Preparation and Properties of Cationic Pigment Dispersions with SMD Random Copolymers

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Abstract

Styrene, methyl methacrylate (MMA) and trimethyl (methyl acryl acyl oxygen) ethyl ammonium chloride were randomly copolymerized to prepare a cationic macromolecular dispersant (SMD) applied in cationic pigment dispersions. The influence of the dispersant concentration on the particle size and centrifugal stability of the pigment dispersions was also studied. The pigment particle size could be as small as 225 nm (Z average) and the centrifugal stability could also be improved, when the dispersant was 1.25 percent the specific absorbency was 97.3%. The influence of the diethylene glycol (DG) dosage on the particle size and stability was also investigated, as the result, the particle size and centrifugal stability was perfect when the DG dosage was 28.2%. Compared with NNO and Tween80, SMD is able to pretend the reassembling of pigment particle more effectively and have better dispersing result.

Introduction

In general, nanoscale pigments can be realized by surface modification of pigment with non-ionic or anionic surfactant, which can improve the wetting ability of pigment surfaces, increase the electrostatic forces of repulsion and steric hindrance, and prevent the nanoscale particles from aggregating each other and stabilize the dispersion. Also, the pigment surface can be modified by compounds of small molecules, and further processed with dispersant to obtain nanoscale pigment dispersions. Many works on the macromolecular dispersants (super dispersants) have been done recently. The studies on nanoscale pigments have been well developed and many patents and papers have been reported [1-8].

There are some problems when non-ionic or anionic dispersant is used in pigment dispersions. For pigment dispersions prepared by non-ionic or anionic dispersant, both surface potential and Zeta potential of the pigment particles are negative. The surface potential of textile and paper made of cellulosic fiber is normally negative, too. Therefore, these electrostatic forces of repulsion between pigments and fibers would result in the weak bonding and poor color fastness when such nanoscale pigments were used to color the fibers. Such bond conditions have to be improved to get the better color fastness. The migration of the pigment particle will often cause problems in pad dyeing. When dip dyeing was used, the fibers had to be cationised first, which quite time should be consumed. Picture bleeding is also a problem as the nanoscale anionic pigment dispersion is used in ink-jet printing.

In comparison with the anionic nanoscale pigment, the cationic one has more favorable fluid, dispersion stability, far better color vividness and dyeing deepness. The preliminary experimental results showed that higher color deepness and vividness and better complete dyeing effects were obtained when the cationic nanoscale pigment was used to dye the cotton fibers. Furthermore, better jet ability and imbibition-preventing property were achieved when it was used in ink-jet printing.

The cationic dispersant has been widely used in many fields [9], but there are only few reports about the preparation of the nanoscale cationic pigment, except for several patents. It has been reported in Japanese patents that cationic dispersant was used in electrodeposits coat [10-13]. Ishwarlal suggested that, being prepared with cationic dispersant, the cationic pigment dispersion could decrease the migration of the pigment, and favorable dyeing deepness and color fastness could be obtained when such pigment was applied to pretreated cotton fabric and terylene-cotton fabric in pad dyeing [14]. Koyanagi appended the cationic surfactant onto the acrylic acid copolymer to attain dispersant and applied it to the anthraquinone pigment to prepare ink for ink-jet printing on paper [15]. In addition, there are many applications of cationic dispersant in many other fields such as papermaking, image thermomigration, ink-jet printing paper, inorganic nanoscale powder [16-20], and preparing hydrophilic ethylene copolymer dispersion [21].

The cationic surfactant is usually used as dispersing agent and cationic agent when dispersing and cationizing the pigment, for example, alkyl ammonium chloride [22]. The cationic polymer electrolyte is used as dispersing agent is the researching hotspot. Compared with the one with a small molecular dispersing agent, the dispersion with macromolecular dispersing agent is more stable and the fastness and coloration effect are better.

