency (%)
St	35.40	53.91
MA	41.24	72.83
MMA	36.74	57.18
BA	34.92	54.43
BMA	40.45	62.27

[a] The weight ratios of pigment to monomer were 1:1.

Table 5 and 6 showed that encapsulation ratios of pigment with polyacrylates were larger than that of with polymethacrylates, and also the encapsulation efficiency. It might be related to the structure of acrylates. With linear structure, the acrylates can well adsorb on the surface of pigment particles. Refer to methacrylates, there was some steric hindrance because of the methyl group in –CH=CH–, so the adsorption of methacrylates on the pigment was not as well as the acrylates.

Conclusions

Pigments are applied as aqueous dispersion due to their water insoluble. Encapsulation of pigments with polymer can protect them from agglomeration and unwanted environmental influences such as UV radiation or acid and alkali. The encapsulation leads to better storage stability, color stability and durability, and the film formation can be adjusted.

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