Modification of SMA Using Epoxypropyl Trimethyl Ammonium Chloride for Carbon Black Dispersing

BAI Fushun，FU Shaohai*，TIAN Anli，WANG Chaoxia; Jiangnan University; Wuxi, Jiangsu/China

Abstract

Poly (styrene-alt-maleic anhydride) (SMA) was modified with epoxypropyl trimethyl ammonium chloride (ETA) through interfacial reaction to prepare an amphoteric dispersant SMG for carbon black dispering. Fourier transforms infrared spectroscopy (FTIR) indicated that the epoxy groups had reacted with anhydride groups. 30.96% anhydride groups in SMA was taken part in the reaction when molar ratio of ETA and SMA was 1.3, mass ratio of p-toluene sulfonic acid and SMA was 14%, and the reaction temperature was 78°C for 6 h. SMG showed an excellent dispersing ability for carbon black when modification degree was higher than 14%, the mass ratio of SMG and carbon black was 7%, and pH value was 9. The change rate of particle size of was only about 3.6% when prepared carbon black dispersion was treated at 60°C for 24 h. The zeta potentials of carbon black dispersion showed amphoteric properties.

Introduction

Pigments are an important group of colorants that have been extensively used in coating, printing and paint industries due to the advantages of photosensitivity, color strength and transparency, etc [1]. Commonly, pigments are dispersed in aqueous media with aid of dispersants for its insolubility in water. In aqueous media, the dispersants adsorbed onto pigment surface via anchor groups to build voluminous shells or intensify the charges around the pigment, thereby preventing flocculation and coagulation of pigments. Poly(styrene-alt-maleic anhydride) (SMA) with excellent dispersing ability was widely used for pigment dispersing[2]. However, SMA is sensitive to metal ions due to –COOH groups in molecular chain [3]. In order to improve the dispersing ability and overcome the shortcomings that stated above, many methods have been developed for SMA modification, such as cation-modified, esterification-modified and anion-modified. Among all of above methods, SMA which modified with cationic agent can not only improve its solubility in water, but also provide some special function groups[4]. Braun[5] modified SMA using quaternary ammonium salt. Dietrich [6] synthesized polystyrene maleimide (SMI) through aminolysis reaction. In this paper, we first modified SMA using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride through interfacial reaction to prepare an amphoteric dispersant (SMG), and further investigated its dispersiability for carbon balck.

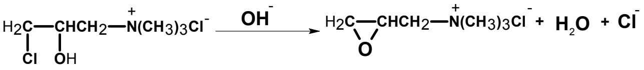
Experimental

Materials

Ethanol (AR), 2-butanone (AR), sodium hydroxide (NaOH, AR), p-toluenesulfonic acid (AR) Hydrochloric acid (HCl, AR) was purchased from Shanghai Chemical Reagent Co., Ltd. of China. 3 - chloro-2 - hydroxypropyl trimethyl ammonium chloride (Content 50%) was provided by Zhuorui Chemical industry, Shanghai, China. Poly (styrene-alt-maleic anhydride) SMA, Mn=13000，molar ratio of styrene to maleic anhydride 1:1）was synthesized in our lab. Styrene (St, CR) was dried by calcium hydride and then distilled before use, 2, 2-AZo-bisiso-butylonitrile (AIBN, AR) was purified by recrystallization with hot ethanol. All the distilled water was used in the experimental.

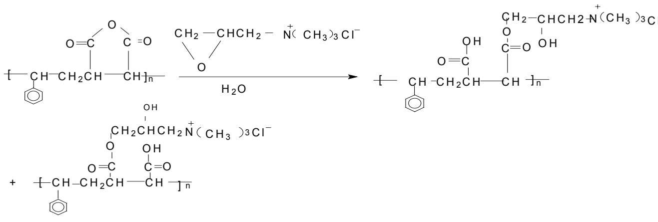
Preparation of SMG

50g 3-chloro-2-hydroxypropyl trimethyl ammonium chloride was put into a three-necked flask equipped with a condenser and then heated to 45°C, and meanwhile, 10g NaOH solution (2mol/L) was dropped into the flask [7]. After reaction for 2h to get epoxy propyl trimethyl ammonium chloride (EPT), the reaction process was illustrated in scheme 1.



(Scheme 1)

Some amount of SMA and corresponding of p-toluenesulfonic acid were dispersed in mixed solvent (mass ratio of 2-butanone and distilled water was 2:1). The mixture was placed into a 250mL four-necked flask equipped with a condenser and heated to certain temperature, and then certain amount of EPT solution was added into the flask, after reacted for some time to get a transparent liquid. Finally, the pH value of the liquid was adjusted to 3 with HCl solution (0.1mol/L), SMA was precipitated, and then SMA was washed three times with ethanol. The reaction process was illustrated in scheme 2.



