

Preparation of a Novel Dispersant for Carbon Black Dispersing and Fixing

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Abstract

The branched poly (styrene-alt-maleic anhydride) (BPSMA) was synthesized by chain transfer polymerization of styrene (St) and maleic anhydride (MA) using (4-vinylphenyl)methanethiol (VPMT) as a chain transfer agent and benzoyl peroxide (BPO) as an initiator. Fourier transforms infrared (FTIR) spectroscopy, ¹H nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) BPSMA confirmed that the copolymer with the branched structure. BPSMA exhibited high dispersing efficiency for CB particles, and prepared CB dispersion showed excellent stability to centrifugal forces and treatment temperature. In addition, BPSMA can also greatly improve the rubbing and washing fastness of the cotton fabrics when cotton fabrics was printed using this dispersion.

Introduction

Inkjet printing on textiles has demonstrated super properties, such as excellent pattern quality, considerably little pollution and especially fast response to the frequent shift of cloth fashion. Inks for fabric printing are usually classified into dyebased and pigmentbased inks. Pigmentbased inks show better waterfastness, smearfastness and lightfastness of the printed fabrics than that of dyebased inks. Moreover, it can also save water and energy and it is also environmentally friendly [1-3]. However, how to prepare dispersion with small particle size, narrow size distribution and excellent stability is still a difficult work.

Dispersing pigments with aid of polymeric dispersants can greatly improve dispersion stabilities [4-6]. In aqueous media, polymeric dispersants are adsorbed onto pigment surface via anchor groups to build voluminous shells or intensify charges around pigment surface, thereby preventing flocculation and coagulation of the pigments. However, dispersing performance of polymeric dispersants may be limited due to some of their defects, such as a polymeric dispersant, commonly having a low molecular weight, can be easily desorbed from pigment surface at a high temperature and tends to tangle together for long-term storage, resulting in poor stabilities. An alternative approach to prepare high performance pigment dispersion is to use the hyper-branched polymers. It is known that the hyper-branched polymers have low viscosity, high solubility and numerous terminal functional groups [7-15]. The use of hyper-branched polymers in aqueous pigment dispersions has recently been attracting increasing attention [16-19].

However, no studies, to the best of our knowledge, have been reported to date to use a hyper-branched poly (styrene-alt-maleic anhydride) (BPSMA) as dispersant for carbon black. In this study, we synthesize a BPSMA via chain transfer polymerization, and further investigated the dispersing efficiency of BPSMA for CB. Meanwhile, the fixing performance of the PBSMA was also studied.

Experimental

Materials

CB with a water content of 3% was purchased from Daxiang Co., Ltd (China) and used after dried. (4-vinylphenyl)methanethiol (VPMT) was synthesized in our laboratory. Styrene (St) and maleic anhydride (MA) had inhibitor removed using an inhibitor-removal column (Aldrich). Benzoyl peroxide (BPO) was purchased from Shanghai Chemical Reagent Co., Ltd. of China, and recrystallized from ethanol before use. 2-butanone (AR grade) and sodium hydroxide (AR grade) were purchased from Shanghai Chemical Reagent Co., Ltd. of China. Sodium hydroxide (AR grade) and inferior sodium phosphate (AR grade) were purchased from Shanghai Chemical Reagent Co., Ltd. of China. Adhesive PBA (Tech grade) and thickening agent (Tech grade) were purchased from Wuxi Changsheng Fine Chemicals Co., Ltd. Distilled water was used in all the experiments. Cotton fabrics (13.8*13.8*248*244) was bleached.

Synthesis of BPSMA

46.3 g St, 43.7 g MA and corresponding amount of VPMT were dissolved in 108.2 g 2-butanone to give a monomer solution. 1.8 g BPO was dissolved in 100g 2-butanone to give an initiator solution. One third of monomer solution and one third of initiator solution were added to a four-neck flask equipped with a mechanical stirrer, a condenser and a thermometer. The mixture was heat to reflux for 1 h. The remaining monomer and initiator solutions were then added dropwise to the four-neck flask, allowing the reaction to continue at reflux for 4h. The product was precipitated by the addition of an adequate amount of ethanol at room temperature. The precipitated product was washed with ethanol for 3 times and then dried in vacuum oven at 30 °C.

Preparation of CB pigment dispersions

1g BPSMA was dissolved in 19 g water at 70 °C. The pH of the polymer solution was adjusted to 8 using 0.1mol/L sodium hydroxide. 5 g CB was added to the solution and then balanced a total weight at 50 g. The mixture was stirred for 15min, and then treated with ultrasonic waves (input power 1100W) for 30 min.

