Preparation of Organic Pigment Encapsulation by Miniemulsion Polymerization

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Abstract

Pigmented ink will be the main developing trend in inkjet printing technology since it is suitable to all kinds of fiber. In this paper, Encapsulation of organic yellow pigment was prepared by miniemulsion polymerization technique. The pigment was first suspended into the monomer phase treated by ultrasonic irradiation, then added to the water system including surfactant,subsequently the mixture converted into stable miniemulsion droplets through ultrasonic irradiation. The pigment monomer emulsion was polymerized using initiator APS. Experimental results showed that the effect of the surfactant on the yields was not very significant, but the encapsulating ratio reduced with an increase of surfactant, the costabilizer hexadecane was the key factor to influence the size of the pigment-polymer particles, and the encapsulating ratio enhanced obviously in the presence of the hexadecane. With the ratio of monomer(styrene) increasing the encapsulating ratio enhanced, and the ratio of polystyrene particles increased too. TEM photographs indicated that the particles have core-shell structure.

Introduction

Textile inkjet printing has demonstrated super advantages over the customary textile printing methods, such as excellent pattern quality, environment friendly, and especially rapid response to the frequent shift of fashion. For textile inkjet printing, inkjet inks are one of the significant factors for perfect product. They are usually classified into two categories as dye inks and pigment inks, according to the colorants in them. Pigment inks are suitable to all kinds of fibres, and their printing procedure is very simple, as final products can be achieved by simple heat curing without steaming and washing. The research and development of pigment inks are the main trend of textile inkjet printing technology[1-2] .

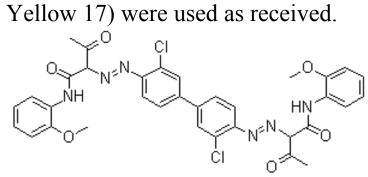
To prepare the stable dispersions of pigment in water is the key technology of the pigment inks. However, after dispersing the water-insoluble pigments in the aqueous phase, they often tend to agglomeration. To encapsulate the organic pigment-nanoparticles with polymer can solve this problem and also protect them from environmental influence like UV radiation or pH. Moreover, the coating leads to better storage stability, color stability and durability.

There are many techniques for encapsulating nanoparticles have been developed, for example emulsion, dispersion and miniemulsion[3-6]. In this paper, Encapsulation of organic yellow pigment was prepared by miniemulsion polymerization technique. The pigment was first suspended into the monomer phase treated by ultrasonic irradiation, then added to the water system including surfactant, subsequently the mixture converted into stable miniemulsion droplets through ultrasonic irradiation. The pigment monomer emulsion was polymerized using initiator APS. TEM photographs indicated that the particles have core-shell structure. The effect of the amount of the surfactant and the costabilizer and the ratio of the momomer/pigment will be studied.

Experimental Part

Materials

The monomer(styrene) was distilled under vacuum and kept under refrigeration until use. The initiator(APS) was recrystallized from water before use. Surfactant(SDS) and pigment (C.I. Pigment Yellow 17) were used as received.



Prearation of polystyrene-encapsulated pigment

Polystyrene encapsulated pigment composite in the form of latex were synthesized through miniemulsion polymerization technique. The pigment was first suspended into the monomer phase treated by ultrasonic irradiation for 10 min, The surfactants SDS was introduced into the reaction into the reaction flask containing distilled water at 40°C, After stirring for 20 min, The mixture of pigment, St and costabilozer, which had been treated by ultrasonic irradiation just before use, was added. Subsequently the mixture converted into stable miniemulsion droplets through ultrasonic irradiation. The temperature was then raised to 80°C, The solution of APS was added to initiate the polymerization. The polymerization proceeded at 80°C for 3 h.

The latex was demulsified with 20wt% $AlCl_3$ solution. The product was collected by cuction filtration, washed thoroughly with hot water, and then dried.

Evaluation of the polymerization

The yield, encapsulating ratio and binding efficiency were used to evaluate the polymerization. The yield was determined by gravimetric method. To partition the PS formed on the pigment surface and the PS in solution, the mixture was centrifuged at 12000 rpm for 15 min. The precipitate was dried in a vacuum oven at 50°C and the weight of the PS on the pigment surface was calculated by subtracting the weight of the pigment. On the other hand, to a somewhat opaque supernatant solution was dried in a vacuum oven at 50 °C and the weight of the PS in the solution was gained. Then the encapsulating ratio and binding efficiency were calculated. The following are the related equations:

$$\text{Yield}(\%) = \frac{\text{Dried total product(g)}}{\text{Total monomer(g) and pigment (g)}} \times 100$$

$$\text{Encapsulating ratio}(\%) = \frac{\text{Polymer formed on the pigment surface}}{\text{Pigment in sample}} \times 100$$

$$\text{Binding efficiency}(\%) = \frac{\text{Polymer formed on the pigment surface}}{\text{Polymer formed}} \times 100$$

Characterization

The latex sample was used directly for the morphology observation using transmission electron microscopy (TEM), the particle size can also be measured by TEM (JEM-2010, JEOL Japan).