(Scheme 2)

Dispersing carbon black with aid of SMG

A certain amount of SMG was dissolved into distilled water, and pH value of the solution was adjusted to 9 by 0.1mol/L NaOH solution. Then corresponding amount of carbon black was added into the prepared solution. After the mixture was stirred for 30min and then treated by ultrasonic waves for 30 min with the input power 1100W to prepare the SMG-dispersed carbon black dispersion.

Characterization of SMG

Fourier-transform infrared spectroscopy (FTIR) spectra of SMA and SMG (in KBr pellet) were recorded on a Nicolet Nexus 560 FTIR spectrometer at the wave number range of 500-4000cm^{-1}, respectively. Acid value (AV) was measured as follows: 1g SMA was dispersed into 99g distilled water, and then excessive amount of KOH solution (0.1mol/L) was added. 3 drops of phenolphthalein was added into the mixture after SMA was completely dissolved. The excessive KOH was titrated by HCl solution (0.1mol/L). AV [8] was calculated according to the Eq. (1).

$$AV = (c_1 v_1 - c_2 v_2) \times 56.1 \tag{1}$$

Where c_1 is the KOH concentration, v_1 is the volume of adding KOH solution, c_2 is the HCl concentration, v_2 is the volume of titrated HCl solution. Modification degree (MD) was calculated according to the Eq. (2).

$$MD = \frac{M(AV_1 - AV_2)}{1000 \times w} \times 100\% \tag{2}$$

Where w is the mass of the measured sample, M is molar mass of EPT, AV_1 is acid value before modification, and AV_2 is acid value after modification.

Properties of the SMG-dispersed carbon black dispersion

The mean particle size (Dm) and Zeta potentials were determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS90 instrument at an angle of 90 °. Stability to temperature (DT) was tested by the change rate of particles. The dispersion was sealed and put in an oven at 60°C for 24h, and DT was calculated to the Eq. (3).

$$S_T = \left(1 - \frac{|d_0 - d_T|}{d_0}\right) \times 100\% \tag{3}$$

where d_0 is the particle size of the starting dispersion and d_T is particle size of the dispersion after treatment, the smaller ST is, the higher stability of the dispersion is.

Experimental

Synthesized of SMG

Table 1 runs 2, 7-9 show that the modification degree of SMA increased with increasing amounts of EPT, and almost reached to its maximum when molar ratio of EPT to SMA was higher than 1.3. Runs 4-6 show that the modification degree increases first and then decreases when mass ratio of p-toluenesulfonic acid to SMA increases. p-toluenesulfonic acid used as catalyst can improve the reaction degree at the same conditions, however, when amount of p-toluenesulfonic acid was high enough, some EPT would be destroyed and then turned into GTA, which result in low modification degree. Runs 1-3 show that the optimal reaction time was about 6 h. Therefore, the optimal modified conditions for SMA was that the molar ratio of SMA to EPT was about 1:1.3, the mass ratio of p-toluenesulfonic acid to SMA was about 14%, and the reaction time was about 6 hours.

Table 1 Effect of modified conditions on modification degree of SMG

NO.	SMA/EPT（wt%）	p-toluenesulfonic acid /SMA(wt%)	Reaction time（h）	MD (%)
1	1:1.2	10	4	4.97
2	1:1.2	10	6	27.54
3	1:1.2	10	8	27.68
4	1:1.2	2	6	24.43
5	1:1.2	14	6	29.04
6	1:1.2	20	6	27.41
7	1:1.0	14	6	22.45
8	1:1.3	14	6	30.02
9	1:1.6	14	6	30.96

The synthesized SMG was confirmed by FTIR (Figure 1). FTIR spectrum of SMA shows that the adsorption peaks at 1774.40cm^{-1}, 1852.37cm^{-1} are respectively symmetric and antisymmetric stretching vibration of C=O, and the peak at 1774.40cm^{-1} is stronger than the peak at 1852.37cm^{-1} , which indicates that the molecules contain annular anhydride. While in FTIR spectrum of SMG, The adsorption peaks at 1774.40cm^{-1}, 1852.37cm^{-1} was disappeared and the adsorption peaks only appeared at 1722.42 cm^{-1}, which indicates that the anhydride was all destroyed in the modification process, and the adsorption peaks at 1722.42 cm^{-1} and 1173.38 cm^{-1} may be attributed to the ester groups in SMG.