Printed cotton fabrics with the CB dispersion

The printing paste based on the weight was prepared according to the following recipes: CB dispersion 2g, Inferior sodium phosphate 0.1g, Adhesive PBA 5g, Thickening agent 2.5g, and water 40.4g. The printing pastes were applied to cotton fabrics through a flat silk screen. The printed fabrics were dried at 80°C for 3min, and then were subjected to hot air at 150°C for 2.5min.

Characterization of BPSMA

Fourier-transform infrared (FTIR) spectroscopy of BPSMA in KBr pellet was performed on a Nicolet Nexus 560 FTIR spectrometer over the wavenumber range of 4000–500 cm⁻¹. BPSMA was dried at 80–90 °C before FTIR measurement. ¹H nuclear magnetic resonance (NMR) spectroscopy of BPSMA was performed on an AVANCE III NMR spectrometer using deuterated acetone as solvent. Gel permeation chromatography (GPC) was used to measure the average molecular weight of BPSMA using a SHI-MAZU GPC analyzer.

Characterization of CB dispersion

The particle size (PS) and Zeta potential (ζ) of CB pigment ink (diluted 100 times with distilled water) were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS90 instrument at an angle of 90°.

The stability to temperature (ST) of CB pigment ink was estimated in terms of the changes in particle size of a dispersion sample for 24h storage at a desired temperature (T).

The centrifugal stability (SC) of CB pigment ink was estimated in terms of relative change in absorbance (A) of a ink sample after centrifugation process, i.e. the ink was centrifuged at 3000 r/min for different time and 0.03 g super dispersion was diluted 2000 times with distilled water. Spectrophotometer was performed on a UNICO UV-2000 spectrophotometer to determine the absorbance at the wavelength for the maximum absorbance (540nm) before and after the centrifugation process, respectively, i.e. A₀ and A_c. The centrifugal stability was then calculated by Eq. (2).

$$S_c = \frac{A_c}{A_0} \times 100\% \quad (2)$$

Characterization of printed cotton fabrics

The printed samples were evaluated for the chromaticity value and the depth of color (K/S), which were measured with Premier 8400 Computer Color Matching System. The color fastness to different environmental features such as rubbing and washing were carried out according to the Standard I.S.O recommendation.

Experimental

Synthesis of BPSMA

In the FTIR spectrum of BPSMA (Figure 1), the absorption peaks at 1778 cm⁻¹ and 1850 cm⁻¹ are assigned to C=O groups for symmetric and antisymmetric stretching vibrations. The symmetric stretching vibration at 1778 cm⁻¹ is much more pronounced than the antisymmetric stretching vibration at 1850 cm⁻¹, indicating the polymer molecule contains annular anhydride groups. The absorption peaks at 1210 cm⁻¹ is assigned to C-S groups and, at the same time, the characteristic adsorption peak of S-H group on VPMT (2565 cm⁻¹) is not found in the FTIR spectrum of the polymer product, indicating VPMT played the role of the chain transfer agent resulting in branched chains on the polymer molecule. In addition, the absorption peaks at 1455 cm⁻¹, 703 cm⁻¹, 1080 cm⁻¹, 3023 cm⁻¹ and 2920 cm⁻¹ can be attributed to vibrations of C=C, C-C, C-H and H-C-H groups.

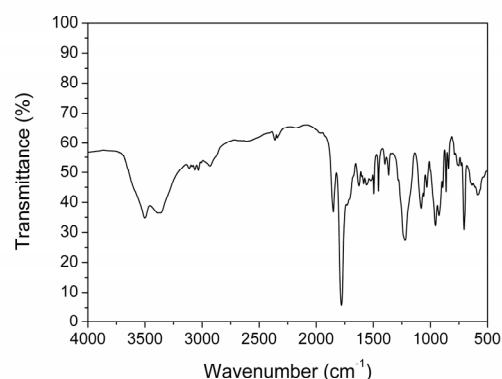


Figure 1. FTIR spectrum of BPSMA

In the ¹H-NMR spectrum of BPSMA (Figure 2), the signals at 3.98 and 1.3 ppm were assigned to the protons of –CH– (1), –CH₂– (2) respectively. The signals at 6.5 to 7.5 ppm were assigned to the protons of benzene rings of St and VPMT (3, 4, 5, 10, and 11). The signals at 3.47 and 2.50 ppm were assigned to the protons of –CH–CH– in MA (6). The signals at 2.30 ppm and 1.98 ppm were assigned to the protons of –CH– (7), –CH₂– (8) in AB respectively, the protons of –CH₂–S– of AB appeared at 1.98 ppm (9). All these results verify the structure of BPSMA as shown in Scheme 1.

