Preparation and Properties of Encapsulated Phthalocyanine for Inkjet Printing Inks

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Abstract

Encapsulated phthalocyanine blue pigment dispersion was prepared by polymerizale dispersant via free radical polymerization, and further was formulated into the inkjet printing ink. The properties of the ink were investigated. TEM and TGA proved that the pigment was encapsulated with some copolymer of Allyloxy Nonyl-phenoxy propanol polyoxyethylene ether ammonium sulfonate and styrene. The ink using these materials had excellent stability to freeze-thaw treatment and centrifugal forces, and its rheological behavior was close to Newtonian fluid. The properties of the ink satisfied with the requirement of Mimaki JV4-180 and can be used on Mimaki JV4-180.

INTRODUCTION

Inkjet printing is one of the fastest growing textile printing technologies, in addition to other advantages, it is more eco-friendly, requires low water and energy consumption, and has no or minimal residue dye water in comparison with conventional printing technologies [1]. The pigment inks that can be applied to all sorts of fabrics have become the main colorant in this technology [2, 3].

In order to prepare the pigment ink with small particle size, narrow particle size distribution and high stability, many methods have been developed. For example, Milling the pigment with the aid of dispersant, especially with polymeric dispersant. In this method, the dispersant would build voluminous shells or intensify the charges on pigment surface, which could effectively avoid flocculation and coagulation of the pigment in the dispersion [4, 5]. Nowadays, many structured polymeric dispersants have been synthesized and applied in pigment dispersing [6-8]. Encapsulation pigment by polymeric materials is another effective way to enhance the pigment properties, such as emulsion polymerization [9-11], phase separation [12, 13], in situ polymerization [14, 15], layer-by-layer assembly [16], and sol-gel [17, 18]. In order to improve the encapsulation efficiency, Nguyen and his co-worker encapsulate pigment using Macro-RAFT copolymers by emulsion polymerization [19]. Bombalski and his co-worker prepare hybrid materials using ATRP in Miniemulsion [20]. Lei Zhao et. al encapsulate organic fluorescent with methyl methacrylate and a polymerizable anionic surfactant [21]. Tatsuo Taniguchi prepared monodisperse fluorescent polymer particles with styrene and a polymerizable surfactant [22].

Although there are so many methods for pigment modification, how to prepare the ink with low viscosity and high stability is still an unresolved problem. In this study, we use polymerizable surfactant as dispersant and prepared phthalocyanine blue pigment dispersion,and further it was formulated into the inkjet printing ink. The properties of the ink were investigated.

EXPERIMENTAL

Materials

Press cake of Phthalocyanine Blue (water content 43%, Wuxi Xinguang Co. Ltd). Allyloxy Nonyl-phenoxy propanol polyoxyethylene ether ammonium sulfonate (ANPS, its chemical structure was shown in Chart 1, Adeka Japan,). Ammonium persulfate (APS, analytical grade). 2, 2'-Azo-bisiso-butylonitrile (AIBN, analytical grade) was purified by recrystallization with hot ethanol. Distilled water was used for all the experiments.

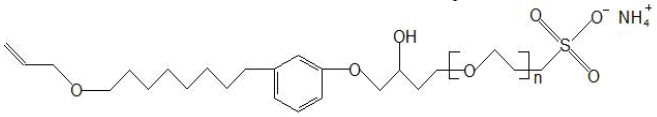

Chart 1 Chemical structure of ANPS

Preparation of encapsulated phthalocyanine blue pigment dispersion

A solution containing certain 7.2g polymerizable dispersant and 262.8g distilled water was prepared and adjusted pH value to 9 using sodium hydroxide solution (0.1mol/L).30g phthalocyanine blue pigment was added into the solution under stirring at 500r/min. The mixture was transferred to a bead mill (0.8 mm, ZrO2 bead as milling medium, the mass ratio of ZrO2 to pigment was about 5:1, Minizeta 03E, Netzsu, Germany), and dispersed for different time to give an nanoscale pigment dispersion.

0.06g APS was dissolved in 60g deionized water, and then 12g initiator solution and 6g styrene was feeding into above dispersion. The dispersion was emulsified with high-speed stirrer machine for 20 min at 25 ^{o}C, and transferred to a 4-neck flask equipped with a stirrer, thermometer and condenser. The temperature was raised to 78 ^{o}C and kept for 30min, and then the remaining initiator solution was injected into the flask in 30 min and remained 78 ^{o}C for 4 hours. The dispersion cooled to room temperature, and then the encapsulated pigment dispersion was obtained.