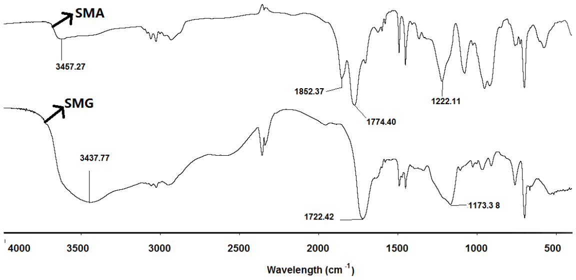


***Figure 1**. FTIR spectra of SMG and SMA*

Preparation of SMG-dispersed carbon black dispersion

Figure 2 shows that the particle size of carbon black dispersion decreases as the modification degree of SMG increases， and reaches to the minimum when the modification degree was about 20%. The larger modification degree was, the more amounts of positive charges were, and the attraction forces was strengthened for different kinds of charges on SMG and carbon black, therefore, the dispersing ability of SMG for carbon black was improved.

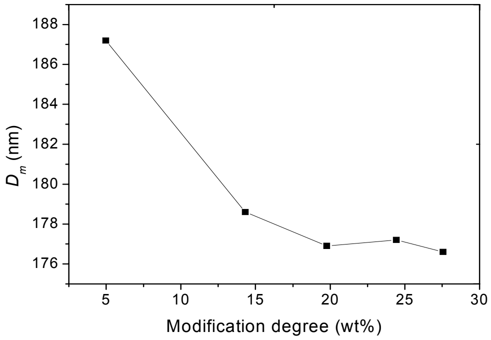


***Figure 2**. Effect of modification degree of SMG on particle size of carbon black dispersion*

Figure 3 shows that the particle size of the carbon black dispersion decreases first and the increases with an increase of amount of SMG, and the reaches to the minimum when mass ratio of SMG and carbon black was about 7%. When amount of SMG was small, the carbon black can not completely encapsulate by the SMG, the repulsive forces was so weak that some dispersed particles will combine again, which led to a poor dispersing ability. However, when amount of SMG was high, some SMG that was not absorbed onto carbon black would dissolve into the aqueous media, as a result, the viscosity of the dispersing media improve greatly, thus led to a poor wetting ability.

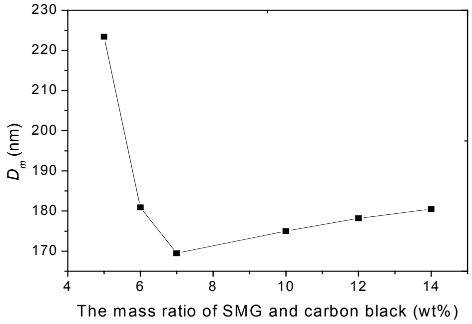


***Figure 3**. Effect amount of SMG on particle size of carbon black dispersion*

Figure 4 shows that the particle size of carbon black dispersion decreased with an increase of the pH value, and reaches to the minimum when pH value was higher than 8. It is known that pH value can influence on the ion degree of -COOH of SMG, thus affected interaction forces between the SMG and carbon black. A small amount of –COOH would be ionized when pH value was lower than 8, therefore, the repulsive forces among the carbon black was small for low ion degree of -COOH of SMG, thus led to a poor dispersing ability.

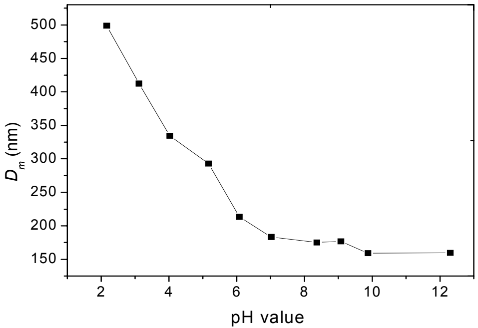


***Figure 4**. Effect of pH value on particle size of carbon black dispersion*

Properties of the carbon black dispersion

Figure 5 shows that the mean particle size was smaller, and the particle size distribution of SMG-dispersed carbon black dispersion was narrower than SMA-dispersed carbon black dispersion, which indicates that SMG has higher dispersing ability for carbon black than that of SMA.

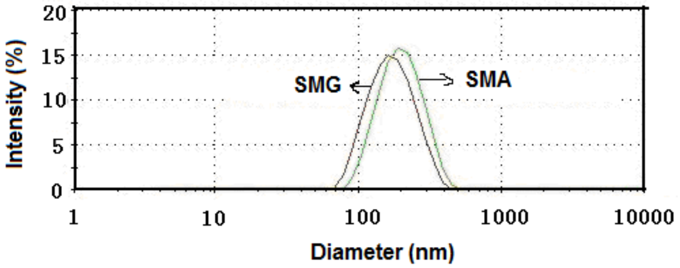


***Figure 5**. Particle size distribution of the dispersion*

Figure 6 shows that Zeta potential of carbon black decreases as pH value increases. The ionization degree of SMG and SMA was related to pH value for –COOH in copolymer. The higher pH value was, and the more amount of –COOH was converted to –COO-, the smaller Zeta potential of carbon black dispersion was. Unlike the SMA-dispersed carbon black dispersion, the SMG-dispersed carbon black dispersion showed amphoteric properties, and the isoelectric point is 6.5. The reason was that small amount of –COOH was turned into –COO-, which could not counteract all the positive charges that produced by –N+(CH3)3, thus the carbon

