

Preparation of Nanoscale Azo Pigment Yellow 13/poly(styrene–maleic acid) Composite Dispersions via Free-Radical Precipitation Polymerization

Shaohai Fu,¹ Changhai Xu²

¹Key Laboratory for Eco-Textile of Ministry of Education, Jiangnan University, 1800 Lihu Road, Wuxi 214122, Jiangsu, People's Republic of China

²Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University, Box 8301, Raleigh, North Carolina 27695

Received 11 December 2008; accepted 19 July 2009

DOI 10.1002/app.31171

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nanoscale azo pigment yellow 13 (PY13) was coated by poly(styrene–maleic acid) (PSMA) with a free-radical precipitation polymerization, followed by the preparation of the dispersion. The effects of the PSMA structure on the particle size and centrifugal stability were investigated. The experimental results revealed that the particle size was large, and the stability of the PY13/PSMA dispersions was high when the molar ratio of the feeding maleic acid to styrene, the weight ratio of the feeding initia-

tor to monomer, and the weight ratio of the feeding monomer to pigment were about 1.0, 0.6, and 20%, respectively. Fourier transform infrared spectroscopy, dynamic light scattering, and transmission electron microscopy indicated that PY13 was coated by PSMA. The PY13/PSMA dispersion was stable in the pH range 5.6–10.5. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1929–1934, 2010

Key words: coatings; dispersions; microencapsulation

INTRODUCTION

Nanoscale pigment/polymer composites are of growing interest to many people because they can greatly improve pigment quality and are useful in industrial applications, such as cosmetics, plastics, inks, and paints.

Several methods have been developed to coat pigments by polymers, such as miniemulsion polymerization,^{1–4} phase-separation techniques,^{5,6} *in situ* polymerization,^{7–9} layer-by-layer assembly techniques,^{10,11} and the sol–gel method.¹² When an organic pigment is coated by a polymer, some novel functions are introduced by the coating polymer. For example, the stability and rheological behavior of composite dispersions were improved when an organic pigment was coated by amphiphilic copolymers,⁶ the lightfastness and solvent resistance were strengthened when an organic pigment was coated by polystyrene,⁵ and the thermal stability and acid and alkali resistance were enhanced when an

organic pigment was coated by some inorganic materials.^{10,11}

In this study, we prepared nanoscale pigment yellow 13 (PY13)/poly(styrene–maleic acid) (PSMA) dispersions via a free-radical precipitation polymerization. The effects of the process conditions on the particle size and centrifugal stability were investigated. The literature indicated that the use of this method for coating an organic pigment has seldom been reported.

EXPERIMENTAL

Materials

Azo PY13 (purity = 99.8%, Wuxi Xinguang Co., Ltd., China) Azobisisobutyronitrile (analytical grade), sodium hydroxide (analytical grade), and maleic acid (analytical grade) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Styrene (chemical grade) was purchased from Shanghai Lingfeng Chemical Reagent Co.; it was distilled *in vacuo* and kept refrigerated for further use. The chemical structure of PY13 is shown in Figure 1.

Preparation of the PY13/PSMA composites

PY13 (20 g) was dispersed in 100 g of toluene. The mixture was treated by ultrasonic waves for 30 min

Correspondence to: S. Fu (shaohaifu@hotmail.com).

Contract grant sponsor: The Natural Science Foundation of Jiangsu Province, China (NSFC); contract grant number: BK2007021.

Contract grant sponsor: Program of Innovative Research Team (PIRT), Jiangnan University, China.

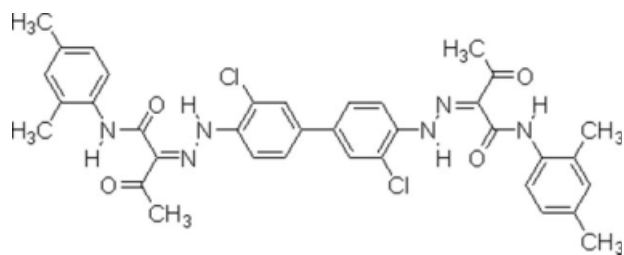


Figure 1 Chemical structure of PY13.

