Synthesis of Novel Encapsulated Pigment Dispersion

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Abstract

Encapsulated Pigment that each pigment particle is coated with water-insoluble polymeric materials has been studied. In spite of e several advantages of encapsulated pigment, there are some issues of applications due to the problems for a synthetic method. There are poor dispersion stability of reactant pigment, low adhesion force between monomer and pigment, and surfactant residue in solution.

To overcome these problems, we adopted emulsion polymerization using anionic self-dispersed pigment, basic monomer, and macromonomer to offer dispersion stability, electrostatic adhesion force and surfactant free reaction

As a result, we developed good dispersion stability, proper size encapsulated pigment.

1. INTRODUCTION

In inkjet printing, ink droplets are ejected from nozzles of a recording head of an inkjet printer onto a recording medium such as a paper. The advantages of inkjet printing beyond other printing methods are its low cost, high quality, and ability to easily produce color images.

Ink used in inkjet printing is prepared by dissolving or dispersing a water-soluble dye or pigment into a solvent including water and a water-soluble organic solvent. If necessary, an additive such as a surfactant may be added.

In order to accomplish good inkjet recording for a long time, water-based ink for inkjet printing must satisfy the following requirements: characteristics such as viscosity, surface tension, and density should have appropriate value, nozzle clogging in an inkjet recording apparatus, precipitate formation due to heat or the like and a change in physical property values should not occur, and recorded images should have excellent water-repellency and light fastness

Aqueous inks are divided into groups by colorant type: dye, pigment, and heterophase colorant. Water soluble dye based inks have strong points of bright and vivid color, wide color gamut and long time storage stability. However when using aqueous dye based ink, print qualities are insufficient in waterfastness, lightfastness and sharpness.

To overcome these problems, aqueous pigmented ink has been developed. They have a clear advantage in lightfastness. The waterfastness of pigmented is also superior. However when using aqueous pigment based ink, print qualities are insufficient in fade color, low color gamut. The rubfastness which is caused by the stacking the pigment particles on the paper surface is also getting worse. Furthermore, the suspended pigments may tend to agglomerate. Because inkjet printers use very narrow nozzle, this cause the nozzle to be clogged.

The way to improve the dispersion stability has been suggested. First, the addition of polymeric dispersant to pigment solution is widely used, but the use of polymer dispersant increases the viscosity and causes kogation in thermal head. Second, the surface modified pigment which has electron rich moiety in the pigment surface has been developed. It enhances the electrostatic repulsion between pigment particles, the dispersion stability is superior. Although self-dispersed pigment improves dispersion stability, rubfastness problem is remained to solve.

Recently, the way to improve dispersion stability, rubfastness and color gamut has been studied. Encapsulated pigment that each pigment particle is coated with water-insoluble polymeric materials is considered as the most efficient way to solve these problems[1]-[3].

In spite of several advantages of encapsulated pigment, there are some issues of application due to synthetic method problems. These are poor dispersion stability of reactant pigment, low adhesion force between monomer and pigment, and surfactant residue in dispersion solution. These problems lead to coagulation of pigment particle, finally nozzle clogging. Moreover, the surfactant residue interferes to adjust adequate surface tension in ink formulation.

To overcome these problems, we adopted emulsion polymerization using anionic self-dispersed pigment, basic monomer, and macromonomer. Anionic self-dispersed pigment offers dispersion stability during polymerization and electrostatic adhesion force with basic monomer. Macromonomer is applied to the surfactant free reaction due to dual activities as function of monomer and surfactant. The strategy to synthesize of encapsulated pigment is presented in Figure 1.

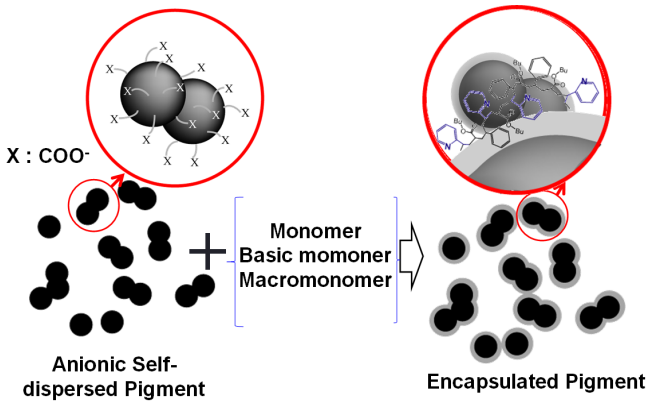

***Figure1**. Schematic synthetic strategy of our novel encapsulated pigment dispersion*

2. EXPERIMENTALS

2.1 Materials

Table 1 shows materials and optimum condition of our synthetic method.

