



Encapsulation of surface-modified carbon blacks by poly(sodium-p-styrenesulfonate) via a phase separation method



Shenbo Jin, Qiuying Li, Chifei Wu*

Polymer Alloy Laboratory, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China

ARTICLE INFO

Article history:

Received 27 June 2014

Received in revised form 29 March 2015

Accepted 7 April 2015

Available online 16 April 2015

Keywords:

Carbon black

Poly(sodium-p-styrenesulfonate)

Phase separation

Encapsulation

Hydrophilic

ABSTRACT

Carbon black (CB) encapsulated by poly(sodium-p-styrenesulfonate) (PSS) via a strong π - π interaction was prepared with the use of ethyl alcohol by a simple phase separation method. Surface treatment was carried out to provide CB particles a better dispersity in water before encapsulation. The result of Fourier transform infrared spectroscopy demonstrated the existence of PSS chains on the surface of coated CB. A nanoparticle with a core/shell structure was clearly observed by transmission electron microscope, while the Raman spectroscopy consequence displayed a structure change of CB after encapsulation. The result of thermal gravimetric analysis indicated that the particle size of CB and the introduction of ethyl alcohol during the experiment are of great importance to prepare hydrophilic carbon black with high encapsulation ratio. Compared to pristine CB, the encapsulated CB exhibited a superb stability in aqueous medium according to the consequence of centrifuging sedimentation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Carbon black (CB) has been widely used as a pigment in the ink, a filler in rubber and plastic industry due to its excellent darkness, chemical stability, heat resistance, and electrical conductivity [1]. However CB particles typically contain 90–99% elemental carbon which makes them strongly hydrophobic. Furthermore, because of the small primary particle size (about 20–60 nm), CB particles are prone to form aggregates and difficult to disperse into matrix [2]. And these aggregates would form agglomerates by van der Waals' forces which are difficult to break up [3], finally leading to the deterioration of material properties [4]. Therefore, preparing stable dispersions of CB in aqueous medium by a low cost, technically straightforward and environment-friendly method is of great importance and in urgent needs [5].

So far, several methods have been developed, such as facial treatment by traditional or novel dispersant [6,7], oxide modification, graft modification and surface coating. Zhou et al. studied the grafting of maleic anhydride onto carbon black surface based on the Diels–Alder addition via ultrasonic irradiation [8]. Li et al. successfully synthesized PVA-g-CB by trapping PVA macroradicals from sonochemical decomposition of PVA molecule [9]. Yang et al. investigated the reversible addition–fragmentation chain transfer (RAFT) polymerizations on carbon black surface, successfully prepared poly(N-isopropylacrylamide) (PNIPAAm) grafted carbon black with a good solubility in water [10].

Jiang et al. fabricated polyvinylpyrrolidone-grafted carbon black (CB-PVP) by a free radical polymerization reaction, and the resultant CB-PVP could disperse well in water [11]. Nevertheless, graft modification involves complicated polymerization reaction and requires harsh terms while the grafting ratio enhances little. Furthermore, oxide modification could not provide CB excellent dispersity in aqueous medium ascribed to the limited number of carboxyl group and hydroxyl group on the surface of CB introduced by oxidation reaction and the quite low degree of ionization of these two groups cannot form enough electrostatic repulsion between CB particles in water. All these drawbacks restrict the application of oxide modification and graft modification.

Surface coating can avoid the complicated polymerization process when a commodity water-soluble polymer is selected as the wall material to encapsulate CB particles [2]. Li et al. selected poly(vinyl alcohol) (PVA) with high hydrolysis degree to encapsulate carbon black (Cabot R99R) nanoparticles via a simple method of coacervation, and the coated CB could keep a stable dispersion in water-based media [12]. However, a large number of additives were required to disperse the carbon black prior to being encapsulated and R99R itself exhibits a better dispersity in aqueous media in comparison with the rubber grade carbon black. In this paper, we report another investigation on this method without employing any other additives during the encapsulation process. Instead of PVA, poly(sodium-p-styrenesulfonate) (PSS) was selected to encapsulate the medium ultra abrasion furnace black in the presence of ethanol. In order to efficiently carry out the encapsulation process, carbon black was modified by use of hydrogen peroxide and sodium hydroxide.