at 90% amplitude with a Branson (Okada, Japan) sonifier W450 Digital and then transferred into a 250-mL, four-necked round flask. Quantities of styrene, maleic acid, and azobisisobutyronitrile were dissolved in 80 g of toluene. Half of this solution was charged into a four-necked round flask and stirred at 1200 rpm for 30 min to get the dispersion. The dispersion was heated to 65°C and kept at this temperature under stirring at 400 rpm for 15 min. The remaining solution was added dropwise to the dispersion within 30 min, and the temperature was kept at 65°C for 4 h under stirring. At the termination of the reaction, the dispersion was centrifuged to give a slurry. The slurry was washed with methanol and then centrifuged; we repeated this process three times. The final product was dried at room temperature to give the PY13/PSMA composite.

The whole coating process included four steps, as shown in Figure 2. First, the monomers and initiator were dissolved in the solvent, and then, the pigment was dispersed into this solution. Second, PSMA was produced and then deposited onto the pigment surface for its poor solubility in the solvent. Third, the amount of PSMA that deposited onto the pigment surface increased with increasing reaction time. Finally, the PSMA was coated onto the pigment after it was dried in an oven.

Preparation of the PY13/PSMA dispersion

The PY13/PSMA dispersion was prepared with 5 g of the PY13/PSMA composite and 95 g of distilled water. After the pH value was adjusted to 8.0 with NaOH (1 mol/L), the mixture was heated to 50°C

and stirred by an Ultra Turrax IKA T18 Basic instrument (Germany) at a rate of 4000 rpm for 30 min.

Preparation of the comparative dispersion

PSMA was prepared under the conditions described for the preparation of the PY13/PSMA composite without the pigment. PSMA (9 g) was dissolved in 203.5 g of aqueous media. After the pH value was adjusted to 9.0 with an NaOH solution (1 mol/L), 37.5 g of PY13 was added to the solution. The mixture was treated by ultrasonic waves until the particle size no longer changed to produce the comparative dispersion (PSMA-dispersed PY13 dispersion).

Characterization

Centrifugal stability

The PY13/PSMA dispersion (0.1 g) was diluted 2000 times. The absorbance spectrum was measured with an ultraviolet-visible spectrophotometer (UV-2000 and UV-2100 models, UNICO Instruments Co., Ltd., Shanghai, China). The wavelength of maximum absorbance was found to be 430 nm, and then, the absorbance was recorded (A_0). After the PY13/PSMA dispersion was centrifuged at 3000 rpm for 30 min, 0.03 g of the upper dispersion in the tube was taken out and diluted 2000 times by distilled water. The absorbance of the dispersion (A_{30}) at a wavelength of 430 nm was measured. The relative absorbance (r_{30}) was calculated according to eq. (1).

$$r_{30} = \frac{A_{30}}{A_0} \times 100\% \quad (1)$$

with r_{30} , the centrifugal stability of the PY13/PSMA dispersion could be evaluated, and the larger r_{30} was, the higher the centrifugal stability was.

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of PSMA (in KBr pellets), original PY13 (in KBr pellets), and the PY13/PSMA composite

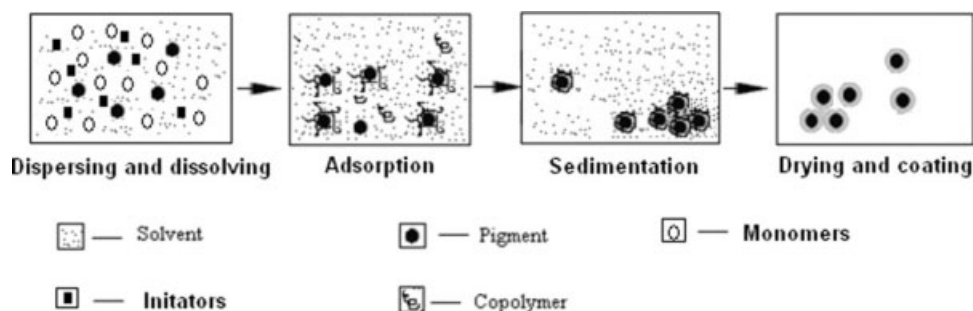


Figure 2 Schematic of the coating course by free-radical precipitation polymerization.