Ink formation

Inkjet printing inks were prepared by above encapsulated pigment dispersion. The formulation in a weight basic was given as follows: encapsulated pigment dispersion 70%, glycerol 17%, and ethylene glycol mono-methyl ether 5%, Tween-80 1% and distilled water 7%. The above components were mixed under stirring until a homogeneous dispersion was obtained. After filtered through a 0.5 μm pore filtering sieve, the inks were prepared and loaded on inkjet printing machine (Mimaki JV4-180, Pizeo-electric inkjet printer, Shinagawa Tokyo, Japan).

Measurement

The encapsulated pigment was proved by transmission electron microscope (TEM) and thermo-gravimetric analyses (TGA). The sample was diluted with water at pH=8 until the suspension was no longer opaque. One drop of the diluted suspension was placed on a copper grid to support the sample, the excess liquid was removed with a tissue, and the grid was left to dry. A Phillips CM12 TEM microscope was used to observe the pigment particles. TGA were performed by Perkin-Elmer instruments Diamond TG/DTA Analyzer, with a heating rate of 5oC/min under air atmosphere.

The ink was evaluated for its properties in terms of viscosity, surface tension, particle size and stability. The viscosity against shear rate was measured using Brookfield DV-III at 25 oC with shear rate 30 s−1. The surface tensions were measured using a ring method in Drop Shape Analysis System DSA100. The particle size distribution was measured by Nano-ZS90. The centrifugal stability and freeze-thaw stability were evaluated by comparing the particle size distribution before and after treatment.

The printing performance of the inks was tested on Mimaki JV4-180. The clogging nozzle rate (B) was calculated according to Eq. (1):

$$B = \frac{C_1}{S} \times 100\% \quad (1)$$

Where C1 is the amount of clogged nozzle, S is the sum of the nozzle on the print head. The cotton fabric (24 cm×24 cm) was printed by Mimaki JV4-180.

RESULTS AND DISCUSSION

Preparation of encapsulated pigment dispersion

Figure 1a, b illustrated the TEM imagines of the original phthalocyanine blue pigment and encapsulated phthalocyanine blue pigment. It can seen that the particle size of encapsulated phthalocyanine blue pigment was bigger and more uniform than that of phthalocyanine blue pigment, which indicated that some copolymer was encapsulated onto pigment surface.

In order to calculate the amount of polymer that encapsulated onto pigment surface, we further investigated the TGA curves of original phthalocyanine blue pigment and encapsulated phthalocyanine blue pigment. It can be seen from Figure 2 that only a small weight losses appeared in the original phthalocyanine blue pigment, which was due to the evaporation of physically adsorbed water. While in the encapsulated pigment, two weight loss peaks appeared, the initial 3.74% weight loss appeared in low temperature range (50 - 128 ◦C) for the evaporation of physically adsorbed water. The subsequent loss of 14.21% (250–450 ◦C) was due to the decomposition of polymers that encapsulated onto pigment. According to the TGA curves, the polymer content of in encapsulated pigment is evaluated to be 14.21%.

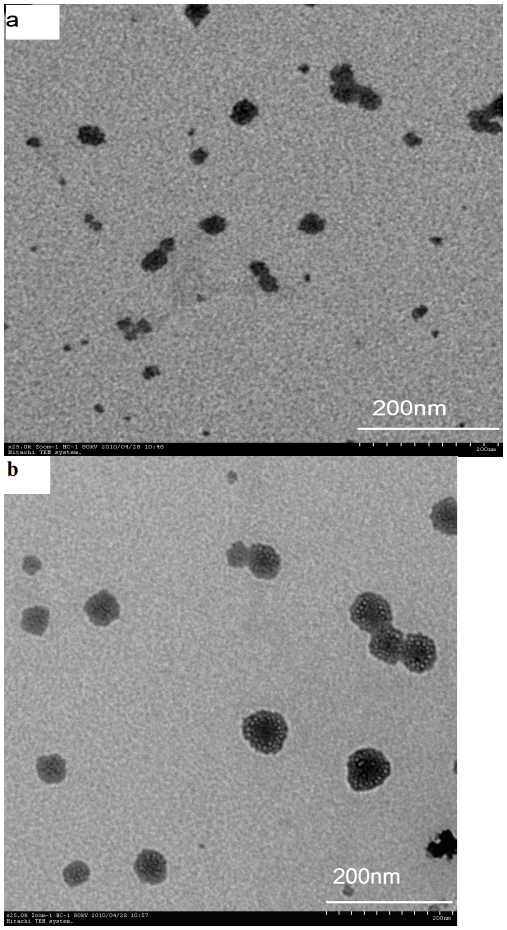

Figure 1 TEM imagine of (a) uncoated phthalocyanine blue pigment and (b) encapsulated phthalocyanine blue pigment.