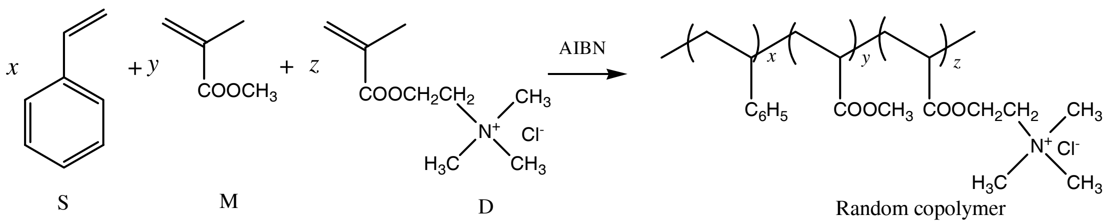
The styrene (S), methyl methacrylate (M) and trimethyl (methyl acryl acyl oxygen) ethyl ammonium chloride (D) were copolymerized in our experiment and a cationic macromolecular electrolyte was obtained and was utilized in the preparation of the pigment dispersion. The properties of the dispersion were studied, and the comparison of the non-ion surfactant, the anionic surfactant and the obtained polymer dispersing agent was also studied.

Experimental

Synthesis and characterization of styrene-methyl methacrylate-methyl acryl acyl oxygen ethyl trimethyl ammonium chloride

Preparation of the SMD random copolymer

The reaction equation of the random copolymerization of styrene, methyl methacrylate and methacryl acyl oxygen ethyl trimethyl ammonium chloride is shown as below,



Scheme 1 The reaction equation of the random copolymerization of the three monomers.

Part of solvent was inpoured into a four-neck flask that was set with thermometer, stirrer, constant pressure drop funnel and condenser tube, the nitrogen was guided into the reaction flask simultaneously. After stirring 20 minutes, the reaction temperature was raised and the mixture of monomer, solvent and initiator that were mixed with a certain proportion was begun to drip. Polymerization was kept going at constant temperature and protected by nitrogen, and the product was taken out after preconcerted time. The product mixture was precipitated by ether, washed by acetone, filtered by decompression and dried to be a constant weight, and finally, the purified white powder product (SMD) was obtained.

The intrinsic viscosity of the copolymer SMD was measured by an Ubbelohde viscometer at 25±0.1°C.

The Infrared spectrum analysis of SMD

The SMD copolymer was dried to be constant weight at 100~105 °C, and then KBr wafer method was adopted to prepare the sample. The sample was analyzed on NEXUS-670 IR instrument. The main parameters were listed: the scanning scope was 400~4000cm^{-1}, the differentiate rate was 0.3cm^{-1}, the scope of the KBr beam splitter was 7400~305 cm^{-1}, and the scope of the DTGS detector was 7600~350cm^{-1}, the light source was EVER-GLOIR.

The molecular weight and molecular weight distribution of SMD copolymer

The molecular weight and molecular weight distribution of the copolymer was tested on Waters 2410 gel permeation chromatography (GPC). The column temperature was 35°C, and the volumetric flow rate was 0.5mL/min (the flowing phase was 0.7 percent of Na_2SO_4/water solution).

The titration of Cl^- in SMD random copolymer

$AgNO_3$ standard solution was utilized to titrate the Cl^- in neutral water solution, and the K_2CrO_4 was used as indicator. The AgCl is precipitated firstly based on the fractional precipitation theory, because the solubility of AgCl is smaller than Ag_2CrO_4. The brick red deposition appears after the AgCl precipitates completely, which is the end point of titration.

The contention of the hydrophilic monomer D in copolymer according to the equation below,

$$F_D = \frac{C_{AgNO_3} \times \Delta V}{W} \times M_D$$

In which, each variable is,

C ($AgNO_3$)-The concentration of $AgNO_3$ standard solution (mol/L)

ΔV-The volume of $AgNO_3$ standard solution that was reacted (mL)

W-The exact weight of SMD copolymer (g)

F_D-The quantity fraction of the hydrophilic monomer D in copolymer

Preparation of the cationic hydrophilic pigment dispersion

The purified pigment red C.I. 22 was mixed with deionized water to be slurry, and the cationic surfactant solution was dropped into it slowly, dispersed by RW20N dispersant to prepare 200g pre-dispersion in which the pigment was 5 percent. Next, the pre-dispersion was miuted by M-110 high pressure micro jet disintegrator (American MICROFLUIDICS Company) at 22000psi. Then the nanoscale pigment dispersion was prepared.