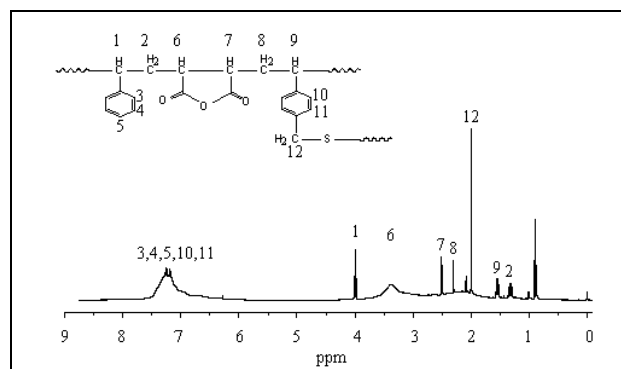


Figure 2. ¹H-NMR spectrum of BPSMA

As suggested by FTIR and ¹H-NMR, VPMT played an important role in branching PSMA. It is believed that a higher amount of VPMT used in polymerization could result in a higher degree of branching in BPSMA that is usually associated with a lower number average molecular weight (M_n) of BPSMA. This is confirmed by GPC analysis shown in Figure 3. Because the M_n of BPSMA is mainly determined by the polymer backbone, branching in BPSMA probably shortened the polymer backbone so as to result in a smaller M_n.

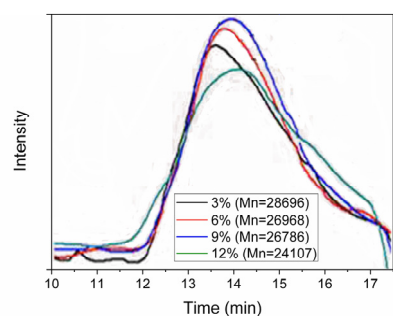


Figure 3. GPC analysis of BPSMA synthesized with the addition of various VPMT amounts in percentage of the total molar amounts of St, MA and VPMT

Performance of the CB dispersion using BPSMA as dispersant

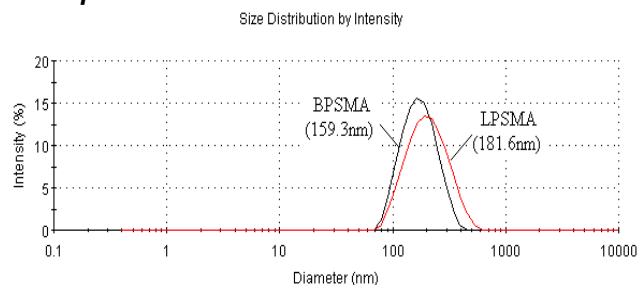


Figure 4. Particle size and its distribution of CB dispersion

In order to understand the dispersing ability of BPSMA, we compared the BPSMA with LPSMA for dispersing CB at pH 8 and mass ratio of polymer to CB 1:5. Figure 4 shows that the particle size was smaller and the particle size distribution of BPSMA-dispersed CB dispersion was narrower than that of LPSMA-dispersed CB dispersion, which indicates that the BPSMA has higher dispersing ability for CB than that of LPSMA.

Zeta potential is an important parameter that determines the long-term stability of the dispersion. It is known that the CB with high Zeta potentials is very stable while the particles with low Zeta potentials tend to coagulate or flocculate. In BPSMA- or LPSMA-dispersed CB dispersion, Zeta potential is closely correlated with the ionization degree of the polymeric dispersant. Figure 5 shows that the BPSMA-dispersed CB dispersion exhibited much higher Zeta potentials than the LPSMA-dispersed CB dispersion. The higher Zeta potentials provided stronger electrostatic repulsion among CB particles and endowed the BPSMA-dispersed CB dispersion higher stability.