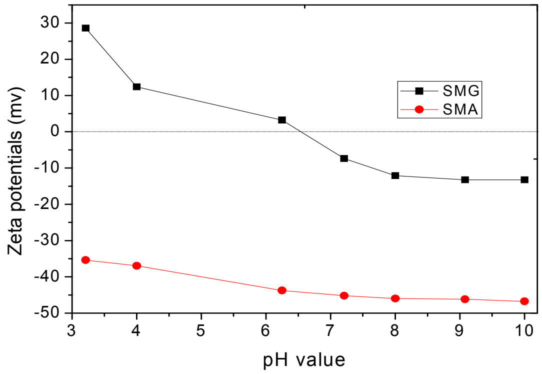


***Figure 6**. Zeta potential of the carbon black based on different pH value*

black shows some positive charges. However, ionization degree of –COOH would increase with an increase of pH value, when the negatives charges was equal to the positive charges which produced by –N+(CH3)3, the Zeta potentials of carbon black was equal to 0.

Figure 7 shows that the storage stability increases with an increase of the amount of SMG, and the particle size changes small when the mass ratio of SMG and carbon black was about 12%. Obviously, when amount of SMG was small, the carbon black can not absorb enough SMG, therefore, the repulsive forces among the particles were small and easily to for aggregates. On the other hand, when amount of SMG was high enough, the excessive SMG that was not absorbed onto the carbon black surface will bridge two or more particles, which also resulted in a poor stability.

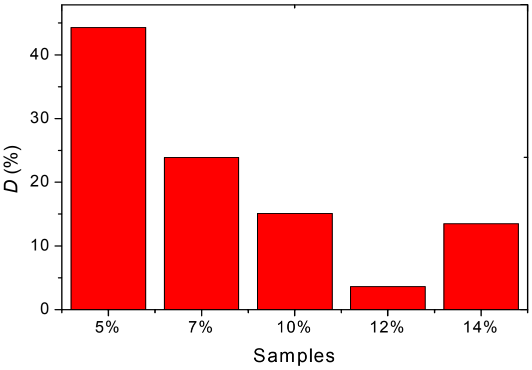


***Figure 7**. Storage stability of carbon black dispersion with different SMG at 40 ℃ for 24h*

Conclusions

The SMA can be modified by interfacial reaction using EPI as the modification reagent, and the modification degree was about 30.96% when molar ratio of SMA to EPT was about 1:1.3, the mass ratio of p-toluenesulfonic acid to SMA was about 14%, and reaction time was about 6 hours. SMG has an excellent dispersing ability for carbon black when modification degree was higher than 14%, pH value was about 9, and the mass ratio of SMG to carbon black was about 7%.

References

[1] Yanli Xu, Yuanlin Zhu. Application of Partial Esterified Esters of Styrene-Maleic Anhydride Copolymer in the Dispersion of Pigment, Dyestuff Industry, 1, 39(2002), 39.

[2] San-yan Zheng, De-shui Lu. Synthesis and Application of Cationic Polymers Containing Quaternary Ammonium Salts, Journal of Functional Polymer, 4, 17(2004).

[3] Lei-li Liu, Zhen-xing Wang. Survey of Development of Cationic Surfactant, Applied Chemistry, 2, 11(1997).

[4] Changrong Zhang, Conglin Jin. The Synthetic Progress of Cation Active Bactericide and the Relation betwen Its Structure and Fungicidal Effectiveness, 5, 30(1997).

[5] Braun D, Sauerwein R, Hellmann GP. Polymer ic surfactants from sty rene comaleic anhydride copolymers, Macromol Symp, 1, 63(2001).

[6] Dietrich B, Rainer S, Goeiz P. Polymeric surfactants from styrene-Comaleic-all decopolymers, Macromoleeular Sym-posia, 3, 16(2001).

[7] Lai-shun Shi, Bo Guo. The Synthesis Research of Epoxypropyl Triethyl Ammonium Chloride Intermidiate, Petroleum Asphalt, 2, 19(2005).

[8] Tsuchida E, Tomono T. Sano H. Solvent effects on the alternating copoly metrication systems Mutation of equilibrium constants by NMR spectroscopy, DieMakromolekulare Chemie, 1, 151(2003).

Author Biography

Bai Fushun received his BE in Light Chemical Engineering from Jiangnan University (2011).Since then he has focused on the development of pigment ink for digital inkjet printing and he is studying for Master's Degree in Textile Engineering at Jiangnan University