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Preparation of Organic Pigment Microcapsules and its Application in Pigment Printing of Silk Fabric

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Abstract. A series of submicron organic pigment microcapsules with high pigment encapsulating efficiency and narrow particles size distribution was prepared via *in-situ* miniemulsion polymerization. The self-adhesive pigment microcapsules were applied to pigment printing of silk fabrics. It was found from printing qualities that, the K/S value, handle, dry and wet rubbing fastness of silk fabrics printed by pigment microcapsules were much better than those printed by traditional pigment paste. The TEM observation of the printed fabrics further indicated that the presence of adhesive polymeric layer on the pigment particles can remarkably improve the dispersion of pigment particles on fabric surface and the adhesion between pigment particles and the target fabric.

Introduction

Pigment printing is widely regarded as a green technology. However, organic pigment is difficult to be wetted and dispersed in water media and then on fabric surface, due to their low polarity and easy aggregation [1]. Thus, massive of disperser and adhesive should be added in pigment printing, which generally brings an irreconcilable conflict between handle and color fastness. Microencapsulation of pigment particles by adhesive polymeric layer was regarded as one of the most effective way to solve this problem [2].

In the past decade, a rapid development occurred in heterogeneous polymerization, and a series of nano- and micro-size composites particles with controllable morphology and structure was prepared via emulsion polymerization [2], miniemulsion polymerization[3,4], suspension polymerization[5, 6], and micro-suspension polymerization [7]. The above technologies can be used to prepare organic pigments microcapsules.

In this paper, a typical organic pigment, copper phthalocyanine blue (PB), was encapsulated by styrene-acrylic co-polymer (P(BA-St)) via *in-situ* miniemulsion polymerization, and a series of organic pigment microcapsules with controllable morphology, particles size and size distribution was prepared. These self-adhesive microcapsules were then applied to the pigment printing of silk fabrics. And the K/S value, handle, dry and wet fastness of fabric printed by microencapsulated pigments were compared with those of the traditional printed fabric in order to reveal the advantages of the microcapsule printing.

Experimental

Materials

Organic pigment copper phthalocyanine blue (PB15:3, cake) was supplied by Zhejiang Lily Group Co., Ltd. Monomers butyl acrylate (BA) and styrene (St) supplied by Shanghai Gaoqiao Chemical Co. were distilled under reduced pressure before polymerization. Cross-linking agent divinylbenzene (DVB) and initiator 2,2'-Azobisisobutyronitrile (AIBN) were obtained from Aldrich Chemical Co., Ltd. Sodium dodecyl sulfate (SDS) and hexadecane (HD) with analytical purity, were purchased from Shanghai No.2 Chemistry Reagent Co., Ltd. Thickener (PTF) was from UK Allied Colloids. Two kinds of silk fabric, georgette and crepe, were kindly supplied by Zhejiang Huatai Silk Co., Ltd.

Preparation of organic pigment microcapsules

A certain amount of organic pigment cake (PB), DVB, AIBN, HD and SDS aqueous solution were gradually added into the monomer mixture (BA: St=9:1) in stirring state. The mixture was then ultra-sonicated for 60 s (output power 400 W, work time 10 s, pause time 5 s) under cooling with ice water to get a stable miniemulsion. The obtained miniemulsion was added into a 200 ml jacket glass reactor. And the miniemulsion polymerization was conducted at 60 ^{o}C for 5 h under a N_2 atmosphere to obtain pigment microcapsules (defined as P (BA+St)/PB). The polymerization process is indicated in Fig. 1.

For comparison, the mixture of organic pigment, poly (butyl acrylate-styrene) latex and SDS aqueous solution was ultra-sonicated for 60 s (output power 400 W, work time 10 s, pause time 5 s) under cooling with ice water, to obtain a stable pigment latex blend (defined as P (BA+St) + PB).

Pigment printing of microcapsules

A certain amount of thickener PTF was added into the pigment microcapsules P(BA+St)/PB and pigment latex blend P(BA+St)+PB under stirring to obtain the corresponding printing paste. The silk fabrics, georgette and crepe, were hand-scraped along the meridional of fabric. The printed fabrics were baked at 80 ^{o}C for 5 min and then at 115℃ for 3 min.

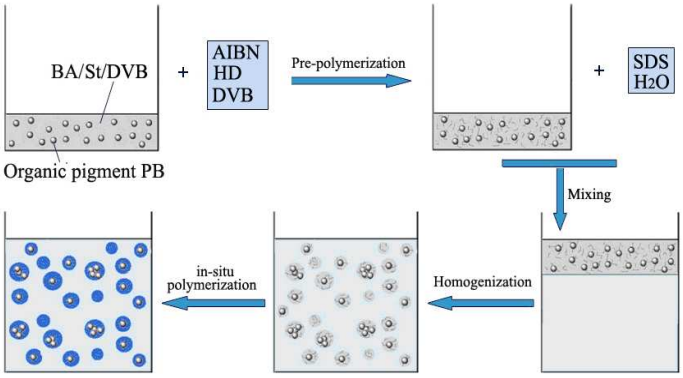


Fig. 1 Schematic diagram of formation of organic pigment microcapsules via *in-situ* miniemulsion polymerization