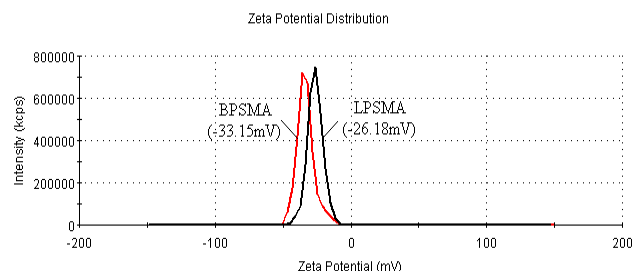


Figure 5. Zeta potential of CB dispersion

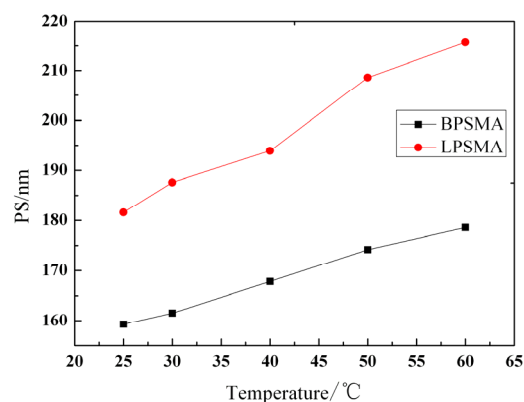


Figure 6. Stability of CB dispersion to temperature

Figure 6 shows that the particle size of both dispersion increased as the temperature increased, indicating that both BPSMA and LPSMA can be desorbed from the CB surface at a higher temperature, and BPSMA is a better choice than LPSMA for preparing a more stable CB dispersion, while the attraction forces between BPSMA and CB particle are stronger than that of LPSMA and CB particle. Moreover, the BPSMA is hard to be desorbed from CB surface, even at high centrifugal speed for its higher attraction forces and the higher Zeta potentials, which can provide an enough repulsive forces among the CB as shown in figure 7, which lead to an excellent centrifugal stability.

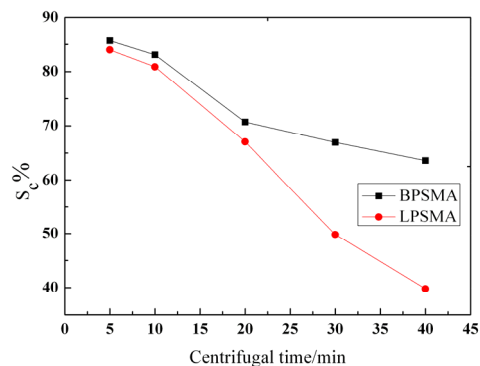


Figure 7. Centrifugal stability of CB dispersion

Fixing performance of the dispersion on the cotton fabrics printing

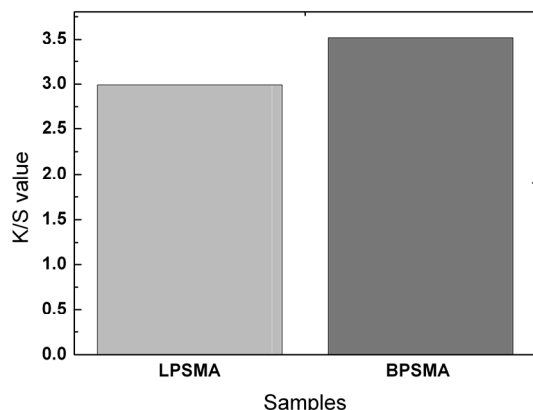


Figure 8. K/S value of the cotton fabrics with different dispersion

Figure 8 shows that the K/S value of fabric printed with BPSMA-dispersed CB dispersion was higher than that of fabric printed with LPSMA-dispersed CB dispersion. On the one hand, the particle size of BPSMA-dispersed CB dispersion is smaller and the surface area is much bigger, which can increase the adsorption for visible light. On the other hand, the BPSMA-dispersed CB dispersion has good miscibility with the printing paste, which can deliver more amount of CB onto the cotton fabrics. Therefore, the printing cotton fabrics using BPSMA-dispersed CB dispersion can greatly reduce the lightness and increases the K/S value of the printed fabrics.

Table 1 Rubbing and washing fastness of printed fabric using different dispersants

Printed fabrics using dispersion with different dispersant	Rubbing		Washing	
	Dry	Wet	Change in color	Staining on cotton
LPSMA	3-4	2-3	3	4
BPSMA	4	3-4	4	4-5

Table 1 illustrates the rubbing and washing fastness of fabrics printed with BPSMA- and LPSMA-dispersed CB dispersion. Just as analyzed above, the particle size of BPSMA-dispersed CB pigment ink was smaller, the surface area was bigger and surface energy was higher, which enhanced the binding forces between the particles and fabrics. Most of all, the anhydride groups of BPSMA could react with the hydroxyl groups of fabric when sodium phosphate was added and baked at high temperature. BPSMA has many branched chains, which could further reinforce the binding force between CB particles and fabrics. These analyses may be

explained that the rubbing and washing fastness to rubbing and washing of fabric printed with BPSMA-dispersed CB pigment ink was higher than that of fabric printed with LPSMA-dispersed CB pigment ink.

Conclusions

BPSMA was successfully synthesized by polymerization of St and MA using VPMT as a chain transfer agent and BPO as an initiator. BPSMA was confirmed by FTIR, ¹H-NMR and GPC. Compared to linear poly (styrene-alt-maleic anhydride) (LPSMA), the CB dispersion using BPSMA as dispersant exhibited a smaller particle size, a more narrow particle size distribution, a higher Zeta potential and higher stabilities. The cotton fabrics printed with CB dispersion prepared with BPSMA exhibited a higher K/S and rubbing and washing fastness than that of LPSMA.

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