Preparation of TiO_2/latex Composite for inkjet white ink

Liping Zhang[1], Fushun Bai[1], Changsen Du[2], Anli Tian[1], Guocheng Mei[2], Shaohai Fu[1]
[1]Key Laboratory of Eco-textiles, Ministry of Education, Jiangnan University, Wuxi, Jiangsu 214122, China
[2] Shi Ming Science and Technology Corporation, Kunshan, Jiangsu 215337, China

Abstract

A TiO_2/latex composite was prepared from KH570-modified TiO_2 and methylmethacrylate (MMA) via miniemulsion polymerization, and further was used to formulate a white inkjet ink. Fourier transform infrared spectrum (FTIR), Transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) indicated that the copolymer of DNS-86 and MMA was successfully coated onto TiO_2 surface and amount of copolymer was about 40%. A white inkjet ink prepared from the TiO_2/latex composite had a small particle size, a narrow particle size distribution and enhanced stabilities to temperature and centrifugal forces. This research may provide a method to prepare a white inkjet ink for textile inkjet printing.

Introduction

TiO_2 is an excellent white pigment due to its high durability and hiding power, which is more suitable for formulation of textile inkjet white ink [1,2]. However, to prepare TiO_2 dispersion with high stability may present a great challenge due to its large specific gravity.

In order to overcome the drawback and to prepare a stable TiO_2 dispersion, many methods have been devised to modify TiO_2. Modification of TiO_2 with silane coupling agent can introduce some lipophilic groups onto TiO_2 surface, which can effectively improve the dispersing performance of TiO_2 in the oil phase [3-5]. However, the stability of TiO_2 in aqueous media has not been improved [6-8]. To fabricate a core-shell composite which used copolymer as shell and TiO_2 as core may be an alternative method for preparation of TiO_2 dispersion with high stability in aqueous media. The copolymer plays important roles in providing strong repulsive static forces as well as reducing the specific gravity of TiO_2 [9-12]. At present, a variety of techniques have been developed for pigment encapsulation, which may also be used for TiO_2 encapsulation [13-15], such as emulsion polymerization [16], in situ polymerization [17], and phase flocculation method [18] and so on.

Although there are many methods for preparation of TiO_2 dispersion, it is still problematic to obtain dispersion with high stability to centrifugal forces and high temperature. In this study, the double bonds were introduced onto TiO_2 surface via silane coupling agent first, and then the TiO_2/latex composite with core-shell structure was prepared from KH570-modified TiO_2 and methacrylate (MMA) via miniemulsion polymerization, and the properties of the TiO_2/latex were further investigated.

Experimental

Materials

TiO_2 (Particle size 50 nm) was purchased from Shanghai Hongyunyuan Co., Ltd., China. γ-methacryloxypropyl trimethoxy silane (KH570) was purchased from Jiangsu Chenguang Co., Ltd., China. Ethyl alcohol, ammonium persulfate (APS), methylmethacrylate (MMA), hexadecane (HD), glycerin and Tween-80 were all of analytical grade, and purchased from Shanghai Chemical Reagent Co. Ltd., China. Distilled water was used in all the experiments. Allyloxy nonylphenol polyoxyethylene ether ammonium sulfate (DNS-86, Chart 1) was supplied by Adeka Co., Ltd., Japan.

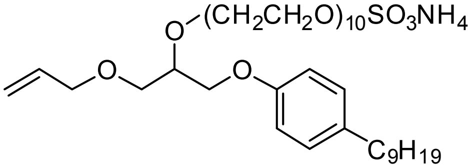

Chart 1. *Chemical structure of DNS-86*

Preparation of TiO_2/latex composite

Modification of TiO_2 with KH570

A mixture of 30 g TiO_2 was dispersed in a mixture solution, with 100 mL ethanol and 10 mL distilled water, followed by addition of 3 g KH-570. The pH value of the dispersion was adjusted to 9 by dropwise adding some amount of ammonia. The mixture was treated with ultrasonic machine for 10 min and then maintained at 30 °C for 24 h under stirring at 500 r/min. The mixture was centrifuged at 12000 r/min until all the particle was precipitated at the bottom of the centrifugal tube. The sediment was washed 3 times with distilled water, and then dried at room temperature under vacuum to get the KH570-modified TiO_2.

