Properties and Application of Carbon Black/Latex Composite via Miniemulsion Polymerization

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Abstract

The core-shell structure composite which used carbon black as core and latex as shell was prepared via miniemulsion polymerization. The morphology of the CB/latex composite have been investigated by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) and thermogravimetic analysis (TGA). It showed that the prepared dispersion had small particle size and better dispersibility. Furthermore, CB/latex composite showed much better stability and printing performance.

Introduction

Carbon black (CB) as an important black pigment has been widely used in the manufacture of Chinese ink, printing ink, paint, etc due to its better light stability and low cost [1]. However, CB is a special kind of carbonaceous material on microstructure, particle configuration and surface behavior, leading to aggregation, poor solubility in organic or inorganic solvents or polymer matrix, which greatly limits its application [2].

Many methods for modification of CB to improve the dispersion properties have been investigated, such as dispersant treatment, oxidation treatment and surface grafting or cladding treatment. Dispersant treatment is most commonly used [3-4], but the way for physical adsorption and desorption of dispersant on CB surface contributes to a low stability. The second is oxidation treatment [5-6]. It has been proved that oxidation treatment can improve hydrophilicity of CB for the introduction some amount of polar groups. However, the stability of CB dispersion prepared using this method is not ideal, due to the lack of steric hindrance. In recent years, surface grafting or cladding treatment was variedly applied. Researchers are trying different approaches to graft or coat polymer layer on CB surface [7-8]. Through this method, the morphology and surface character, electrostatic repulsion of CB can be greatly enhanced, thus greatly improve the compatibility with the substrate materials. In addition, the coating polymer can also take part in the film-forming, thus can improve the adhesive force for the substrate.

In recent years, miniemulsion polymerization not only has the advantages of emulsion polymerization such as high polymerization rate, high molecular weight and low viscosity, but also has unique characteristics [9-10], especially its unique nucleation and its one-to-one replica during polymerization. In our previous work, we have studied on miniemulsion polymerization for some years and had many achievements in coating dyes and pigments including carbon black [11-12]. In this study, CB/latex composite suspension was prepared via miniemulsion polymerization by using oil-soluble initiator and polymerizable emulsifier, and then further investigated its performance, encapsulation mechanism and application for textile printing.

Experimental Section

Materials

Carbon black (CB) was purchased from Wu Xi Shuangcheng Carbon Black Co., Ltd, China; Allyloxy nonyl alcohol polyoxyethylene (10) ether sulfate (DNS-86, Chart 1) was a gifted from Qingxin Haner Chemical Technology Co., Ltd, China; Hexadecane (HD, AR grade), methyl methacrylate (MMA, AR grade) were all provided by Sinopharm Chemical Reagent Co., Ltd, China; Azobisisobutyronitrile (AIBN, CR grade) was provided by shanghai Shisihewei Chemical Co., Ltd, China.

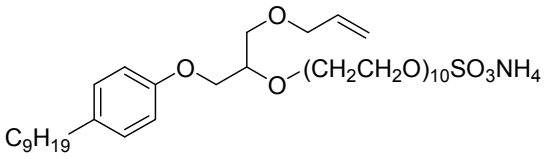

Chart 1. *Chemical structure of DNS-86*

Preparation of CB/latex composite suspensions

The aqueous phase was prepared by dissolving DNS-86 (14.4 mmol/L) in water. And then CB was added into it to get DNS-86 dispersed CB. The organic phase was prepared by dissolving HD and AIBN in the acrylic monomer MMA. The concentrations of the two to MMA were both 2 wt % and MMA to CB was 25 wt%. Both phases were mixed using a mechanical stirrer at 500 rpm agitation. The coarse emulsion was then sonified for 30 min in Ultrasonic JY98-3D homogenizer (NingBo Scientz Biotechnology Co., Ltd, China). Finally, CB/O/W miniemulsion was prepared. During the polymerization process, the miniemulsion was placed into the reactor and allowed to polymerize over 2.5 h. The reaction temperature was 70 °C.

Measurement

Transmission Electron Microscopy (TEM)

The morphology of the sample was investigated by TEM using a H-7650 equipment. The samples were prepared by depositing a drop of diluted colloidal solution on carbon grid (230 meshes) and allowing the water to evaporate at room temperature.

