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Original Research Paper

Analysis of dispersion and aggregation behavior of carbon black particles in aqueous suspension by colloid probe AFM method

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ABSTRACT

To clarify the role of polymer dispersants at the carbon black (CB) nanoparticle/liquid interface, the adsorbed structure of the dispersants and the interactions between particle surfaces was evaluated using colloid probe AFM. As it is difficult to prepare stable spherical granules consisting of CB nanoparticles with diameters on the scale of several microns, for a colloidal probe by spray drying and sintering, CB nanoparticles were uniformly coated on the surface of spherical resin particles using a physical composing process. In order to establish the mechanism of action of the CB polymer dispersant by using the prepared colloid probe, polyethyleneimine (PEI) and PEI functionalized with a hydrophobic toluoyl group (T-PEI) were compared. It was found that on the adsorption of T-PEI, the viscosity of the aqueous CB suspension and the size of the aggregates were remarkably decreased in acidic conditions. Although the amounts of PEI and T-PEI adsorbed onto the CB were almost the same, a larger repulsive interaction was observed in the case of the T-PEI. CB nanoparticle dispersion was promoted by the increase in steric repulsion due to the structure of the adsorbed T-PEI.

1. Introduction

Carbon black (CB) possesses excellent coloring, electroconductive, and thermal characteristics. These, in addition to its weather resistance, make it ideal for use in a number of applications, for example as a black pigment in coatings, ink-jet ink, or in aqueous pigments [1,2]. In the print business, the market for the production of black ink for inkjet printers is huge. When used as a pigment, CB particles have a number of properties that can significantly affect the performance of the ink. For instance, the smaller the particle diameter is, the higher the degree of blackness is; however, this makes stabilization in the solvent more difficult. The success of these applications strongly depends on the availability of CB nanoparticles that are effectively stabilized in solution. Research regarding aqueous suspensions of CB nanoparticles is also carried out in the field of electroconductive coatings and paints, and their electroconductivity makes them suitable for use as an electrode material in lithium ion batteries [3,4]. However, the dispersion stability of the CB nanoparticles in these cases has a powerful impact on the product performance. In particular, the hydrophobicity of the CB surface causes particle aggregation when water is used as the solvent. Various physical and chemical techniques have been used to overcome this problem.

For aqueous suspensions, one approach to increasing dispersion stability is to increase the hydrophilicity of the CB particle surface. Recently, many studies have been carried out with the aim of simplifying the processes and ensuring the safety of various surface modification techniques. Oxidation treatment can be used to change the functional groups present on the CB surface and improve the compatibility with water [5,6]. Graft processing can be used to introduce a polymer onto the surface of CB using a chemical reaction [7,8]. Another highly useful technique is the adsorption of a polymer dispersant to the CB particles [9,10].

Some surface modification techniques have been combined with top-down routes such as milling and grinding in order to destroy the strong aggregates among primary particles [11,12]. Using these modification methods, a number of researchers have successfully prepared CB nanoparticles dispersed in solvents, almost to the level of primary particle size. However, it should be noted that these CB nanoparticles were designed to be dispersed in specific solvents depending on their surface chemical structures. For instance, CB nanoparticles can be dispersed in neutral aqueous solutions since most surface modification protocol such as oxidations generates many carboxyl groups and resulted to possess negatively charged surfaces due to their dissociation. However, under acidic conditions, negatively charged sites will be reduced and the CB nanoparticles would therefore be difficult to disperse in an aqueous suspension under acidic conditions. This significant

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limitation means that there are still aggregation problems that need to be overcome when processing CB in aqueous suspensions under acidic conditions.

In a previous report, in order to break down the strong aggregates of CB nanoparticles, the adsorption of polyethyleneimine (PEI) functionalized with a hydrophobic toluoyl group (T-PEI) was conducted together with a high agitation bead milling process in aqueous media [13]. Although many reports have presented some effective processes for CB surface modification by adsorption of polymer dispersants [14,15], few studies have demonstrated the effect of these agents on the dispersion stability and CB nanoparticle interactions.

From the view point of controlling the dispersion stability of nanoparticles in liquid media, Kamiya et al. and Kakui et al. studied the microscopic interactions between a variety of ceramic surfaces using an atomic force microscope (AFM) and the macroscopic behaviors of suspensions, such as viscosity and flow, on the addition of polymer dispersants with various molecular structures [16–18]. These studies involved analysis of both the adsorbed structure and the mechanism of action of the polymer dispersants. For example, Kakui et al. investigated the mechanism by which linear and branched PEI affect a dense ethanol suspension of alumina using colloid probe AFM. In comparison with linear PEI, the branched chains that were adsorbed on the alumina surface facilitated a short-range steric repulsive force between the particles, effectively reducing the viscosity of the dense suspension [18]. Although the effect of polymer dispersants on ceramic nanoparticles has been systematically presented, their effect on CB nanoparticles in aqueous solution has not been reported thus far. In previous work, a colloid probe was used to characterize surface interactions between fine particles and nanoparticles with diameters of less than 1 μm. Spherical granules with diameters of several microns were prepared using a spray drying process of suspension and heat treatment. However, stable spherical granules consisting of CB nanoparticles for colloid probe analysis could not be prepared by spray drying due to the difficulty in dispersing large aggregates using a physical milling process.