Preparation of TiO_2/latex composite

The procedure for preparing TiO_2/latex composite involves an oil phase consisting of 10 g KH570-modified TiO_2, 5 g MMA and 0.3 g HD, an aqueous phase consisting of 59 g deionized water, 0.05 g $NaHCO_3$ and 1 g DNS-86. The oil phase was slowly dropped into the aqueous phase at room temperature under stirring. The suspension was emulsified in an ice bath for 15min by ultrasonic waves (input power 1100 W) to give O/W miniemulsion.

The miniemulsion was transferred into a 250 mL four-neck flask equipped with stirrer, thermometer and condenser. When the temperature of the O/W miniemulsion was raised to 70 °C and maintained for 30 min, 10 g aqueous solution with 2% mass concentration of APS was added to the flask under nitrogen. After finishing the addition of the initiator, the temperature of the mixture was kept at 70 °C for 4 h to obtain TiO_2/latex composite dispersion.

The TiO_2/latex composite was obtained by cooling the mixture to room temperature. The prepared dispersion was centrifuged at 12000 r/min until all the TiO_2/latex composite was precipitated at the bottom of the centrifugal tube. The sediment was washed 3 times with methanol and dried at room temperature under vacuum to prepare the TiO_2/latex composite.

Formulation of white inkjet ink

A white inkjet ink was prepared with the TiO_2/latex composite particles. The formulation in a weight bases was given as follows: 30% TiO_2/latex dispersion, 30% glycerol, 1.2% Tween-80, and 38.8% distilled water. The above components were mixed under ultrasonic waves (input power 1100 W). The white ink was obtained after filtered through a 500 nm pore filtering sieve.

Characterization

Transmission electron microscope (TEM)

One drop of dispersion was diluted to 2000 times with distilled water, and then was coated on a 400-mesh carbon-coated copper grid and dried in the air. TEM observations were performed using a Hitachi H-7000 transmission electron microscope.

FTIR spectrum

The samples were ground and pressed into KBr pellets. FTIR spectrum was recorded on a Nicolet Nexus 560 FTIR spectrometer. For each spectrum, it was collected at 4000-500 cm^{-1} range with an 8 cm^{-1} resolution and 32 scans.

Thermogravimmetric analysis (TGA)

Thermogravimmetric analysis was performed on a Perkin-Elmer instrument Diamond TG/DTA analyzer. 3-5 mg samples were placed in ceramic pot and heated from room temperature to 800 °C at a rate of 5 °C /min under air atmosphere.

Physical properties of the white ink

The apparent viscosity of the dispersion was measured using Brookfield DV-III at 25°C with shear rate 30 s^{-1}. The surface tension was measured using a ring method in Drop Shape Analysis System DSA100. The particle size of the white ink was measured by DLS method.

Hiding power

Hiding power (X) was tested according to the standard method ISO2814-1976 and evaluated using Eq. (1),

$$X = \frac{R_B}{R_W} \times 100\% \qquad (1)$$

Where R_B is the reflectance of sample coated on the black plate, R_W is the reflectance of sample coated on white plate.

Stability

Stability to temperature (S_T): The dispersion was stored in a sealed container at 60 °C for 24 h. ST was evaluated using Eq. (2),

$$S_T = (1 - \frac{|d_0 - d_T|}{d_0}) \times 100\% \qquad (2)$$

Where d_0 is the particle size of the original sample, and d_T is the particle size of the sample stored at 60 °C.

Centrifugal stability (Sc): The dispersion was centrifuged at 2000 r/min for 30 min. 0.03 g super dispersion in centrifuge tube was taken out to dilute 2000 times with distilled water. Spectrophotometry was performed on a UNICO UV-2000 spectrophotometer to determine the absorbance at the wavelength for the maximum absorbance (410 nm) before and after the centrifugal treatment. Sc was calculated according to the Eq. (3),

$$S_C = \frac{A_{CS}}{A_0} \times 100\% \qquad (3)$$

Where A_0 is the absorbance before centrifugal treatment, A_{CS} is the absorbance after centrifugal treatment.