Results and Discussion

Effect of the Amount of surfactant

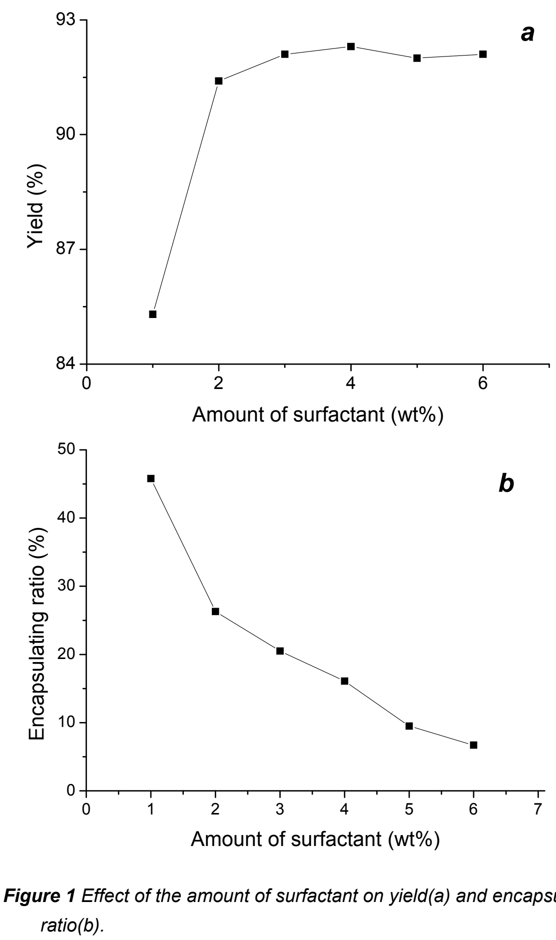


Figure 1 *Effect of the amount of surfactant on yield(a) and encapsulating ratio(b).*

In this work, we use SDS as emulsifier, the effect of the amount of the surfactant on the yield and encapsulating ratio were studied. Large amount of the surfactant was used and the amount of the surfactant had significant effect on the encapsulating ratio, but the effect of the surfactant on the yields was not very significant. As shown in the Figure 1. The optimal amount of the surfactant is about 2-3% where both the yield and encapsulating ratio were superior. Obvious precipitate was observed when using surfactant less than 1%, and the yield dropped sharply, when use 1%, the yield was 85.3%, but the encapsulating ratio was relatively high. When the surfactant was added more, the yield was maintained at more than 90%, but the encapsulating ratio was decreased. Because with more surfactant, some free PS micelles were formed in the system.

Effect of the costabilizer hexadecane

It is known that the presence of small amounts of an appropriate costabilizer is a prequisite condition to obtain stable miniemulsion droplets. The main action of the costabilizer is to build up an osmotic pressure in the monomer droplets which counterbalances the Laplace pressure inside the original emulsion, and retards the Ostwald ripening effect characterized by diffusion of monomer from small droplets to larger ones. In an 'ideal' miniemulsion process, the monomer droplets and the latex particles are expected to have about the same size since the former are converted into the later. In this experiment we used hexadecane as the costabilizer, the result was showed in Figure 2, It was initially obvious that the addition of small amount of an hexadecane significantly increased the encapsulating ratio. As we can see form the Figure 2(b), when use 0.6% costabilizer, the encapsulating enhanced 15.8% to 40.3%. From figure2(a), we could see that the hexadecane had no effect on the yield.