Table1. Material Condition

Material	Species	Optimum Condition
Pigment	CB-COO$^-$	10% to medium
Monomer	Styrene Butyl acrylate	44% to pigment
Basic Monomer	2-VP, AAM	20% to monomer
Macromonomer	PEG-Ether	2~20% to monomer
Initiator	KPS,	1~2% to monomer

Carbon black, CB-COO$^-$ whose surface was modified to carboxylic acid group was employed for pigment. It has the prior dispersion stability by electrostatic repulsion between carboxylic acid moieties. The surface modified carbon black was used in-house products or commercially available pigment such as Cab-O-Jet 300, Cab-O-Jet 400 (Cabot Co.), Bonjet black CW-1, Bonjet black CW-2, Bonjet black CW-3 (Orient Chemical Co). The monomer was consists of 3 parts which are monomer, basic monomer and macromonomer. Basic monomer contains nitrogen atoms in the molecule that can indroduce electrostatic attraction. Macromonmer has median molecular size compared with monomer or surfactant. In the molecular structure, macromonomer has hydrophilic part and polymerizable hydrophobic tail that can be applied as the surfactant free reaction due to dual activities as function of monomer and surfactant. In this experiment, PEG-Ether (Mw :246g/mol) was employed.

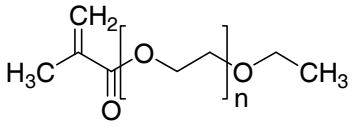

***Figure2**: structure of macromonomer*

At the beginning, our experiment was to determine the effective amount of materials by conventional ionic surfactant method. To maintain the dispersion stability in the process of encapsulation, anionic self-dispersed pigment, Cab-O-jet 300, whose surface was modified to carboxylic acid was introduced. The carboxylic acid group has lone pair electron which leads electrostatic repulsion between pigment particles, therefore it enhances the dispersion stability without dispersant.

It was also important to use appropriate ratio of monomers and pigment to polymerize on the pigment surface. When the total monomer ratio including monomer, basic monomer and macromonomer was increased or the basic monomer ratio was decreased, the spherical free polymer was appeared and the particles tended to agglomerate, then the particle size increased. In contrast, if the total monomer ratio decreased, the polymer could not cover the pigment surface, the strong points of encapsulated pigment would be weakened.

After determination of material species and amount, the conventional surfactant was replaced by macromonomer. In general, the surface active force of ionic surfactant is higher than non-ionic surfactant. The surface active force is important to form a suitable monomer droplet size. We concerned about the lower surface active force of macromonomer than ionic surfactant, but macromonomer carried out its dual activity as surfactant and monomer successfully.

2.2 Preparation of Encapsulated pigment dispersion by emulsion polymerization

The solution of monomer, basic monomer and macromonomer and pigment dispersion was sonicated at the 0℃ for 5min to make homogenous solution. Then, nitrogen purge gas introduced for 30 min. Then the temperature was increased to 70~90℃ and the initiator solution was added and stirred for 1~24 hour.

2.3 Particle Size

Pigment dispersions were diluted to 10000 times and balanced at 25 degree Celsius for 5min, and then particle size was measured by ELS-8000 (Otsuka Electronics, Japan)

2.4 Measurements of Stability of pigment dispersion

Centrifuging stability [4] : Pigment dispersion was centrifuged at 20000 r/min for 5min, then the decantant in the centrifugal tube was taken out and diluted to 10000 times with deionized water. Absorbency of pigment dispersion was measured at 300nm wavelength and calculated changes of absorbance before the centrifugation.

Freeze-thaw stability: the pigment dispersion was sealed and placed at -40℃ for 2hours and then temperature was increased to 60℃ for 2hours. This thermo cycle was carried out for 10 times and measured the change of particle size.

2.5 Particle shape of encapsulation pigment

The dispersion was dried for 1day in vacuum oven at 50℃. The dried powder was observed by scanning tunneling microscope (S-3500, Hitachi, Japan)

2.6 Measurement of Glass transition temperature

In ink jet head, ink droplet is formed from vapor-bubble pressure by electrical heating or mechanical force by piezoelectric materials. If there is reactivity or thermal unstable materials in the ink composition, the head surface can damaged by the adhesion of ink residuals. The phenomenon is called 'Kogation' which leads misdirection or failure to form ink droplet. The factors of kogation are colorant, polymer, cosolvent and so on. To avoid kogation, the polymer in encapsulated pigment has to have high Tg to reduce the cohesion into the head materials. In contrast, the media requires low Tg due to the binding affinity into the media. It is essential that the control of the effective position of Tg to prevent kogation and maintain the media binding affinity.

Fox equation (1) is known for the regulation method of Tg based on the homopolymer Tg.

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} + \frac{w_3}{Tg_3} \qquad (1)$$

where in

w_1, w_2, w_3 is *w/w%* of monomer in copoymer

Tg_1, Tg_2 Tg_3 is Tg of each homopolymer

After the encapsulated pigment dispersion was dried in the vacuum oven, the residual solid contents were collected and analyzed the glass transition temperature by Differential Scanning Calorimeter. (TMA Q100, TA instruments)

3. Result and Discussions

From this research, the results are summarized in two stages, which will be explained the following each article in more detail. Briefly, the first stage is the merits of our novel synthetic method. The second stage is the application effort to a thermal inkjet ink by variation of glass transition temperature of polymer.