The test of the properties of pigment dispersion

The pigment dispersion was put into centrifugal tube and centrifugal separated by a centrifuge (80-1 style) at 4000rpm and for 30 min. Then 1mL centrifugal separated dispersion was taken out by suction pipet and diluted 2000 times, and the absorbency (A_{30}) at the most absorb wavelength was tested on 722 spectrophotometer; the same means was applied to test the absorbance (A_0) of the sample that was not centrifugal separated. The centrifugal separation stability was characterized by the ratio of the both (r_{30}).

$$R_{30} = \frac{A_{30}}{A_0} \times 100\%$$

Results and Discussion

IR and GPC Characterization of SMD

The SMD copolymer was characterized by IR and GPC respectively.

The IR was shown in Figure 1. Wherein the peak at 3427.01cm^{-1} is vibration absorption of the quaternate ammonium salt, the peak at 1726.59cm^{-1} is the flexing vibration absorption of the carbonyl group, the peak at 1632.95cm^{-1} is the absorption of asymmetric and symmetric bending vibration of methyl, the peak at 1478.37cm^{-1} is the absorption of angle change vibration of the methyl, and the peaks at 764.87cm^{-1} and 708.03cm^{-1} are the characteristic absorption of the single substitute absorption of the benzene.

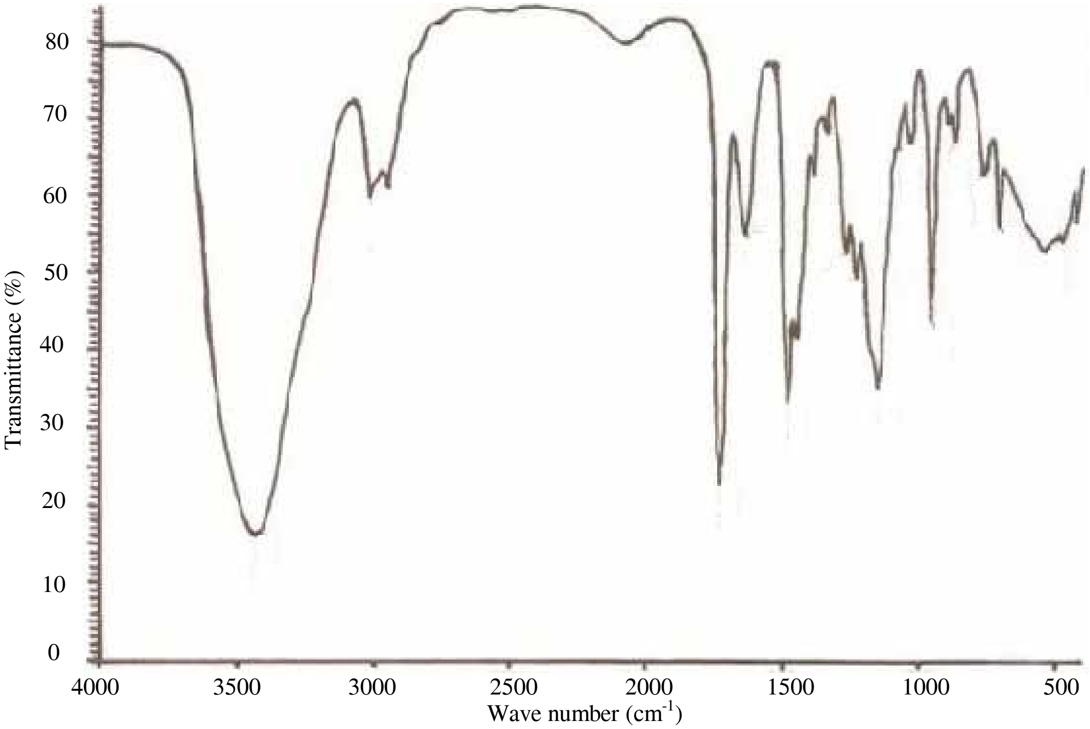


Figure 1 The IR spectrum of SMD copolymer

The molecular weight and molecular weight distribution profile was tested by GPC. The molecular weight distribution profile showed that SMD copolymer contained two parts, wherein the main part of polymer's molecular weight was about 5943, and the molecular weight distribution index was 1.32.

The Z-average particle size of the pigment dispersion

The recycling times of the pigment pre-dispersion in high pressure and high shear force micro jet disintegrator has important influence on the particle size of the pigment dispersion. The relationship between the both is listed in Figure 2. It shows that the pigment particle size is increased with the recycling times' increasing. But the particle size increases only a little when the recycling times are over 25. For example, the particle size just diminishes 3 nm as the recycling times increases from 25 to 30.