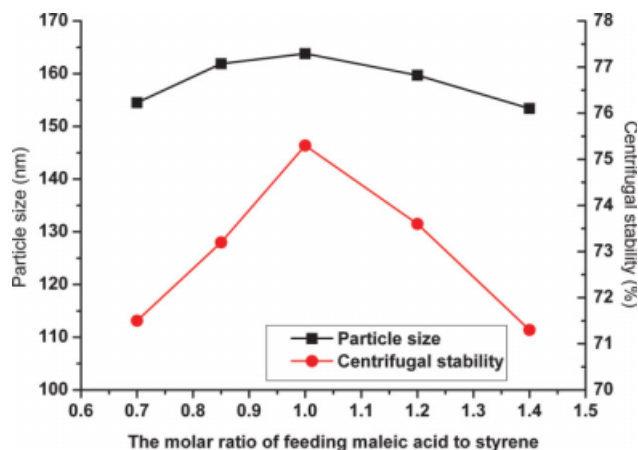


Figure 3 Effect of $M_{m/s}$ on the particle size and centrifugal stability of the PY13/PSMA dispersion (particle size maximum standard deviation = 1.2, centrifugal stability maximum standard deviation = 0.8, $R_{i/m} = 0.6\%$, $R_{C/P} = 20\%$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(in KBr pellets) were recorded on a Nicolet Nexus 560 FTIR spectrometer (Thermo Electron Corp., USA).

Particle size analysis

The PY13/PSMA dispersion was diluted 2000 times, and its pH value was adjusted to 8.0. The particle size was measured by a Nano-ZS90 (Malvern Instruments, Ltd., Worcestershire, England), and each sample was measured three times to obtain an average particle size.

Morphological analysis

One drop of the dispersion was diluted by water, then placed on a 400-mesh carbon-coated copper grid, and dried in air. The morphologies of original PY13 and PY13/PSMA in the dispersion were characterized with a transmission electron microscope (Jeol JEM-100SX, Akishima, Japan).

Contact angle analysis

The sample was uniformly coated onto a glass slide and then pressed slightly with another glass slide to ensure a flat surface. The contact angle of water on the sample was tested by a Krüss DSA 100 (Hamburg, Germany). Each sample was measured three times to obtain an average contact angle.

Freeze–thaw stability

The sample was sealed and stored at -5°C for 12 h and then transferred to an oven set at 60°C . The particle size of the dispersion was measured after stor-

age for different times. The freeze–thaw stability was evaluated by the changing rate of particle size (S_T) as given by eq. (2).

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

where d_0 is the starting particle size and d_T is the particle size of the dispersion after the freeze–thaw treatment at a specific time. The smaller S_T was, the higher freeze–thaw stability of the dispersion was.

Stability of the pH values

The pH values of the dispersions were adjusted by HCl (1 mol/L) and NaOH (1 mol/L), respectively, and then, the dispersions were stored at room temperature for 24 h. The changing rate of the particle size (S_{pH}) was calculated by eq. (3):

$$S_{pH} = \frac{|d_0 - d_{pH}|}{d_0} \times 100\% \quad (3)$$

where d_0 is the starting particle size and d_{pH} is the particle size of the dispersion at different pH values. The smaller S_{pH} was, the higher the stability of the pH value of the dispersion was.

RESULTS AND DISCUSSION

Preparation of the PY13/PSMA dispersion

Figure 3 shows that the particle size reached its maximum when the molar ratio of the feeding maleic acid to styrene ($M_{m/s}$) was equal to 1.0. It is known that styrene and maleic acid tend to alternate

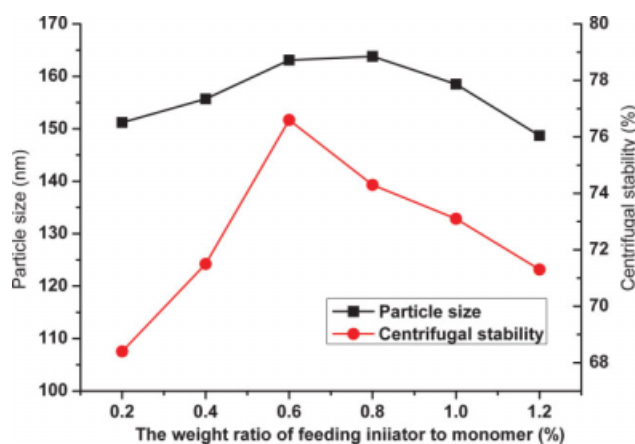


Figure 4 Effect of $R_{i/m}$ on the particle size and centrifugal stability of the PY13/PSMA dispersion (particle size maximum standard deviation = 0.9, centrifugal stability maximum standard deviation = 0.5%, $M_{m/s} = 1.0$, $R_{C/P} = 20\%$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