Fourier Transform Infrared (FTIR)

The samples were ground and mixed with KBr to make pellets. FTIR spectra were recorded on a Nicolet Nexus 560 FTIR

spectrometer. For each spectrum, it was collected at 4000–500 cm−1 range with an 8 cm−1 resolution and 32 scans.

Thermogravimetic Analysis (TGA)

The composite particles were collected by centrifuging the suspension and drying in the vacuum oven for 12 h at room temperature. The residual amounts of composite particles were measured by TGA on a Perkin-Elmer TGA-7 instrument by heating from 25 to 650 °C at the rate of 20 °C/min in a nitrogen flow.

Stability

The centrifugal stability is tested by the ratio of absorbency value (R) before and after centrifugation. The samples were centrifuged at different speed for 30 min and then measured the absorbency value (A) at wavelength of 510 nm.

$$R = \frac{A_1}{A} \times 100\% \qquad (1)$$

The samples were removed to room temperature after standing at -5 °C. The particle size of the sample before and after thaw is d0 and d1, respectively. The freeze-thaw stability is measured by change rate of particle size (Td) as shown in Eq (2).

$$T_d = (1 - \frac{|d_0 - d_1|}{d_0}) \times 100\ \% \qquad (2)$$

Printing performance

Printing paste was consist of 15 wt% thickener, 40 wt% adhesives, 2 wt% colorant and deionized water. Pigment printing was a three-step process: printing, drying and curing (180 °C, 150 s). The CIE L*A*B* color and K/S value were measured by spectrum-measuring which is in model Premier 8400 computer color testing and matching instrument. The morphology of the fabric was observed by using scanning electron microscope (SEM).

Results and Discussion

Morphology of the CB/latex composite

Fig.1 shows the TEM images of CB/ latex composite. It can be seen that the DNS-86-dispersed CB is aggregated seriously. While, CB/latex composites are well disperse in aqueous media. Comparing Fig. 1b to Fig. 1d, a layer about 30 nm on CB is found in CB/latex composite, demonstrating that CB/latex is prepared successfully via miniemulsion polymerization.

Fig.2 shows the FTIR and TGA of the CB/latex composite. It can be seen from Fig. 2a, except all the characteristic absorption of original CB, some new absorption peaks at 1730 cm^{-1} (the vibration of ester bond of PMMA), 620 cm^{-1} and 1109 cm^{-1}(the vibration of sulfonic groups) are appeared in the CB/latex composite, which indicate that the latex is the copolymer of MMA and DNS-86.