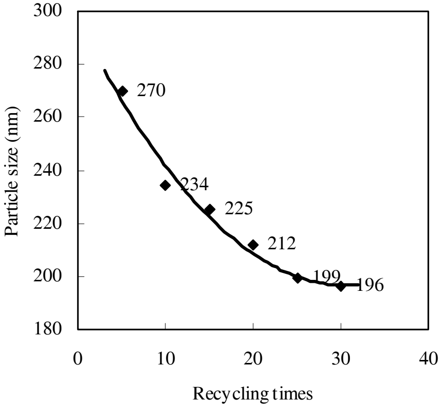


Figure 2 The influence of the recycling times on the average particle size of pigment dispersion. The pressure was 22000 psi, the pigment's concentration was 5% and the SMD dosage was 1.25%.

Figure 3 shows that the influence of the SMD dosage on the particle size in the pigment dispersion. The particle size was decreased apparently with the decreasing of the SMD dosage. The trend of decreasing was postponed after the dosage was smaller than 1.25%

The jet ability of the ink should be optimized by acceding to a certain quantity of polyhydric alcohol when preparing the ink-jet printing pigment ink. We tested effect of the diethylene glycole (DG), shown as Figure 4. It can be concluded from Figure 4 that the pigment particle size was diminished steply by the increasing of the DG. The particle size arrived the smallest when the DG was dosed 28.2%, and it was increased when the DG dosage was higer than 28.2%.

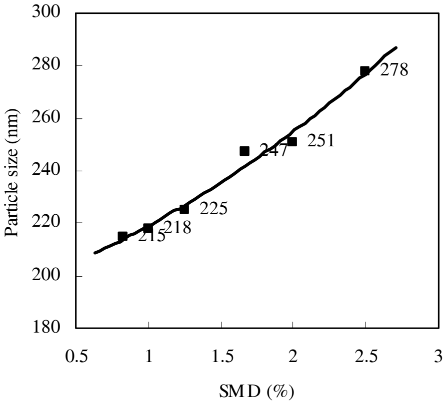


Figure 3 The influence of the SMD dosage on the average particle size of the pigment dispersion. The pressure was 22000 psi, the recycling times was 15 and the pigment's concentration was 5%.

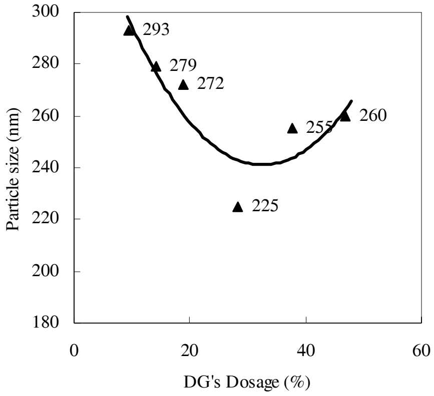


Figure 4 The influence of the DG's dosage on the average particle size of the pigment dispersion. The pressure was 22000 psi, the recycling times are 15, the pigment's concentration was 5% and the SMD dosage was 1.25%.

The dispersion stability of the pigment

The milled pigment dispersion was put into centrifuging field to accelerate the pigment particle's sedimentation. The dispersion stability can be characterized by the change of pigment's concentration of the superstratum dispersion in centrifugal tube. The relation of absorbency and concentration of pigment dispersion is accordant with Lanber-Beer Law in low concentration range. Thus the pigment's concentration can be demonstrated by the absorbency of the dispersion.

The influence of the recycling times of high pressure micro-jet disintegrator on the sediment stability in centrifugal field was shown in Figure 5. The nanoscale pigment dispersion appeared the highest specific absorbency when the recycling times were 15. It showed that the dispersion has the best sediment stability when the recycling times were 15.

Figure 6 is the relationship between the SMD dosage and the sediment stability in centrifugal field of the pigment dispersion. It is obvious that the nanoscale pigment dispersion's specific absorbency R_{30} was increased with the SMD dosage's reducing. The specific absorbency arrived at the max when the SMD dosage was 1.25%, and it was decreased with the continuously reducing of SMD dosage.