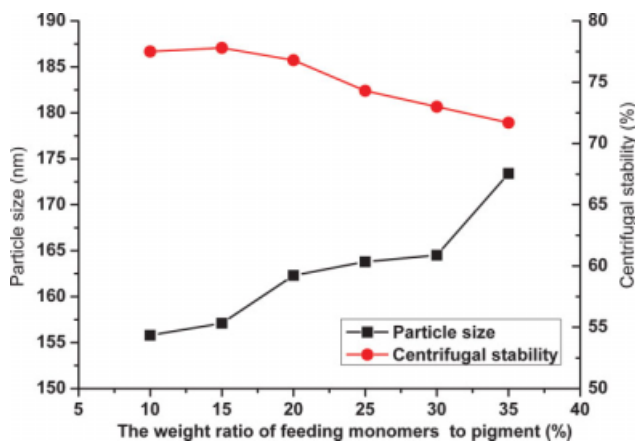


Figure 5 Effect of $R_{C/P}$ on the particle size and centrifugal stability of the PY13/PSMA dispersion (particle size maximum standard deviation = 1.1, centrifugal stability maximum standard deviation = 0.9%, $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in a free-radical copolymerization.¹³ Therefore, more copolymers were coated onto the pigment surface when $M_{m/s}$ was equal to 1.0, which led to a thicker coating layer. Similar to the change of particle size, the centrifugal stability reached its maximum as well when $M_{m/s}$ was equal to 1.0; this indicated that the centrifugal stability was closely related to the thickness of the coated layer. Generally, the thicker coating layer was, the stronger steric repulsion was.¹⁴

Figure 4 show that both the particle size and the centrifugal stability reached their maximum when the weight ratio of the feeding initiator to monomer ($R_{i/m}$) was about 0.6%. It is known that under the same conditions, a smaller amount of initiator produces a higher number-average molecular weight (M_n) of

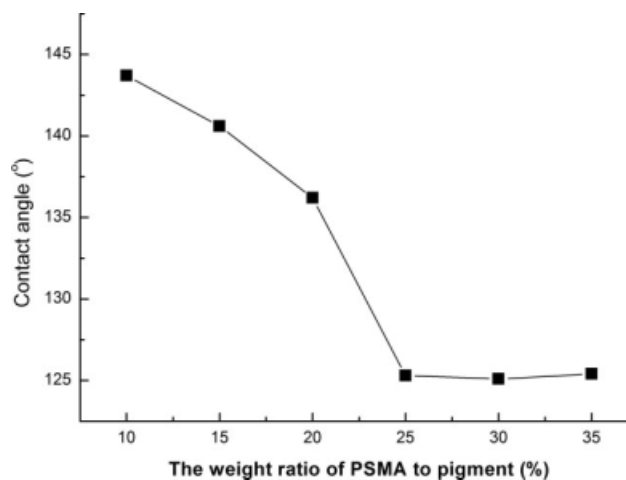


Figure 6 Effect of $R_{C/P}$ on the water contact angle of the PSMA/pigment composite (maximum standard deviation = 1.2, $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$).

PSMA, and the higher M_n caused a quicker sedimentation speed.¹⁵ When $R_{i/m}$ was lower than 0.6%, M_n was high enough to cause a high sedimentation speed during the coating process. As a result, some PSMA could not coat onto PY13; this resulted in a small particle size. When $R_{i/m}$ was higher than 0.6%, however, the attractive forces between the PY13 and PSMA were small for low M_n ; in that way, some PSMA was washed off, which led to the small particle size.