* Corresponding author. Tel.: +86 21 64251844; fax: +86 21 64252569.
E-mail address: wucf@ecust.edu.cn (C. Wu).

2. Experiment

2.1. Materials

A commercial medium ultra abrasion furnace black (N234, obtained from Cabot Co.) with a mean diameter of about 20–25 nm was chosen for this study. The CB particles were dried for 24 h at 105 °C under vacuum before use. PSS solution with a content of 20 wt.% was purchased from Shanghai Herochem Co. Ltd. Hydrogen peroxide and sodium hydroxide were obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd., while ethyl alcohol was purchased from Shanghai Titan Scientific Co. Ltd. All the chemicals were used without further purification.

2.2. Oxidation and neutralization reaction of carbon black

Oxidation was carried out by refluxing 25 g N234 with 350 ml 30% hydrogen peroxide solution in a 500 ml three-necked round-bottom flask with a 300 rpm stirring rate at 100 °C for 24 h. The oxidation product was filtered, washed with deionized water several times, and finally dried under vacuum at 80 °C for 24 h. Then the dried oxidized carbon blacks (CBO), 300 ml deionized water and 30 ml 20 wt.% sodium hydroxide solution were added into the three-necked round-bottom flask and stirred at a rate of 300 rpm at 50 °C for 3 h. The product was filtered, washed with deionized water until the pH value of filtrate remained unchanged. After being dried under vacuum at 80 °C for 24 h, neutralized carbon blacks (NCB) were obtained.

2.3. Preparation of PSS-encapsulated carbon black

The encapsulation process was carried out in a 250 ml three-necked flask equipped with a stirrer and a condenser. Firstly, 0.8 g pristine CB or NCB was dispersed into 60 ml deionized water by an ultrasonic cleaner (JP-020, Shenzhen Jiemeng Cleaning Equipment Co. Ltd.) for 30 min at a stirring rate of 300 rpm under room temperature. Then, 2 ml PSS solution was dropped into the three-necked flask. After another 30 min treatment under ultrasonic, ethyl alcohol (20 ml), as a nonsolvent of PSS, was added into the above dispersion drop by drop to induce coacervation of PSS. Finally, the obtained dispersion was kept standing for 12 h, and the encapsulated CB was separated from aqueous solution by ultracentrifuge (CP80MX, Hitachi) at a speed of 38,000 rpm for 1 h. In order to study the impact of ethyl alcohol on encapsulation ratio, encapsulated NCB without adding ethyl alcohol was fabricated, and was abbreviated as PNCB-1 here. Similarly, the encapsulated CB and encapsulated NCB with treatment of ethyl alcohol were named as PCB and PNCB-2, respectively.

2.4. Characterizations

A laser particle analyzer (ZEN3600, Malvern) was utilized to acquire the information of particle size distribution and zeta potential of CB. To prepare the dispersion (0.02 g/l), CB particles were scattered into deionized water under ultrasonic for 20 min.

Fourier transform infrared (FTIR) spectrum was used to detect the presence of polymer on the encapsulated CB and recorded by Nicolet 5700 spectrometer.

The thermal gravimetric analysis (TGA) was tested by TGA analyzer (STA449 F3 Jupiter, NETZSCH, Germany). Each sample was heated from room temperature to 800 °C at a heating rate of 10 K/min under nitrogen atmosphere.

A Raman spectrometer (inVia + Reflex, Renishaw, UK) was used to study the structure information of CB. Accurately profiling the contribution of D bands (~1340), G bands (~1600) and A bands (~1550) of CB was accomplished by a He–Ne laser at an excitation wavelength of 633 nm [13].

