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

Shaohai Fu*, Chunxia Wang, Key Laboratory of Science & Technology of Eco-Textile of Ministry of Education, Jiangnan University. 1800 Lihu Road, Wuxi 214122, Jiangsu, P. R. China

Abstract

The copolymer-encapsulated pigment dispersion was prepared by phase separation technique with 2-[(2-Methoxy-4-nitrophenyl)azo]-N-(2-methoxyphenyl)-3-oxobutyramide (P.Y.74) and copolymer of styrene and maleic acid (PSMA). The surface-modified pigment dispersion was prepared by milling method with P.Y.74 and dispersant of PSMA, and further the two dispersions were applied to formulate into pigment ink, respectively. The colloidal properties of these two dispersions were compared, and the printing performance of prepared inks was also investigated. The results showed that the particles in PSMA-encapsulated pigment dispersion were smaller than that of surface-modified pigment dispersion. The stability to NaCl concentration, pH value and temperature of PSMA-encapsulated dispersion was superior to surface-modified pigment dispersion. The apparent viscosity of PSMA-encapsulated pigment dispersion changed small, while changed greatly in surface-modified pigment dispersion with increasing the shear rate. Printing performance indicated that the PSMA-encapsulated pigment dispersion was more suitable to preparation of inkjet printing inks than that of surface-modified pigment dispersion.

1. Introduction

Textiles inkjet printing 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 were hard to be wetted and dispersed in aqueous media, so the organic pigments should be modified before using. The organic pigment dispersed with aid of dispersant is a common method to prepare the pigment dispersion. Polymeric dispersants are a class of specially designed, structured materials which have good properties in stabilizing pigments [2-6]. In aqueous media, polymeric dispersants build a voluminous shell around organic pigment particles and also intensify charges on the particle surface. The pigment was encapsulated into copolymer is another important modification method [7-10]. In the last decade, a variety of techniques have been developed, such as miniemulsion polymerization [11]; graft method [12, 13]; layer-by-layer assembly technique [14, 15] and phase separation technique [16].

In this study, the PSMA-encapsulated pigment dispersion was prepared by phase separation technique; the surface-modified pigment dispersion was prepared by milling method with aid of PSMA. The colloidal properties of the two dispersions were compared, and the printing performance of the ink which prepared above dispersion was also investigated.

2. Experimental

2.1 Materials

Copolymer of styrene and maleic acid copolymer (PSMA, made by ourselves, Mn=9000, the molar ratio of styrene to maleic acid 1:1); Hydrochloric acid (HCl, analytical grade) and sodium hydroxide (NaOH, analytical grade) were purchased from Shanghai Chemical Reagent Co., Ltd. P.Y.74 (purity 99.8%) was supplied by Wuxi Xinguang Co., Ltd.

2.2 Preparation of the PSMA-encapsulated pigment dispersion

10g PSMA was dissolved in solvent and then 50g P.Y.74 was added into the solution under stirring. After that the mixture was dispersed by Ultra Turrax IKA T18 Basic (IKA Instruments Ltd, German) at 4000r/min for 1 hour, 250mL water (pH<5) used as coacervation agent was dropped into the mixture at the rate of 10mL/min. The mixture was centrifuged to get some slurry, and the slurry was washed 3 times using distilled water to remove PSMA which was not absorbed onto the P.Y.74 surface, and then dried at 60℃ to get the powder of PSMA-encapsulated pigment. The dispersion was prepared with 10g PSMA-encapsulated pigment powder and 90g distilled water. pH value was adjusted to 8 using sodium hydroxide (0.01 mol/L). The system was kept at 60 °C for 30 min under stirring at the rate of 4000r/min.

2.3 Preparation of the surface-modified pigment dispersion

10 g PSMA was hydrolyzed in 440g water, and adjusted pH value to 8; then 50g P.Y. 74 was added to the solution and then milled on a bead miller (0.8 mm ZrO bead as milling medium, stirring speed of 2000r/min) for 3 hours.

2.4 Preparation of ink for inkjet printing

Ink formulation based on the weight was given in Table 1. The components were mixed together under stirring at 300r/min until a homogeneous dispersion was obtained. After filtered through a 500nm pore filtering sieve, the inks were prepared and loaded for inkjet printing.

Table1. Formulation of inks for inkjet printing

Component	Weight Content (%)
Dispersion^a	50
Glycerol	15
Ethylene glycol monomethyl ether	10
Urea	2
Tween-80	1.2
Distilled water	21.8

^{a}Note: the dispersion refers to PSMA-encapsulated pigment dispersion and surface-modified pigment dispersion, respectively.

2.5 Measurement

The particle size distribution of dispersion was tested by DLS (dynamic light scattering) method using Nano-ZS90 (Malvern Instruments Ltd, UK).