Characterization and measurements

The morphology of pigment and pigment microcapsules were observed by a JEM-1230 type transmission electron microscope (TEM, JEOL). Their particles size was measured by dynamic light scattering on a LB-550 particle size analyzer (DLS, Horiba). The surface morphology of printing fabrics was observed by a JSM-5610 type scanning electron microscope (SEM, JEOL). The color depth (K/S value) was measured by a SF600X type spectrophotometer color measurement (DataColour). The stiffness was measured by a LYB-05 automatic fabric stiffness tester. The wet and dry rubbing fastness was tested using GB/T3920-1997 and GB251-1995 standards.

Results and Discussion

Morphology of organic pigment microcapsules

The distribution of organic pigment PB and inorganic pigment TiO_2 in water/monomer phases is shown in Fig. 2. It showed that almost all of PB particles can be homogeneously dispersed in monomer phase, while TiO_2 mainly in water phase, which implies that PB is hydrophobic and compatible with monomer. Thus, organic pigment is very suitable to be encapsulated by adhesive polymer via non-homogeneous polymerization, such as miniemulsion polymerization.

The appearances of PB aqueous dispersion, pigment latex blend (prepared via traditional technology) and pigment microcapsule (prepared via *in-situ* miniemulsion polymerization) are shown in Figure 3. Compared with PB+H_2O and P(BA+St)+PB, P(BA+St)/PB had darker color and excellent pigment dispersion. The corresponding morphology observed from TEM image in Fig. 4 showed that almost all of pigment particles (dark-colored) were encapsulated by soft polymer (light-colored), indicating the microencapsulation appearance. Furthermore, as can be seen from the DLS curves in Fig. 5, the particles size distribution of P(BA+St)/PB was narrow, and the particles size was obviously greater than the one of PB, also implying the compounding between pigment particles and adhesive polymer.

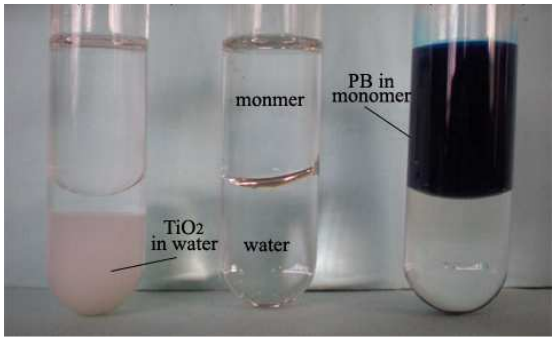


Fig. 2 Distribution of inorganic pigment TiO_2 (left) and organic pigment PB (right) in water/monomer phases

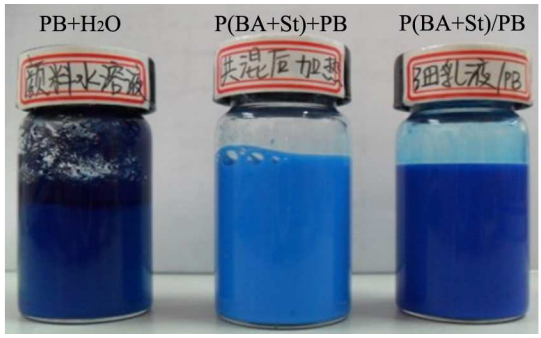


Fig. 3 Appearance of PB aqueous dispersion ($PB+H_2O$), pigment latex blend (P(BA+St)+PB) and pigment microcapsule (P(BA+St)/PB) under similar pigment content

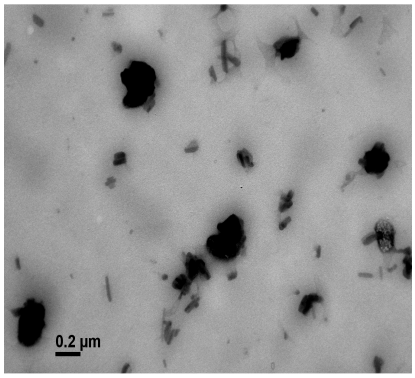


Fig. 4 Typical TEM image of P(BA+St)/PB pigment microcapsules

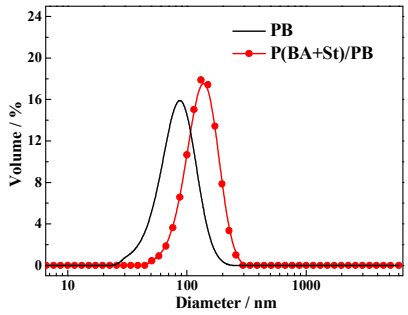


Fig. 5 Size distribution of PB particles and P(BA+St)/PB microcapsules particles

Microcapsules printing for silk fabric

Two kinds of pigment pastes containing P(BA+St)+PB and P(BA+St)/PB were applied to the pigment printing of silk fabrics via a pigment printing process. The effects of paste form on printing qualities, such as K/S value, handle, dry and wet rubbing fastness, were investigated and the results are shown in Table 1.