Results and discussion

TEM

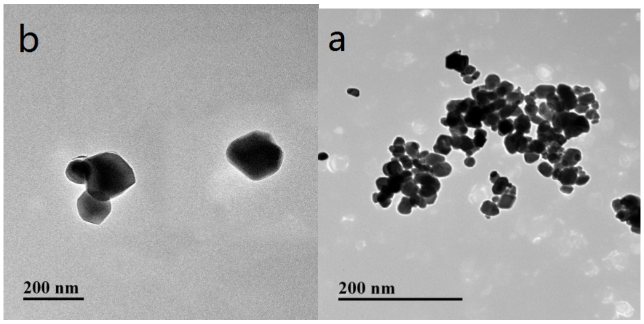

Fig.1 TEM photos of (a) KH570-modified TiO_2 and (b) TiO_2/latex composite

As shown in Fig. 1, the diameter of TiO_2/latex composite was much greater than that of the KH570-modified TiO_2, and a core-shell structure was observed in the TEM photos with the particle size of 185 nm. The result indicates that the latex was successfully coated onto TiO_2 surface.

FTIR

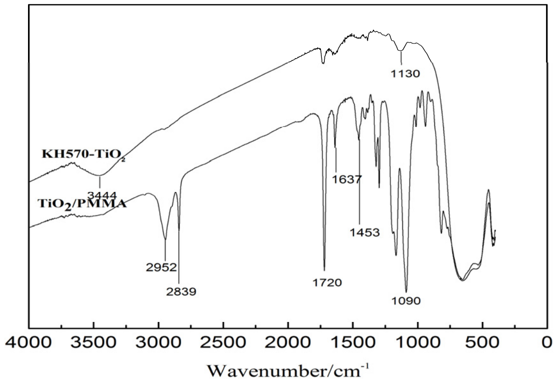

Fig. 2 *FTIR of KH570-TiO$_2$ and TiO$_2$/latex nanoscale composite particles*

Fig.2 shows FTIR spectra of TiO$_2$/latex composite. Compared with the spectra of KH570-modified TiO$_2$, the new absorbance bands appeared on TiO$_2$/latex composite at 1720 cm^{-1} assigned to C=O stretching vibration, 2952 cm^{-1} and 2839 cm^{-1} assigned to -CH$_2$ stretching vibration, 1637 cm^{-1}, 1453 cm^{-1} and 1402 cm^{-1} assigned to benzene ring stretching vibration, and 1090 cm^{-1} assigned to C-O stretching vibration. There are all characteristic frequencies of the copolymer formed from MMA and DNS-86, which indicates that the latex encapsulated on TiO$_2$ is the copolymer of DNS-86 and MMA.

TGA

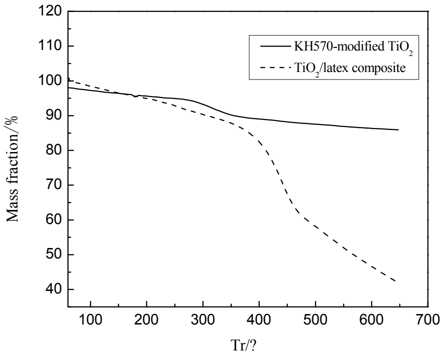

Fig.3 *TGA of KH-570-TiO$_2$ and TiO$_2$/ latex nanoscale composite particles*

The amount of latex coated onto TiO$_2$ surface was determined by TGA. As shown in Fig.3, the TiO$_2$/latex composite had a small weight loss in the temperature range of 50 to 200 °C, which was ascribed to the evaporation of physically adsorbed water. The TiO$_2$/ latex composite had higher water content than the KH570-modified TiO$_2$ because latex contained sulfate groups (-COO$^-$) that imparted better hydrophilic performance. In the temperature range of 250 to 350 °C, the KH570-modified and the TiO$_2$/ latex composite had a weight loss of 10%, which may be ascribed to the decomposition of the KH570 that was grafted onto TiO$_2$. A subsequent weight loss of 40% in the TiO$_2$/ latex composite in the temperature range of 380 to 550 °C, which may be ascribed to the decomposition of the latex coated onto the TiO$_2$. Therefore, it can be concluded that latex was successfully encapsulated onto TiO$_2$ and the latex content was evaluated to be 40%.

Properties of white ink prepared from TiO$_2$/Latex composite dispersion

The basic physical properties of the white ink

The physical properties of the white ink prepared from the TiO$_2$/latex composite and conventional TiO$_2$ respectively are summarized in Table 1. It can be seen that the viscosity, surface tension and particle size of the white ink prepared from TiO$_2$/PMMA composite was found to be 3.86 mPa.s, 34.4 mN/m and 183.5 nm, which were satisfied with printing requirements of Mimaki JV4-180.