The dispersion was treated by adding different dosages of NaCl to determine the change rate of the particle size (d) as given in Eq.(1), where D_1 and D_2 are the average particle size before and after treatment at certain temperature for some time, respectively. The smaller d, and the higher stability to NaCl was.

$$d = \frac{|D_2 - D_1|}{D_2} \times 100\% \tag{1}$$

The pH value of the dispersion was adjusted by HCl (1%) and NaOH (1%) respectively, and the change rate of the particle size(d) was calculated as given in Eq. (1). The smaller d, and the higher stability to pH value was.

The dispersion was sealed and stored at different temperature for 1 hour, then the change rate of particle size was calculated from Eq.(1). The smaller d, and the higher stability to temperature was.

The apparent viscosity of the dispersion at 25°C was measured with a programmable rotational viscometer (Brookfield, America).

The printing performances of the inks prepared from pigment dispersions were tested on an inkjet printing machine (Mimaki JV4-180, Japan, pizeo-electric inkjet printer). The clogging nozzle rate (B) was calculated according to Eq. (2):

$$B = \frac{C_1}{S} \times 100\% \tag{2}$$

Where C_1 is the amount of clogged nozzle, S is the sum of the whole nozzle on the print head. The greater B, the poorer printing performance of ink is.

3. Results and discussions

3.1 The particle size distribution of the dispersions

Figure1 indicated that the particle size of PSMA-encapsulated pigment dispersion was smaller, and its distribution was narrower than that of surface-modified pigment dispersion. These results suggested that the phase separation technique was suitable to preparation of nanoscale pigment dispersion.

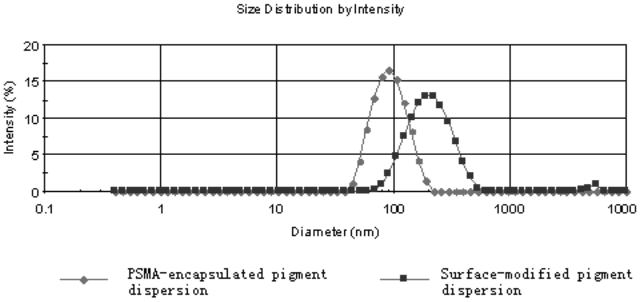

Figure1. *The particle size distribution of the dispersion, ■- PSMA-encapsulated pigment dispersion, ●- Surface-modified pigment dispersion*

3.2 The stability of the dispersions

3.2.1 The stability to NaCl concentration

Figure2 showed that the change rate of particle size about dispersion increased with an increase of the NaCl concentration, especially in surface-modified pigment dispersion. It is known that the cationic ions could compress the electric double layer, the more amount of cationic ions, the higher compress effect of the electric double layer was. In addition, In the surface-modified pigment dispersion, the electric double layer was higher than that of PSMA-encapsulated pigment dispersion, which could be more affected by NaCl concentration. Figure2 also indicated that the stability to NaCl concentration of the PSMA-encapsulated pigment dispersion was better than that of surface-modified pigment dispersion.

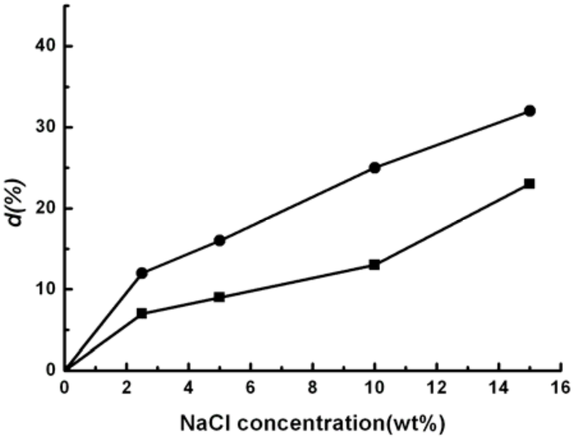

Figure2. *Effect of NaCl concentration on stability of the dispersion, ■- PSMA-encapsulated pigment dispersion, ●- Surface-modified pigment dispersion*

3.2.2 The stability to pH value

Figure3 indicated that the stability of the dispersion was greatly influenced by pH value, especially in surface-modified pigment dispersion. The neutralization degree of PSMA in the dispersion would increase with increasing the pH value, thus the more amount of –COO- would be produced onto the pigment surface, which resulted in enhancing the repulsive force among the particles. On the contrary, when the pH value was high enough, PSMA molecular would neutralize completely and then dissolve into the water, which would result in poor stability. The particle size changed sharply when the pH value was higher than 10, suggesting that the stability was destroyed and the particles combined each another at these conditions. Figure3 also indicated that the stability to pH value of the PSMA-encapsulated pigment dispersion was better than that of surface-modified pigment dispersion.