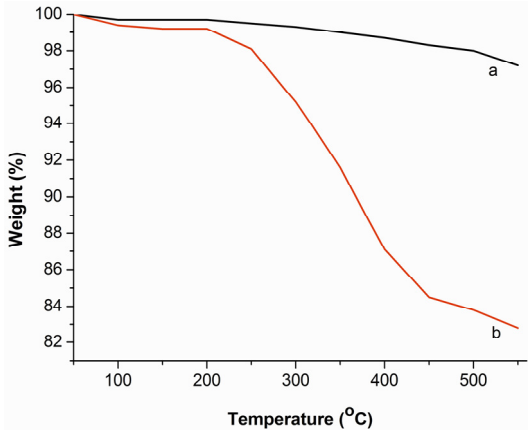

Figure 2 TGA curves of (a) original phthalocyanine blue pigment and (b) encapsulated phthalocyanine blue pigment

Properties and its printing performance of the ink
Particle size distribution

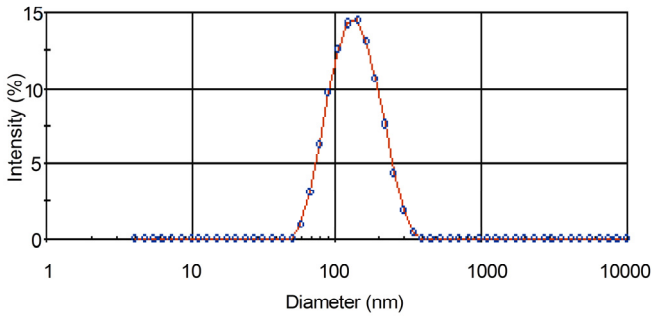

Figure 3 Particle size distribution of the ink

The small particle size and narrow Particle size distribution of the ink can obtain the excellent color performance and stability of the ink. Figure 3 showed that the smallest particle size was about 40nm and the largest particle size was about 400nm, the mean particle size was about 120.6 nm, which was far smaller than the diameter of the nozzle (40μm). These results indicated that the encapsulated disperse dye can be used to formulate inkjet printing ink.

Rheological behavior

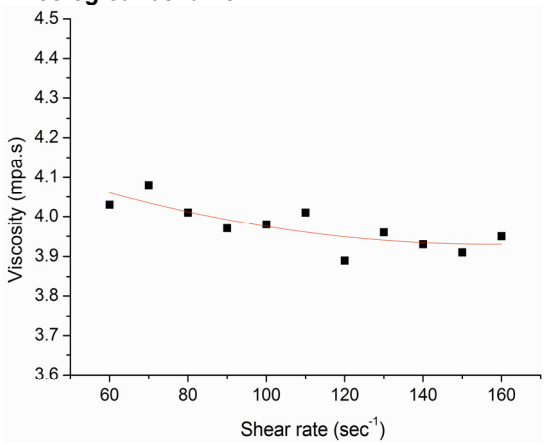

Figure 4 Effect of shear rate on viscosity of encapsulated disperse dye dispersion

The rheological behavior of an excellent ink needed to be as close to Newtonian as possible. As a result, the flow performance of the ink could not be disturbed by the piezoelectric pulse. Figure 4 showed that the ink exhibited a quite stable viscosity when the shear rate was in the range of 60 to 160 sec^{-1}. These results indicated that it was suitable for inkjet printing machine.

Stability of the ink

Figure 5 indicated that the particle size of the ink became narrow and small after the ink centrifugal treatment. The sedimentation speed of the small pigment particles would be offset by the Brownian motion at centrifugal speed, while some large particles would be deposited for centrifugal forces, thus led to the above changing of the particle size distribution.