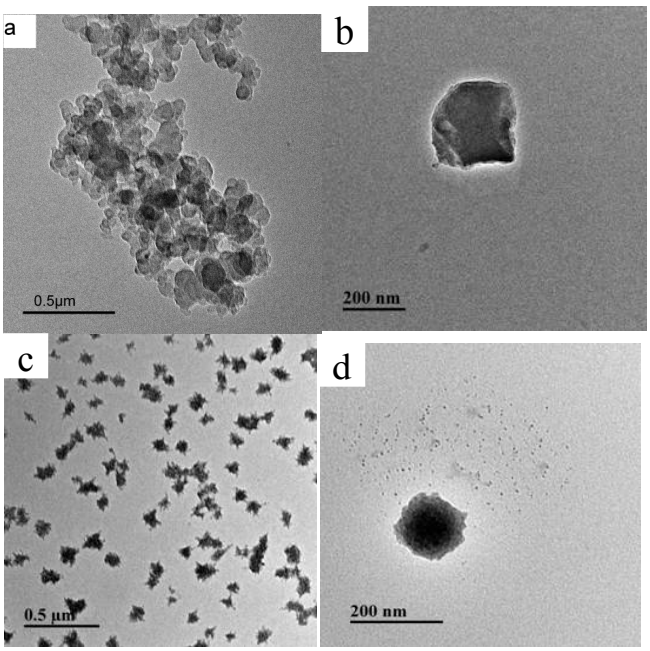

Fig. 1 *TEM images of (a、b) DNS-86-dispersed CB and (c、d) CB/ latex composite*

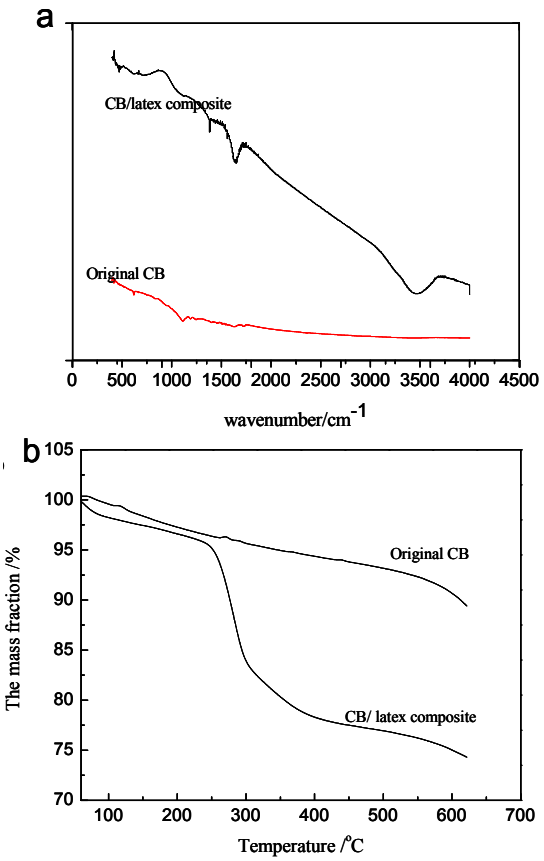

Fig. 2 *(a) FTIR spectra and (b) TGA analysis of CB/ latex composite*

Fig. 2b shows about 2.5% mass loss appears in the original CB when temperature increases from room temperature to 200 °C, which is due to the water and impurities adsorbed on the surface of CB. However, in this temperature range, 5% mass more loss is observed in the CB/latex composite, which may be caused by $SO3^-$ in the CB/latex. Moreover, 20% mass loss appears during 250 °C to 400 °C, which may be attributed to the decomposition of latex. Therefore, it may be concluded that the content of latex is nearly 20% in the CB/latex composite.

Based on above results, it is concluded that the latex was successfully encapsulated on CB surface, and the encapsulation process may be divided for three steps as shown in Fig. 3. First, CB is dispersed with DNS-86 by ultrasonic method. Second, the costabilizer and monomer are added into the DNS-86 dispersed dispersion to prepare the minemulsion. Third, the temperature is improved and initiated the polymerization.

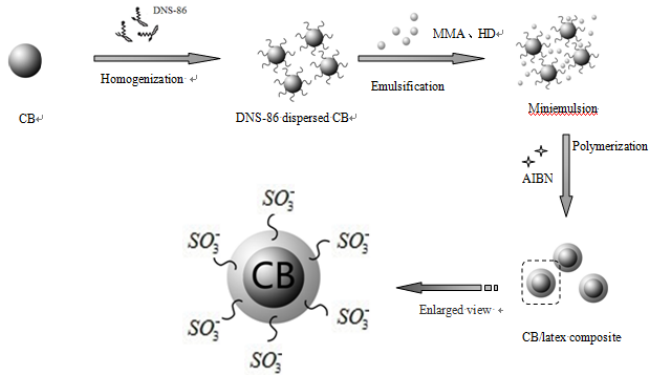

Fig.3 *Encapsulation process for prepare the CB/latex composite*

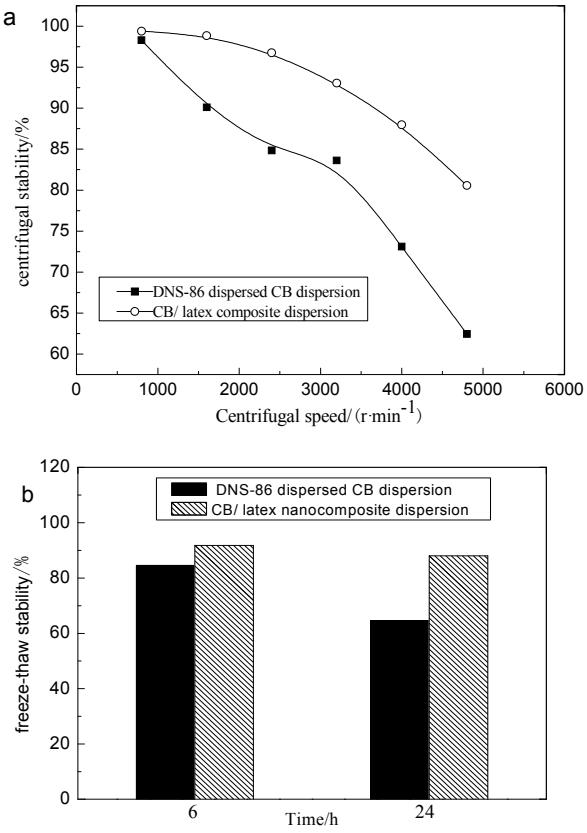

Fig. 4 *Stability of CB/ latex composite dispersion (a) centrifugal stability (b) freeze-thaw stability*