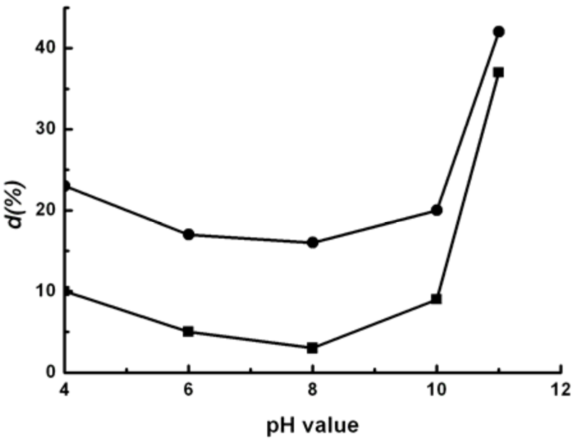

Figure3. *Effect of pH value on stability of the dispersion, ■- PSMA-encapsulated pigment dispersion, ●- surface-modified pigment dispersion*

3.2.3 Stability to temperature

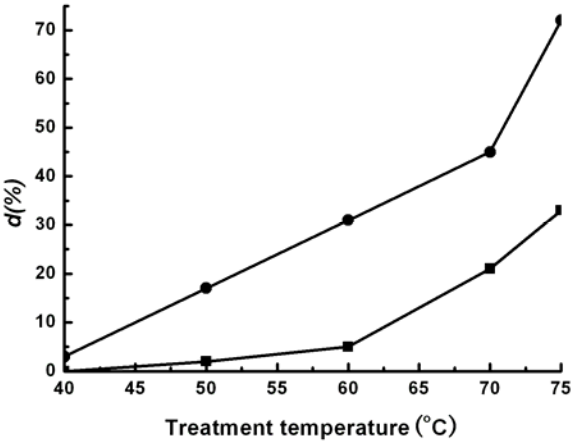

Figure4. *Effect of treatment temperature on stability of the dispersion, ■- PSMA-encapsulated pigment dispersion, ●- surface-modified pigment dispersion*

Figure4 indicated that the stability of the PSMA-encapsulated pigment dispersion is better than that of surface-modified pigment dispersion, and the particle size of PSMA-encapsulated pigment dispersion changed small when the dispersion was treated at the temperature from 40℃ to 60℃. The reason for these may be due to the action forces and action mode between PSMA and pigment particle were different in the two dispersions, in PSMA-encapsulated pigment dispersion, the action forces were large for completely absorption while in the surface-modified pigment dispersion, the action forces were small for partly absorption.

3.3 Rheological performance of the dispersion

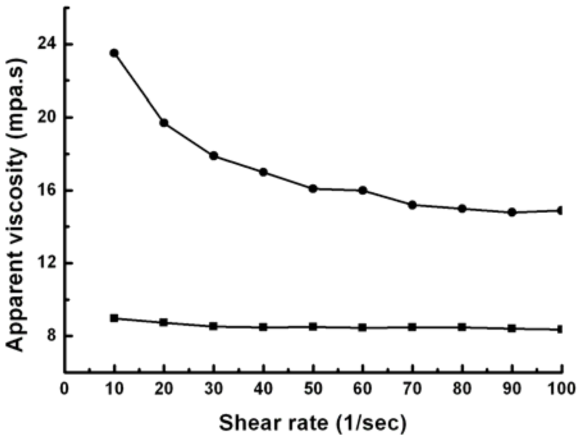

Figure5. *Effect of treatment temperature on stability of the dispersion, ■- PSMA-encapsulated pigment dispersion, ●- surface-modified pigment dispersion*

Figure5 showed that the PSMA-encapsulated pigment dispersion had an apparent viscosity which was much different from that of surface-modified pigment dispersion. Unlike the PSMA-modified pigment dispersion, the apparent viscosity of which dropped a lot from 10 to 50 1/sec and became stable at higher shear rate, the PSMA-encapsulated pigment dispersion exhibited a quite stable apparent viscosity regardless of the changes of shear rate from 10 to 100 1/sec.

The reason for these may be caused by the status of PSMA molecules in two dispersions. In surface-modified pigment dispersion, lots of the PSMA were dissolved in aqueous media, which could greatly increase the apparent viscosity, and the PSMA molecular chains would be uniformly aligned under raising shear rate, thus resulting in the decrease of apparent viscosity. In the PSMA-encapsulated pigment dispersion, the PSMA molecules were completely absorbed on the pigment surface that there was no obvious fluctuation on apparent viscosity as increasing shear rate. These results indicate that the PSMA-encapsulated pigment can effectively improve the fluidity of the dispersion.