The change in the centrifugal stability with the weight ratio of the feeding initiator may have been due to the chain length of PMSA. When the chain of PSMA was long enough, the stretching chain could bridge two or more particles; therefore, the particles easily deposited under centrifugal forces. On the contrary, when the chain was short, the repulsion

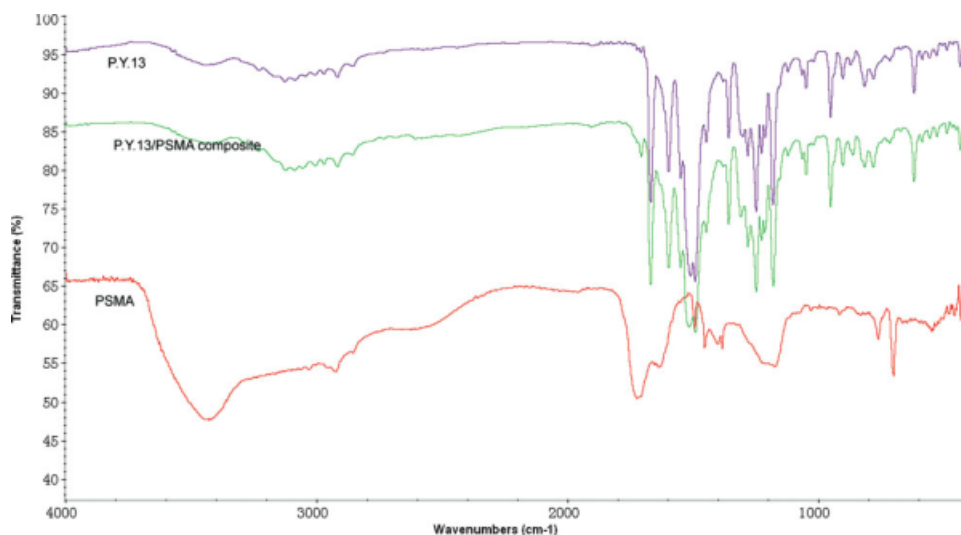


Figure 7 FTIR spectra of the PSMA, original PY13, and PY13/PSMA (process conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

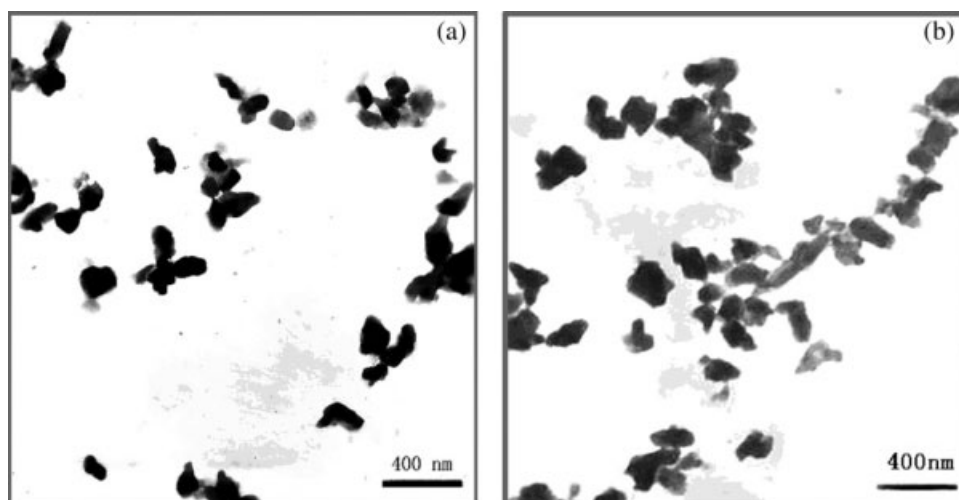


Figure 8 Transmission electron micrographs of the (a) PSMA-dispersed PY13 dispersion and (b) PY13/PSMA dispersion (process conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$).

among the particles was small because some PSMA was washed off of the pigment surface; this led to poor centrifugal stability.

Figure 5 shows that the increase in the weight ratio of the feeding monomer to pigment ($R_{C/P}$) brought about an increase in the particle size and a decrease in the centrifugal stability. These results indicate that the amount of PSMA deposited onto the pigment surface increased with increasing $R_{C/P}$. Moreover, the changes in particle size and centrifugal stability were interrelated. According to Stokes' law, the particle's settling velocity is directly proportional to the square of the particle size and inversely proportional to the fluid's dynamic viscosity.¹⁶ Therefore, the centrifugal stability decreased with increasing particle size, whereas the viscosity changed little.