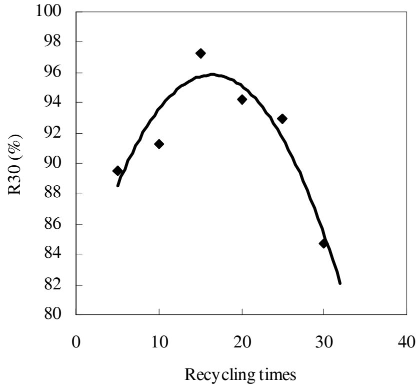


Figure 5 The influence of the recycling times of the high-pressure micro-jet disintegrator on the specific absorbency of the pigment dispersion. The pressure was 22000 psi, the pigment's concentration was 5% and the SMD dosage was 1.25%.

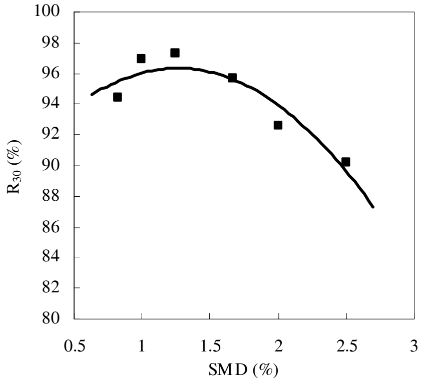


Figure 6 The influence of SMD dosage on the specific absorbency of the pigment dispersion. The pressure was 22000 psi, the recycling times are 15, and the pigment's concentration was 5%.

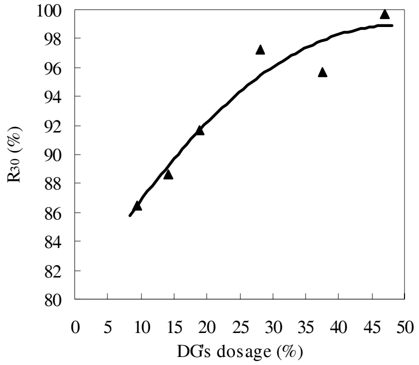


Figure 7 The influence of the DG's dosage on the specific absorbency of the pigment dispersion. The pressure was 22000 psi, the recycling times are 15, the pigment's concentration was 5% and the SMD dosage was 1.25%.

It is the relation of the DG and the specific absorbency in Figure 7. It shows that the specific absorbency of dispersion was raised by the DG dosage's increasing. It is because that the DG raised the viscosity of the dispersion.

Properties of the pigment dispersion prepared by different surfactant

The pigment red C.I. 22 was dispersed in water in high pressure and high shear force micro-jet disintegrator, in which the non-ion surfactant Tween80, the anionic surfactant NNO and the synthesized cationic polymer SMD were utilized as dispersing agent respectively. The Nano-ZS90 nanometer particle size and Zeta potential analyzer was adopted on measuring the dispersion's specific absorbency, viscosity and Zeta potential. The results are shown in Table 1.

It is shown in Table 1that the absolute value of Zeta potential is the highest when SMD is used as dispersing agent, arriving at 36.0mV. The anionic surfactant NNO is a little lower, which is about 31.0mV. The Zeta potential of the dispersion with Tween80 is the lowest, only 3.1mV. The static repulsion energy is very strong when the surface potential is over 30mV, the Brownian motion energy can not overcome the energy barrier, thus the particle repulses each other and the dispersion is stabilized. The anionic surfactant NNO stabilized the dispersion by the static repulsion and the non-ion surfactant Tween80 stabilized the dispersion by the steric hindrance. However, the macromolecular dispersing agent SMD has both functions when it is adopted on dispersing pigment, so that it can pretend the reassembling of the pigment particle.

Table 1 The Zeta potential of the pigment dispersion with different dispersing agent

Dispersing agent	SMD	Tween80	NNO
R_{30} (%)	97.3	86.5	81.0
Viscosity (cp)	8.8	5.5	4.6
Zeta potential (mV)	+36.0	3.1	31.0

Conclusions

The research result showed that the particle size could be as small as 225 nm (Z average) and the centrifugal stability could also be improved when the dispersant was 1.25 percent, the specific absorbency was 97.3%, in C.I. 22 dispersion. The influence of the diethylene glycole (DG) dosage on the particle size and stability was also studied, as the result, the particle size and centrifugal stability was perfect when the DG dosage was 28.2%. The study of NNO, Tween80 and SMD verified that, compared with NNO and Tween80, SMD is able to pretend the reassembling of pigment particle more effectively and have better dispersing result.

Acknowledgement

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