Table 1. the basic physical properties of the white ink

White ink prepared with	η (mPa.S)	σ (mN/m)	D (nm)
TiO$_2$	3.26	29.5	203.6
TiO$_2$/ latex composite	3.86	34.4	183.5

The hiding power of the white ink

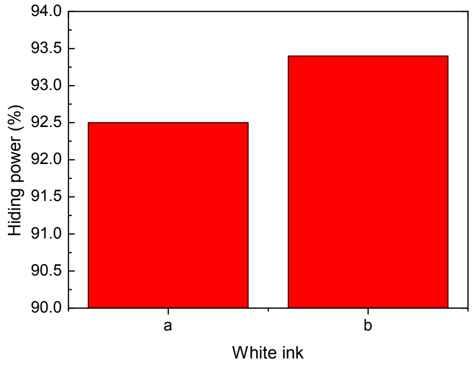

Fig. 4 Hiding power of the white ink prepared from (a) commercial TiO$_2$ (b) TiO$_2$/ latex composite

Fig. 4 shows the hiding power of the white ink prepared from TiO$_2$/ latex composite and commercial TiO$_2$, respectively. It can be seen that with the same amount of TiO$_2$, the hiding power of the white ink prepared with TiO$_2$/ latex composite is higher than that of commercial TiO$_2$. The reason may be due to that the particle size of TiO$_2$/ latex composite is smaller than commercial TiO$_2$, leading to a high hiding power for cover area was increased.

The stability of the white ink

Fig. 5 shows that the stability of white ink prepared from TiO$_2$/ latex composite is much better than that of commerical TiO$_2$. In TiO$_2$/ latex composite, some amount of -SO$_3^-$ groups were introduced onto the TiO$_2$ surface, and moreover, DNS-86 was attached onto TiO$_2$ surface via covalent bond. Therefore, it was hard to desorbing from TiO_2 surface, even at high temperature or strong centrifugal forces.

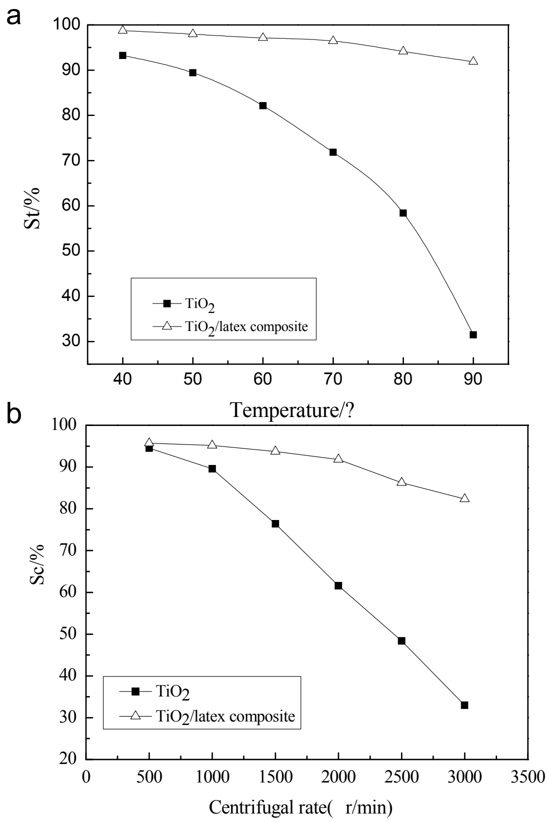

***Fig.5** Stability of the white ink prepared from TiO_2/ latex composite (a) stability to temperature, (b) centrifugal stability*

Conclusions

TiO_2/ latex composite with core-shell structure were prepared by miniemulsion polymerization method. The TiO_2/ latex composite were found to have particles at 185 nm and the latex content was evaluated to be 40%. The white ink prepared from TiO_2/ latex composite had a small particle size and enhanced stabilities to temperature and centrifugal forces, and was suitable for textile inkjet printing.

Acknowledgements

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Author Biography

Shaohai Fu received his PhD in College of Textiles and Clothing from Jiangnan University (2006). Since then, he has worked in Key Laboratory of Eco-Textiles of the Ministry of Education, Jiangnan University. His work has focused on textile dyeing and printing, digital textile inkjet printing and pigment modification. Now, He is the vice President of College of Textiles and Clothing, Jiangnan University, and a member of SDC and AATCC.