3.1 Particle Size and Shape

The shape and size distribution of encapsulated pigment are shown in Figure 3.

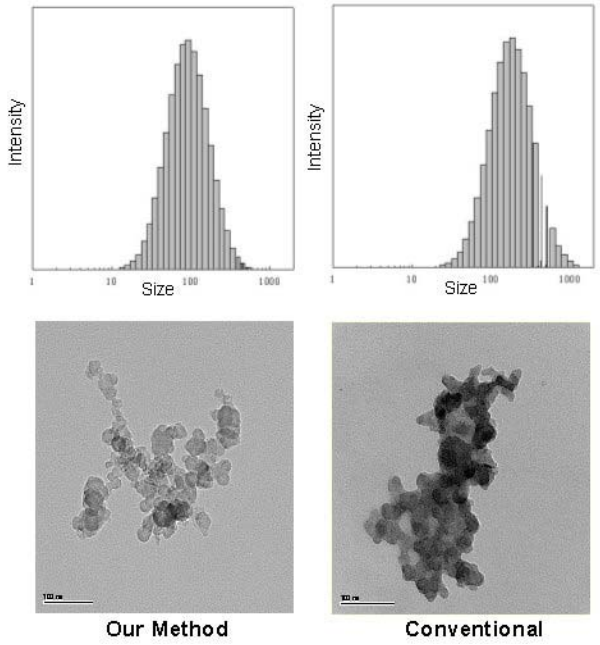

***Figure 3**: Size distribution and SEM image of Encapsulted pigment*

Encapsulated pigment applied to this method had smaller size and more narrow size distribution than conventional method combined non-self-dispersed pigment and neutral monomer. From this result, the dispersion stability of the anionic self-dispersed pigment maintained until the end of reaction. The spherical free polymer which was originated from the polymerization of monomer droplet itself, not in the pigment surface, was not observed in optimum condition. This phenomenon described by the electrostatic interaction took place efficiently between pigment and basic monomer, and offered effective driving force of monomer diffusion from monomer droplet to pigment surface.

3.2 Stability of pigment dispersion

The pigment which has low dispersion stability is apt to precipitate by gravity. So centrifugal is one of the ways to measure dispersion stability. Freeze-thaw stability represented the accelerated storage stability of pigment.

Table2: Stability test result

Test	Carbon Black	Our method	Conventional
Centrifugal stability Δ UV absorbance (%)	34	43	92
Freeze-thaw stability Δsize (%)	12	15	120

After centrifugation, encapsulated pigment dispersion produced by the method had little precipitation in the bottom of tube. The smaller changes of relative UV absorbance, after centrifugation, indicated that the encapsulated pigment made from basic monomer had efficient electrostatic repulsion between the particles. Also, the smaller size of particles enhanced the buoyancy of pigment particles. These factors had also influences on the superior freeze-thaw stability.

3.3 Glass Transition temperature (Tg) Controls

Considering above issues, we synthesized various encapsulated pigment based on the Fox equation. The resulted Tg was presented in table3 and Figure4.

Table 3: The result of Tg.

material	2-VP	AAM
Tg(℃)	22	20
	46	48

We thought that Tg of 20~50℃ would be satisfied both suitable media binding affinity and preventing the formation of kogation on the printer head. The type of polymer was important to kogation because the heat resistant and softness was different. So, we synthesized various encapsulated pigments by controlling the kinds and ratio of monomer which were styrene, butyl methacrylate and basic monomer.

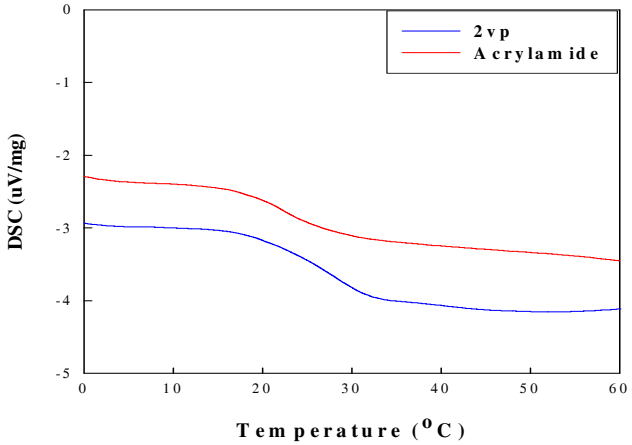

***Figure 4:** Glass transition temperature (Tg) of encapsulant*

These dispersions will be made ink formulation and be studied which is effective Tg, and which materials are suitable in printer head.

4. Conclusion

The adoptation of self-dispersed pigment and basic monomer and macromonomer was an efficient way to synthesis of encapsulated pigment. This method improved the dispersion stability during polymerization and adhesion force between pigment and monomer. The pigment dispersion prepared in our method has higher stability, proper sizes without coagulation, and the free polymer.

We expect this encapsulate pigment is to cover the disadvantages of the existing inks, paints and coating solution and so on.

5. Acknowledges

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6. Reference

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