Table 1 Effect of paste form on the printing qualities of silk fabrics

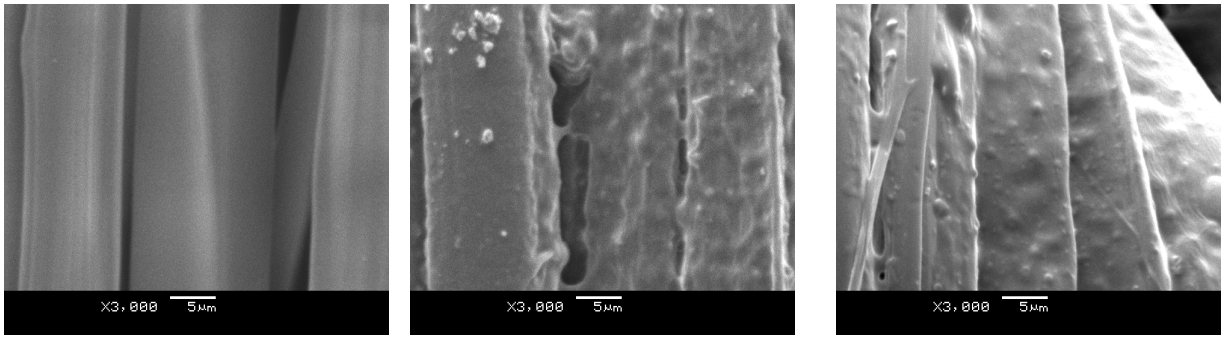
Paste form	Georgette				Crepe			
	K/S	Stiffness	Rubbing fastness		K/S	Stiffness	Rubbing fastness	
			dry	wet			dry	wet
PB	1.29	2.16	2-3	2-3	2.33	1.60	1-2	2
P(BA+St)+PB	1.87	1.99	4	4	3.70	1.61	3-4	4-5
P(BA+St)/PB	3.63	1.79	3	4-5	6.58	1.65	3-4	4-5

It can be found that the paste form played an important role in the printing quality of silk fabrics. Both for georgette and for crepe, the K/S value, handle, dry and wet rubbing fastness of silk fabric printed by microencapsulated pigments were better than those printed by traditional paste.

The corresponding surface morphology was observed by SEM, and the typical SEM images are shown in Fig. 6.

The surface of crepe was smooth and no adhesion phenomenon can be found between silk fibers. While for P(BA+St)+PB printed crepe, the surface was coarser and many mass pigment aggregation can be found on the surface of silk fibers. For pigment microcapsules P(BA+St)/PB printed crepe, the surface was relatively flat and the adhesion phenomenon between fibers had been partly inhibited.

All of them implied that the presence of soft polymer layer on the pigment particles can remarkably improve the dispersion of pigment particles on silk fabric surface, and simultaneously the binding force of pigment particles with fabric.



Crepe Crepe printed by P(BA+St)+PB Crepe printed by P(BA+St)/PB

Fig.6 Typical SEM images of the raw crepe fabric (a), the blend P(BA+St)+PB printed crepe fabric (b) and the microcapsule P(BA+St)/PB printed crepe fabric (c)

Mechanism of pigment microcapsules printing

The above results can be explained by the following schematic diagram (Fig. 7).

For traditional pigment printing, the pigment particles and adhesive latex particles are separated in paste [1]. Both on paste preparation process and on film-forming process, the pigment particles are easily to aggregate into clusters and then be excluded from adhesive film, which finally decrease the cover rate and the adhesion fastness of pigment particles remarkably.

For pigment microcapsules printing, almost all of small pigment particles have been effectively encapsulated by adhesive polymer layer before paste preparation. Thus, both the pigment aggregation and stripping can be remarkably prevented.

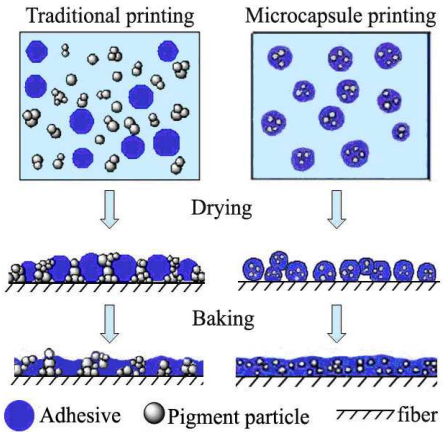


Fig.7 Schematic diagram of film formation of traditional pigment printing and pigment microcapsule printing

Conclusions

The microencapsulation of pigment particles by adhesive polymer via *in-situ* polymerization can remarkably improve the adhesion between the pigment and the target fabric, and simultaneously the dispersion of pigment particles on the matrix surface. Thus, this technology can be regarded as one of the effective way to obtain excellent printed fabrics with better handle and rubbing fastness.

Acknowledgments

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