In addition, when $R_{C/P}$ was high enough, some PSMA dissolved in the media bridged two or more particles, which also led to the large particle size and poor centrifugal stability. As shown in Figure 5, the optimal $R_{C/P}$ was observed to be 20–25%. These results were further confirmed by the relationship between the contact angle of water on the PY13/

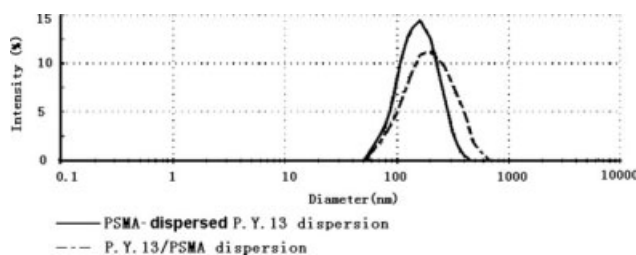


Figure 9 Particle size distribution of the (a) PSMA-dispersed PY13 dispersion and (b) PY13/PSMA dispersion (process conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$).

PSMA composite and $R_{C/P}$ (Fig. 6). PSMA was more hydrophilic than PY13, therefore, as more PSMA was coated onto the pigment, the PY13/PSMA composite displayed a decreased water contact angle.

Characterization of the PY13/PSMA composite and its dispersions

FTIR spectra

Figure 7 shows the spectra of PY13 and the PY13/PSMA composite. The absorbance bands, which were assigned to PSMA ($-\text{COOH}$ stretching vibration at 1710 cm^{-1} and $\text{C}=\text{C}$ on the benzene ring stretching vibration at 1454 , 1495 , and 1601 cm^{-1}) were present in the spectra of the PY13/PSMA composite. Comparing the spectra, we found that the spectra of PY13 and the PY13/PSMA composite

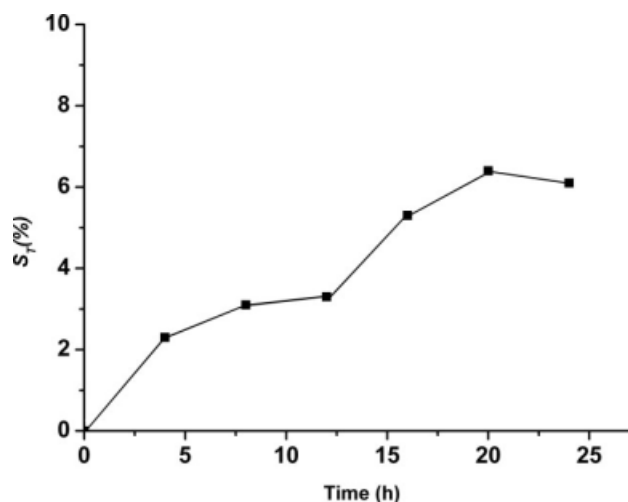


Figure 10 Freeze–thaw stability of the PY13/PSMA dispersion (process conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$).

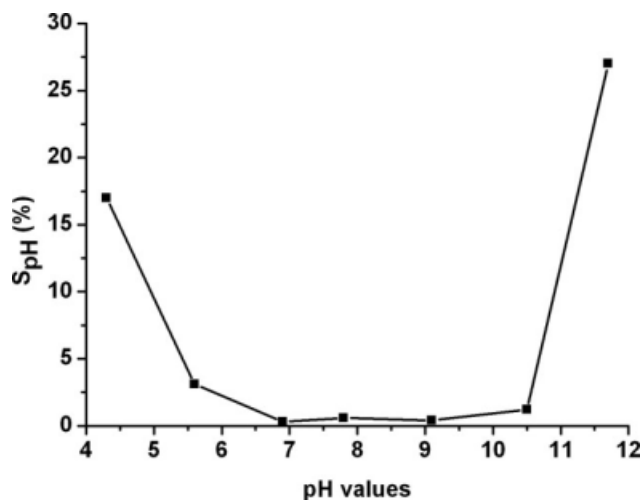


Figure 11 Stability of the PY13/PSMA dispersion to pH value (process conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$).

were similar except for the peak at 1710 cm^{-1} , which suggested that PSMA was coated onto the pigment.