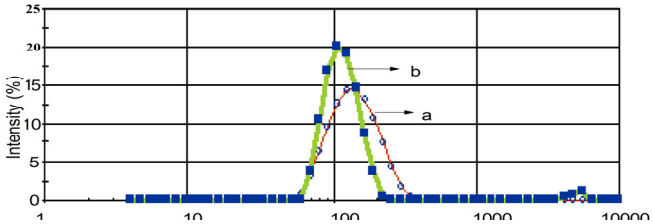

Figure 5 Particle size distribution of the ink (a) before and (b) after centrifugal treatment, centrifugal speed 3000r/min, and time 30 min

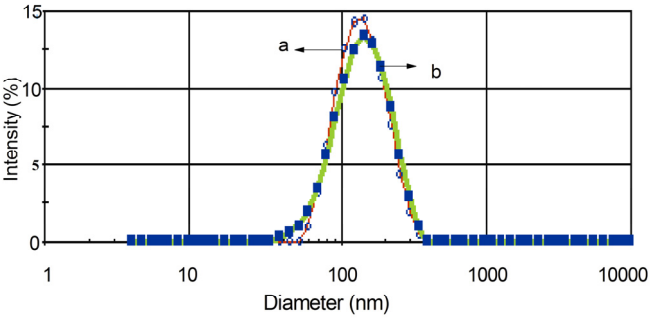

Figure 6 Particle size distribution of the ink (a) before and (b) after freeze-thaw treatment, the dispersion first put in -5oC for 12h, and then put in 60 oC for another 12h

Figure 6 showed the particle size distribution of the ink before and after freeze-thaw treatment. It can be seen that the particle size distribution changed small after freeze-thaw treatment. The reason may be due to that the attractive force between polymer and pigment was large for completely encapsulation, and it was hard to be peeled off at freeze-thaw treatment temperature. From Figure 5 and Figure 6, we may conclude that the ink had an excellent stability to storage and can be used on inkjet printing machine.

Printing performance of the ink

Physical properties of the ink, such as particle size, stability, viscosity and surface tension have great influence on many aspects of the printing process including choice of printing system, printing performance and printed images. For example, Surface tension and viscosity has major effects on wetting of nozzle surface, wetting width of printing substrates, penetration speed and depth into substrates. Generally, a high surface tension and viscosity are desirable for the ink for a uniform and stable drop formation on the nozzle. However, if surface tension and viscosity was high enough, a poor printing performance would be gotten. Therefore, the surface tension and viscosity should adjust according to the requirement of the printing machine. In this paper,

the surface tension and viscosity of the ink were found to be 31.7mNm−1 and 4.01mPa.s, respectively. This printing ink can be used on Mimaki JV4-180. The relationship between the clogging nozzle rate of the printing ink and the printing time was shown in Figure 7, only 2.5% nozzle was blocked after printing 60min, these results indicated that the printing performance was excellent when the printing ink was formulated with encapsulated pigment.

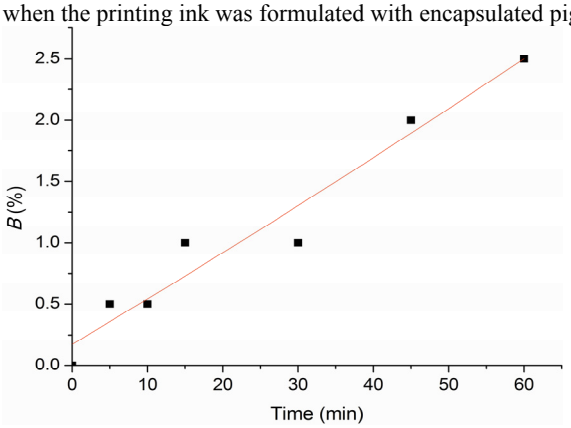

Figure 7 Effect of printing time on clogging nozzle rate

CONCLUSIONS

The encapsulated pigment dispersion could be prepared when ANPS was used as dispersant, styrene was used as co-monomer, and APS was used as initiator. The inkjet printing ink which prepared with encapsulated pigment had an excellent stability and narrow particle size distribution, which can be suitable for Mimaki JV4-180.

Acknowledges

This work is supported by Ph.D Science Foundation for industry of Jiangsu province (BK2009582) and we also thank the Jiangnan University for supporting in the course of research.

References

[1] Kosolia, C.T.; Tsatsaroni, E.G. "Synthesis and characterization of hetarylazo disperse colorants: Preparation and properties of conventional and microemulsified inks for polyester ink-jet printing". Journal of applied polymer science. 116, 1422(2010).

[2]Y. Chun, J.H. Choi, "Syntheses of polymeric dispersants for pigmented ink-jet inks", Coloration Technology. 124, 355 (2008).