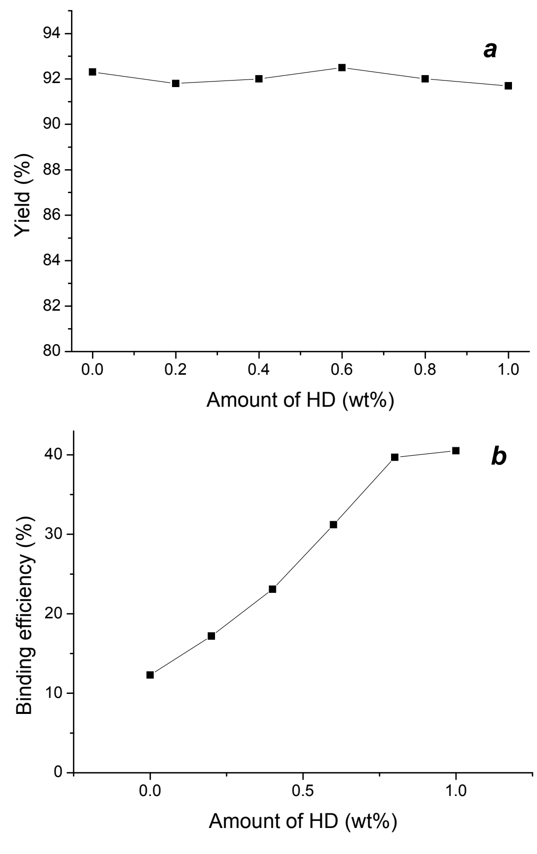


Figure 2 *Effect of the amount of costabilizert on yield(a) and binding efficiency(b).*

Effect of the ratio of the St/pigment

Different recipes containing different amount of St and pigment were examined, we changed the ratio of St/pigment from 1:1 to 16:1, the results were shown in table 1, When the amount of the St increased, the yield was increasing slowly, when the ratio of the St/pigment raised to 8:1, the amount of the pigment had no effect on the polymerization of styrene, the yield was stable at 91-93%. With the increasing of the St, the encapsulating ratio enhanced, but the binding efficiency dropped obviously, indicating the formation of the free polystyrene in the latex. No matter how many styrenes added, the encapsulating ratio could not reach 50% and the binding efficiency is lower.

Table 1 Effect of the ratio of the St/pigment

Ratio of St/pigment	Yield (%)	Encapsulation ratio (%)	Binding efficiency (%)
1:1	70.5	6.8	9.6
2:1	83.6	8.4	5.0
4:1	86.8	16.8	4.8
6:1	90.5	26.5	4.9
8:1	91.0	34.6	4.7
10:1	91.8	42.3	4.6
12:1	92.1	43.5	3.9
14:1	92.0	43.8	3.4
16:1	92.3	43.3	2.9

Morphology

The TEM photographs of final latex showed the morphology and the particle size of the particles. TEM is a useful means to study morphology of a given object. The TEM picture Figure 3(a) showed that there were both pigment particles and many spherical polystyrene particles in the latex. As seen in Figure 3(b), the pigment particles are contained into polymer pockets. Comparing the Figure 3(a) and the Figure 3(b), we can see that the costabilizer were the key factor of the polymerization process. Figure 3 (c) is the photos of a highly magnified encapsulated pigment, as we can see the pigment are coated with a thin layer of polystyrene. And the diameter of the particle was about 500nm.

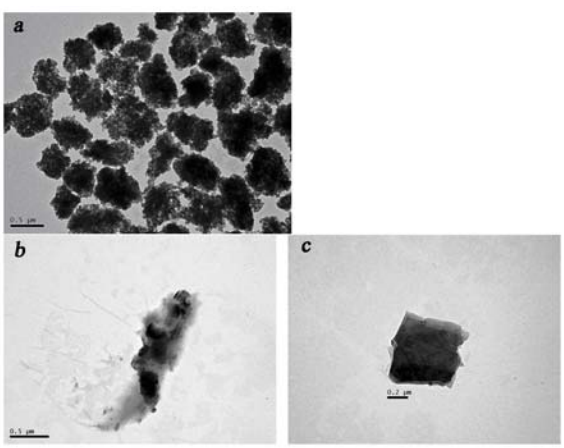


Figure 3. *TEM images of the pigment polystyrene latex particles, (a)without costabilizer, (b)in presence of costabilizer, (c)highly magnified encapsulated pigment*

Conclusion

Encapsulation of an organic yellow pigment could be achieved under the experimental conditions. The pigment could be embedded satisfactorily into the preservation of the polystyrene latex particles. The morphology of the composite particles studied by TEM showed successful encapsulation. The costabilizer hexadecane was the key factor to influence the size of the encapsulating ratio, with a little costabilizer the encapsulating ratio enhanced obviously. No matter how many monomer added, the encapsulating ratio were not more than 50%, with more and more free PS particles formed, the binding efficiency decreasing as well.

Although an acceptable level of encapsulation of pigment has been achieved, better results could be surely obtained if the surface of the pigment were modified prior to polymerization in order to increase stability.

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Xia Zhang, postgraduate. She has worked in the College of Textiles & Clothing, Jiangnan University. Her research interest focused on the development of pigment inkjet printing inks.