The particle size and morphology of pristine CB particles and encapsulated CB particles were investigated by transmission electron microscopy (TEM) (JEM 1400, JEOL). Testing samples were prepared by heavily

diluting the obtained dispersion with deionized water (500 times) and transferring one drop onto a 200-mesh copper grid, finally being dried by an infrared lamp.

The stability of dispersion was tested on an ultraviolet–visible spectrophotometer (759S, Shanghai Jinghua Technology Instruments Co. Ltd.) at a wavelength of 430 nm. The obtained dispersion was diluted for 10 times with deionized water, and then centrifuged (LDZ4, Beijing Medical Centrifuge Company) for a period of time at a speed of 4000 rpm. Finally, 1 ml liquid taken from the centrifuged dispersion under liquid level by 1.5 cm was diluted into 50 ml deionized water for test. In view of the comparability among all the samples, dispersions containing different kinds of CB were prepared under the same condition (being treated under ultrasonic for 60 min, in a mixture of deionized water and ethyl alcohol).

3. Results and discussion

3.1. Characterizations of oxidized and neutralized carbon black

Oxidation of medium ultra abrasion furnace black could provide it much more hydrophilic groups such as carboxyl and phenolic hydroxyl, which can prevent CB particles from agglomeration by the electrostatic repulsion. As shown in Fig. 1, the result of particle size distribution demonstrates this. Compared to CB, the distribution curve of CBO moves to left (small size), while the average particle size decreased from 214 nm to 109 nm. However, a more obvious movement of the curve of NCB is observed and the size distribution becomes relatively narrow, which indicates that NCB displays a preferable dispersion in water. The difference in particle size between CBO and NCB could be explained by the number of anions on the surface of CB. Although the hydrophilic groups introduced by oxidation could improve the dispersity of CB in water, the limited groups and low degree of ionization of carboxyl and phenolic hydroxyl weakened its electrostatic repulsion. However, neutralized carbon black, whose hydrolysis degree of carboxylate and phenolate was low, could form stronger electrostatic repulsion among NCB particles ascribed to the presence of more anions.

A natural sedimentation experiment was used to evaluate the stability of the dispersion of CB, CBO and NCB. In view of the comparability, all the samples were scattered and kept under the same conditions. As seen in Fig. 2, unlike CBO and NCB, pristine CB sank to the bottom quickly within 1 day and completely settled to the bottom after 2 days. Furthermore, some noticeable precipitates were discovered on the bottom when the bottle filled with CBO dispersion was inverted, while NCB kept a homogeneous dispersion in water during the same time. The results further indicate that the NCB particles, which contain more anions in comparison with pristine CB and CBO, possess a better solubility in water. The results of zeta potential are well consistent with the above discussion. As a result of the increase of anion content on its surface, zeta potential of CBO and NCB decreases to –15.9 mV and –24.9 mV respectively, while that of pristine CB is positive charged (about 8.8 mV). The dispersion stability of NCB was improved by reason of the enhancement of electrostatic repulsion, which displayed a positive correlation with the absolute value of zeta potential.

3.2. Characterizations of PSS-encapsulated carbon black

Thermal gravimetric analysis (TGA) was used to evaluate the encapsulation ratio of CB nanoparticles. Fig. 3 shows the TGA results of pristine CB, NCB, PCB, PNCB-1, PNCB-2 and PSS. As we can see, the weight loss of NCB is larger than that of pristine CB. It can be attributed to the creation of functional groups in the material as a result of chemical treatment [14]. Generally, the weight loss of encapsulated CB is much heavier than the pristine CB ascribed to the decomposition of polymer coating on it. It can be seen from Fig. 3 that PNCB-2 (the yield of PNCB2 particles is 65%) exhibits a heavier weight loss in comparison with the parent material (NCB) while the weight loss of PCB and PNCB-1 decreases little. The

Download English Version:

<https://daneshyari.com/en/article/235572>

Download Persian Version:

<https://daneshyari.com/article/235572>

[Daneshyari.com](https://daneshyari.com)