[3]A. Hladnik and T. Muck, "Characterization of pigments in coating formulations for high-end ink-jet papers", Dyes and Pigments. 54, 253 (2002).

[4]Y.M. Chen, R.S. Hsu, H.C. Lin, S.J. Chang , S.C. Chen and J.J. Lin., "Synthesis of acrylic copolymers consisting of multiple amine pendants for dispersing pigment", Journal of Colloid and Interface Science. 334, 42 (2009).

[5]N. Faouzi, A. Naceur and Y. Chevalier, "Selection of dispersants for the dispersion of C.I. Pigment Violet 23 in organic medium", Dyes and Pigments. 74, 133(2007).

[6]H.J. Spinelli. "Group transfer polymerization and its use in water based pigment dispersants and emulsion stabilizers", Prog. Org. Coat.. 27, 255 (1996).

[7]Y. Zhou, D. Yu , P.Xi , S.L.Chen, "Influence of styrene-maleic anhydride copolymers on the stability of quinacridone red pigment suspension", Journal of dispersion science and technolog., 24, 721(2003).

[8]E. Reuter, S. Silber and C. Psiorz, "The use of new blockcopolymeric dispersing agents for waterborne paints: theoretical and practical aspects", Progress in Organic Coatings. 37, 161(1999).

[9]N. Steiert and K. Landfester, "Encapsulation of organic pigment particles via miniemulsion polymerization", Macromol. Mater. Eng., 292, 1111(2007).

[10]F. Tiarks, K. Landfester and M. Antonient, "Encapsulation of carbon black by miniemulsion polymerization", Macromol. Chem. Phys.. 202, 51(2001).

[11]S. Lelu, C. Novat, C. Graillat, A. Guyot and E. Bourgeat-Lami, "Encapsulation of an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process", Polym Int.. 52, 542(2003).

[12]T.Y. Zhang, X.N. Fei, J. Song and C.L. Zhou, "Properties of copper phthalocyanine microencapsulated in polystyrene by phase separation", Dyes and Pigments. 44, 1(2000).

[13]S. H. Fu and K. J. Fang, "Preparation of copolymers and its application in encapsulated pigment red 122", Journal of Applied Polymer Science. 105, 317 (2007).

[14]M.A. Tasdelen, J. Kreutzer and Y. Yagci, "In situ Synthesis of Polymer/Clay Nanocomposites by Living and Controlled/Living Polymerization", Macromolecular Chemistry and Physics. 211, 279(2010).

[15]V. V. Vodnik, D.K. Bozanic, E. Dzunuzovic, "Thermal and optical properties of silver-poly (methylmethacrylate) nanocomposites prepared by in-situ radical polymerization", Eurppean Polymer Journal. 46, 137-144(2010).

[16]J.J. Yuan, W.T. Xing, G.X. Gu. and L.M.Wu, "The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique" , Dyes and Pigments. 76, 463(2008).

[17]J.J. Yuan, S.X. Zhou, L.M. Wu and B. You, "Organic pigment particles coated with Titania via Sol-Gel process". J. Phys. Chem.B. 110, 388(2006).

[18]P. Palumbo, "Surface modification of pigmented colorants and applications to digital printing", International Congress of Imaging Science. 559 (2002).

[19]D. Nguyen, H.S. Zondanos, J.M.Farrugia, A..K. Serelis, C.H. Such and B.S. Hawkett, "Pigment encapsulation by emulsion polymerization using Macro-RAFT copolymers", Langmuir. 24, 2140(2008).

[20]L. Bombalski, K. Min, H. Dong and C. Tang, " Preparation of well-defined hybrid materials by ATRP in Miniemulsion", Macromolecules. 40, 7429(2007).

[21]L. Zhao, Z. Lei, X. Li, S. Li, J. Xu, B. Peng and W. Huang, "novel approach of preparation and patterning of organic fluorescent nanomaterials", Chemical Physics Letters. 420, 480 (2006).

[22]T. Taniguchi, N. Takeuchi, S. Kobaru and T. Nakahira, "Preparation of highly monodisperse fluorescent polymer particles by miniemulsion polymerization of styrene with a polymerizable surfactant ", Journal of Colloid and Interface Science. 327, 58 (2008).

Author Biography

Associate professor Shaohai Fu received his PhD in textiles from Jiangnan University (2006). Since then he has worked southern Yangtze University. His work has focused on the development of inkjet printing technolog