In this study, in order to analyze the dispersion stabilization mechanism of CB nanoparticles and their interactions in aqueous media with a polymer dispersant, PEI and T-PEI were adsorbed on the surfaces of a colloid probe and substrate, and their surface interactions were measured. CB nanoparticles were uniformly coated on the surface of spherical resin particles several microns in diameter using a physical composing process to prepare the colloid probe and plate substrate. The suspension viscosity, aggregated particle size, zeta potential, and amount of polymer dispersant adsorbed onto the CB nanoparticles, were examined in order to investigate their aggregation and dispersion behavior in aqueous solutions at pH 7 and pH 3. The effects of the pH of the suspension and the structure of the polymer dispersant on the behavior of the CB nanoparticle suspensions are discussed herein with reference to the relationships between the macroscopic suspension viscosity and the microscopic surface interactions measured by colloid probe AFM.

2. Materials and methods

2.1. Materials

CB nanoparticles (TOKABLACK #5500, specific surface area measured by BET method, 212 m^2/g, average particle size ca. 25 nm) and cross-linked polystyrene (PS) spherical particles were purchased from Tokai Carbon Co. Ltd., Japan, and Sekisui Plastics Co. Ltd., Japan, respectively. Fig. 1 shows FE-SEM images of original CB nanoparticles and PS particles. PEI ($M_W = 10{,}000$) was purchased from Wako Pure Chemical Industry Ltd., Japan. Acetone was purchased from Kanto Chemical Co. Inc., Japan, and *o*-toluoyl chloride was obtained from Tokyo Chemical Industries Co. Ltd., Japan. Fig. 2 shows chemical structures of PS, PEI and *o*-toluoyl chloride. All chemicals were used without further purification.

2.2. Synthesis of PEI functionalized with toluoyl group (T-PEI)

The synthesis of T-PEI was carried out in a manner similar to that described in our previous report [13] with the exception that here the molecular weight of the PEI was 10,000 rather than 1800. Briefly, 2.0 g of PEI was dissolved in 100 g of acetone. Following this, 1.84 g of *o*-toluoyl chloride dissolved in 20 g of acetone was quickly added with vigorous stirring in an ice bath, and then, left to stir for a further 3 h. The generated white pasty product was collected by centrifugation, rinsed with 40 g of acetone, and centrifuged again. The resulting substance was again dissolved in 20 g of distilled water and stirred at 65 °C for 16 h. The final product was collected by drying the aqueous solution at 105 °C for 24 h. The structure of the obtained cationic PEI was analyzed using Fourier transform infrared (FT-IR) spectroscopy (Nexus 470, Thermo Electron Co.) and CHN organic element analysis (JM-10 Micro coder, J Science Lab. Co., Ltd., Japan).

2.3. Analysis of suspension behavior

In order to determine the best additive content of PEI and T-PEI, a controlled amount of each dispersant (0.25–3.0 mg/m^2, based on total surface area of CB in the suspension) was dissolved in 50 g of water with the pH adjusted to pH 7 and 3 with HNO_3 and NH_3 (total counter ion concentration = 1.07×10^{-3} mol/l adjusted with NH_4NO_3). Following this, 0.05 g of CB nanoparticles were dispersed in the different solutions with 2 min ultrasonic irradiation and then stirred for 24 h to allow the adsorption of the dispersants onto the CB nanoparticles. To analyze the size of the aggregated CB particles in aqueous media, samples were subjected to 1 min of ultrasonic irradiation, and then, dynamic light scattering (DLS) measurements were performed (HPP5001, Malvern Instruments Ltd.). The CB nanoparticles were then collected by strong centrifugation (10,000 rpm, 30 min). The obtained powder was dried under vacuum at room temperature for 19 h. The zeta potential of the CB nanoparticles was analyzed (Zeta Potential Analyzer Model 502, Nihon Rufuto Co. Ltd., Japan) using a solution in which the supernatant from the centrifugation process was diluted 1000 times in pH-adjusted water (pH 3 or 7, adjusted with HNO_3 and NH_3, total counter ion concentration = 1.07×10^{-3} mol/l adjusted with NH_4NO_3). The adsorbed content of cationic dispersant was analyzed using TG–DTA (Thermo Plus EVO, Rigaku Co. Ltd., Japan) of the collected powder under nitrogen flow.

To analyze the behavior of the suspensions, a controlled amount of each dispersant (1.0 mg/m^2, based on total surface area of CB in the suspension) was dissolved in 50 g of pH-adjusted water (pH 3 or 7, adjusted with HNO_3 and NH_3). Following this, 2.8 g of CB nanoparticles were dispersed into the solution, and the mixing process was conducted on a planetary mill (Rentaro Thinky Mixer AR-100, THINKY Co. Ltd., Japan) and stirred for 24 h. After 10 min of planetary mixing with the aid of defoaming, the suspension viscosity was measured on a cone-plate viscometer (RS1, HAAKE Co. Ltd., Germany).

2.4. Preparation of CB coated spherical polystyrene particles

In order to prepare the CB colloid probe and substrate, CB nanoparticles were coated and fixed on the surface of spherical PS particles, as shown in Fig. 1b, using a physical composing process (Theta composer, Tokuju Co. Ltd., Japan). Firstly, 13.65 g of SBX-8