Transmission electron micrographs and particle size distribution

Figure 8 showed that particle size of PY13/PSMA [Fig. 8(b)] was uniformly distributed and was a little larger than that of PSMA-dispersed PY13 [Fig. 8(a)] in the dispersion. This result was further confirmed by the particle size distribution measured by the dynamic lightscattering (DLS) method (Fig. 9). The particle size of the PY13/PSMA composite mainly distributed in the range 50–700 nm and was a little larger than that of PSMA-dispersed PY13 dispersion. These results indicated that PY13 was coated by PSMA.

Freeze–thaw stability

Figure 10 indicates that the dispersion had a quite high thermal stability, even with a long-term freeze–thaw treatment. When PSMA was completely absorbed onto the pigment, the attractive forces between PSMA and PY13 were so strong that PSMA was hardly peeled off, even at high temperatures.

Stability with the pH value

Figure 11 indicated that the dispersion was stable in the pH range 5.6–10.5, and the changing rate of the particle size increased sharply when the pH value was out of this range. As discussed previously, because PSMA was completely absorbed onto PY13 via hydrophobic chains, the attractive forces became

stronger so that the PSMA was hardly peeled off. However, when the pH value was below 5.6, few $-\text{COOH}$ groups reacted with OH^- , the electric repulsion was small for few $-\text{COO}^-$ groups on the pigment surface, and thus, the particles could easily combine each other. On the other hand, almost all of the $-\text{COOH}$ groups reacted with OH^- when the pH value was high enough. The attractive forces between PSMA and the pigment were small for the high solubility of PSMA; thus, the PSMA was easily desorbed from the pigment surface, which led to poor stability and a large S_{pH} .

CONCLUSIONS

A nanoscale PY13/PSMA dispersion was prepared with free-radical precipitation polymerization. Both the particle size and the stability of the dispersion attained satisfactory results when it was prepared under the following conditions: $M_{m/s} = 1.0$, $R_{i/m} = 0.6\%$, and $R_{C/P} = 20\%$. Some PSMA was successfully coated onto the pigment surface. The PY13/PSMA dispersion showed excellent thermal stability.

The authors thank Southern Yangtze University for supporting the course of this research.

References

- Lelu, S.; Novat, C.; Graillat, C.; Goyot, A.; Bourgeat-Lami, E. *Polym Int* 2003, 52, 542.
- Tiarks, F.; Landfester, K.; Antoniet, M. *Macromol Chem Phys* 2001, 202, 51.
- Zhou, J.; Zhang, S. W.; Qiao, X. G.; Li, X. Q.; Wu, L. M. *J Polym Sci Part A: Polym Chem* 2006, 44, 3202.
- Zeng, Z.; Yu, J.; Guo, Z. X. *Macromol Chem Phys* 2004, 205, 2197.
- Zhang, T. Y.; Fei, X. N.; Song, J.; Zhou, C. L. *Dyes Pigments* 1999, 44, 1.
- Fu, S. H.; Fang, K. J. *J Appl Polym Sci* 2007, 105, 317.
- Xun, Y. J.; Liu, Y. N.; Shu, W. G.; Xiong, L. M. *Paint Coat Ind* 2003, 33, 15.
- Feng, W.; Wang, S.; Wang, L. *Fine Chem (China)* 2002, 19, 538.
- Xu, W. J.; Chen, H. Z.; Li, H. Y.; Wang, M. *Colloids Surf A* 2005, 266, 68.
- Yuan, J. J.; Xing, W. T.; Gu, G. X.; Wu, L. M. *Dyes Pigments* 2008, 76, 463.
- Yuan, J. J.; Zhou, S.; You, B.; Wu, L. *Chem Mater* 2005, 17, 3587.
- Yuan, J. J.; Zhou, S.; Wu, L. M.; You, B. *J Phys Chem B* 2006, 110, 388.
- Tian, A. L.; Cai, Y. Q.; Fang, K. J.; Zhang, X. *Polym Mater Sci Eng (China)*, 2005, 11, 103.
- Elias, H. G. *An Introduction to Polymer Science*; VCH: New York, 1997.
- Fu, S. H.; Fang, K. J. *J Dispersion Sci Technol* 2008, 29, 1085.
- Lamb, H. *Hydrodynamics*; Dover: New York, 1993.