Stability of the CB/latex composite dispersion

Fig. 4 shows that freeze-thaw and centrifugal stability of the CB/ latex composite dispersion are much better than that of DNS-86 dispersed dispersion. Unlike DNS-86 dispersed CB dispersion, the DNS-86 attaches to CB surface via covalent bond during polymerization, which effectively avoids desorption of the DNS-86, even at high/low temperature or high centrifugal force.

Printing performance with CB/latex dispersion

Table 1 illustrates that the K/S value and rubbing fastness of fabrics printed by CB/ latex composite dispersion are higher than that of DNS-86 dispersed CB dispersion. Desorption of DNS-86 will take place during the process of printing, thus leading to CB aggregation. When DNS-86 dispersed CB dispersion was used as colorant, it will lead to the low K/S value and poor rubbing fastness. For CB/ latex composite dispersion, DNS-86 cannot be desorption from CB surface, and furthermore, the latex can also take part in the film-forming, which can improve the K/S and rubbing fastness.

Table 1. Comparison of K/S value and robbing fastness of fabrics printed by ultrafine CB and CB/ latex composite

Printing fabric	L	a	b	K/S value	robbing fastness	
					dry	wet
DNS-86 dispersed CB dispersion	21.7	0.5	2.1	16.4	4	3-4
CB/ latex composite dispersion	20.7	0.5	1.8	17.4	4-5	4

Surface morphologies of printed fabrics with CB were determined by SEM. As illustrated in Fig.5, the CB/ latex composite printed fiber has a smooth surface. While, the surface of DNS-86-dispersed CB printed fiber is very rough with the presence of cavities and wrinkles.

Conclusion

CB/latex composite with core-shell structure has been prepared via miniemulsion polymerization. Calculated from TEM image and TGA, 30 nm latex layer was attached on the CB surface, which is nearly 20% concentration of CB/latex composite. CB/latex composite has better stabilities and printing properties

than that of DNS-86-dispersed CB, which can be widely used for textile print and so on in future.

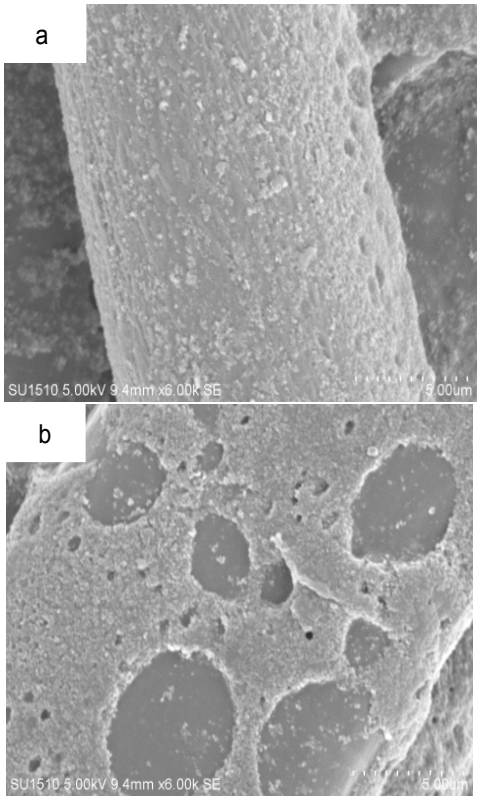

Fig. 5 *SEM images of printed fabrics. (a) CB/ latex composite (b) DNS-86-dispersed CB*

Acknowledgements

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Author Biography

Shaohai Fu received his PhD in College of Textiles and Clothing from Jiangnan University (2006). Since then, he has worked in Key Laboratory of Eco-Textiles of the Ministry of Education, Jiangnan University. His work has focused on textile dyeing and printing, digital textile inkjet printing and pigment modification. Now, He is the vice President of College of Textiles and Clothing, Jiangnan University, and a member of SDC and AATCC.