3.4 Printing performance of the inks prepared by two dispersions

Table2 shows the physical properties of the pigment inks which made from PSMA-encapsulated and surface-modified pigment dispersion, respectively. It was noted that the apparent viscosity of PSMA-encapsulated pigment ink was smaller than that of surface-modified pigment ink, and the surface tension of surface-modified pigment ink was lower than that of PSMA-encapsulated pigment ink. These differences may be due to the different absorption status between the pigment and the PSMA.

Table2. Physical properties of the pigment inks

Pigment ink	D (nm)	η_a(mpa.s)	σ (mNm^{-1})
Surface-modified pigment ink	226.0	6.24	28.9
PSMA-encapsulated pigment ink	110.8	4.72	29.7

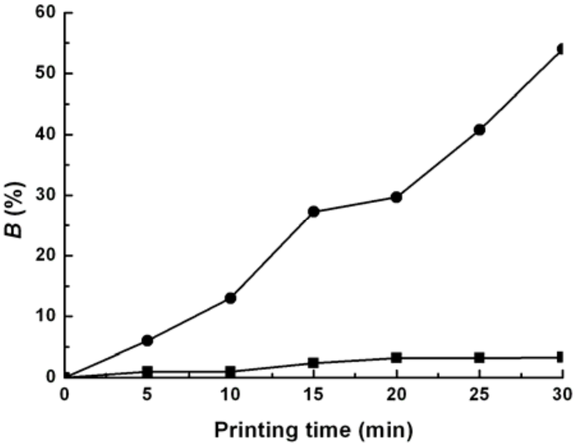

Figure6. *Printing performance of pigment ink, ■- PSMA-encapsulated pigment ink, ●- Surface-modified pigment ink*

Figure6 indicated that the printing performance of PSMA-encapsulated pigment ink was better than that of surface-modified pigment ink. The difference may be due to that the larger particle size the easier clogging the nozzle of print head was, moreover, the higher apparent viscosity might also lead to poorer printing performance. These results indicated that the PSMA-encapsulated was more suitable for preparation of the pigment ink for inkjet printing.

Conclusions

Phase separation technique is an effective method to prepare the nanoscale pigment dispersion. The PSMA-encapsulated pigment with small particle size have excellent stability to NaCl concentration, pH value and treatment temperature. The rheological behavior of PSMA-encapsulated pigment dispersion was close to Newton fluidity and was suitable for preparation of pigment ink for inkjet printing.

Reference

[1] Fu, S.H., Zhang, X., Zhu H. M. and Fang K.J., Dyestuffs and Coloration, pg.32. (2005).
[2] Banash, M.A. and Stuart, G.C., Prog. Org. Coat., pg.34. (1999).
[3] Chang, C.J., Chang, S.J., Tsou, S., Chen, S.I., Wu, F.M. and Hsu, M.W., J. Polym. Sci. Pt. B-Polym. Phys., pg.1909. (2003).
[4] Zhou, Y., Yu, D., Wang, C.L. and Chen, S.L., J. Dispersion Sci. Technol., pg.721. (2003).
[5] Annabelle, P., Evelyne, N., Bruno, F. and Pierre, D., Colloid Surf. A-Physicochem. Eng. Asp., pg.375. (1999).
[6] Lin, Y., Smith, T.W. and Alexandridis, P., J. Colloid Interface Sci., pg.1. (2002).
[7] Viala, Ph. Bourgeat-Lamy, E., Guyot, A., Legrand, P. and Lefebvre, D., Macromol. Symp., pg. 651. (2002).
[8] Batzilla, T. and Tulke, A., J. Coat. Technol., pg.77. (1998).
[9] Aslam, M., Fu, L., Li, S. and Dravid, V. P., J. Colloid Interface Sci., pg.444. (2005).
[10] Tiarks, F., Landfester, K. and Antonietti, M., Macromol. Chem. Phys., pg.51. (2001).
[11] Lelu, S., Novat, C., Graillat, C., Guyot, A. and Bourgeat-Lami, E., Polym Int., pg.542. (2003).
[12] Palumbo, P., International congress of imaging science, pg.559. (2002).
[13] Fei, X., Zhang, T. and Zhou, C., Dyes Pigment, pg.75. (2000).
[14] Yuan, J., Xing, W., Gu, G. and Wu, L., Dyes Pigment., pg. 463. (2008).
[15] Yuan, J., Zhou, S., You, B.and Wu, L., Chem. Mat., pg.3587. (2005).
[16] Fu, S.H. and Fang K.J., J. Appl. Polym. Sci., pg.317. (2007).

Author Biography

FU Shao-hai, PHD, Key Laboratory of Science & Technology of Eco-Textile Ministry of Education, Southern Yangtze University, Wuxi 214122, P. R. China.

E-mail: shaohaifu@hotmail.com