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Notes

Production of Carbon Black/Silica Composite Particles by Adsorption of Poly(vinyl pyrrolidone)

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Introduction

To reinforce the mechanical and electrical properties of materials, carbon black has been widely used as a filler in polymer industry because of its excellent properties such as heat, chemical, and weathering resistance, lightweight, electroconductivity, and low thermal expansion.[1,2] The dispersibility of carbon black is important to show such abilities in organic solvents and polymer matrices. Therefore, many researches have been reported that the dispersibility of carbon black in solvents and polymer matrices is remarkably improved by grafting of polymers on the surface of carbon black.[3,4] Silica offers a unique combination of tear strength, abrasion resistance, and aging resistance compared to carbon black.[5] In tire treads, silica yields a lower rolling resistance at an equal wear resistance and wet grip than carbon black.[6] Therefore, the use of a dual filler system separately composed of carbon black and silica in polymer matrices can give the benefits from each component.[7] To the best of our knowledge, carbon black/silica hybrid composite particles have not prepared to date.

Herein, we aimed to synthesize the carbon black/silica composite particles by a sol-gel process to simultaneously use the properties of each material. In this study, we have found a simple and fast method to produce the carbon black/silica composite using poly(vinyl pyrrolidone) (PVP) as a coupling agent. This amphiphilic, nonionic polymer adsorbs onto the surface of various materials[8-10] such as metals,[11] polystyrene,[12] and graphite.[13] PVP stabilizes colloidal particles in water and nonaqueous solvents.[14] And it can interact with the hydroxyl-rich silica through the hydrogen bond or by electrical attraction.[15]

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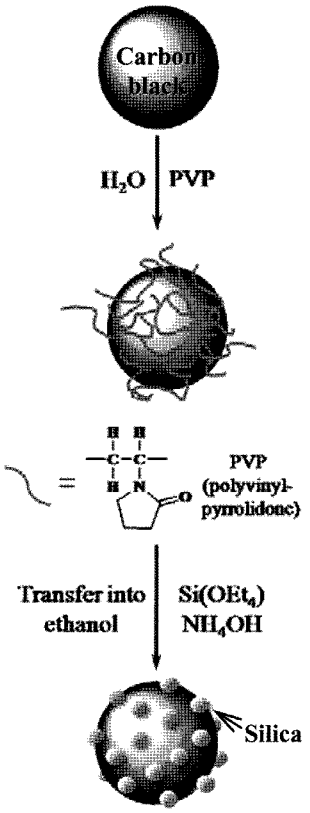
Experimental

Carbon black (N762, Degussa, Germany) and tetraethyl orthosilicate (TEOS, Samchun, Korea) were used without further purification. The carbon black has the surface area of 29 m^2/g and average particle size of 70 nm, respectively. Poly(vinyl pyrrolidone) (PVP K-30, M_w=40,000 g/mol, Aldrich, USA) was used as a coupling agent. Highly pure ethanol and ammonia (25-30 wt% NH_3 in water) were purchased from Duksan Chemical Co., Korea and used as received.

The carbon black/silica composite particles were produced via the following two steps; adsorption of PVP onto the surface of carbon black particles and synthesis of silica. The procedure is shown in Scheme I.

The adsorption of PVP on carbon black was carried out in a 500 mL flat bottom flask with magnetic stirring at 500 rpm for 24 h at room temperature. 250 mL of distilled water was first poured into the flask and PVP was charged. The amount of PVP was varied from 1.0 to 2.0 g. After PVP completely dissolved in water, 1 g carbon black was charged. To transfer the PVP-adsorbed carbon black into ethanol after 24 h, the solutions were filtered out. The filtered carbon black was redispersed in a solution of ammonia in etha-



Scheme I. Procedure to synthesize carbon black/silica composite particles.

nol (4.4 vol% ammonia in ethanol) and then TEOS was charged under stirring at 500 rpm. The amount of TEOS was varied from 3 to 5 g and the reaction was carried out at room temperature for 24 h.

The morphologies of the carbon black/silica composite particles were characterized by Transmission Electron Microscope (TEM, CM200, Philips). The elementary analysis of the composite was performed using the energy dispersive X-ray spectroscopy (EDAX) equipped in TEM. The surface coverage of carbon black particles by silica was simply measured using Scion image analyzer (Scion Co., USA).

Results and Discussion

Due to the amphiphilic character of PVP, it can be adsorbed onto many different surfaces.[14,16,17] Therefore, we used it as a coupling agent and examined firstly the effect of concentration of PVP. Usually, carbon black has plenty of polar groups such as carboxylic acid and hydroxyl group on its surface. These polar acidic groups promote the adsorption of basic PVP on the surface, finally resulting in the well-defined silica shell layer.

Figure 1 shows the TEM images of raw carbon black and PVP-adsorbed carbon black. At 0.8 wt% PVP relative to the medium (water), the thickness of adsorbed PVP onto carbon black was about 2.3 nm (Figure 1(b)). Figure 2 represents the TEM microphotographs of carbon black/silica particles with various PVP concentrations. At 0.4 wt% PVP relative to the medium (water), the amount of PVP adsorbed onto carbon black was too small and the PVP on carbon black cannot sufficiently interact with the hydroxyl-rich silica through the hydrogen bond or by electrical attraction.[15] Therefore, silica particles were not synthesized on the surface of carbon black. The size of synthesized silica particles was about 100 nm (Figure 2(a)). Contrastively, at 0.8 wt% PVP relative to the medium, the PVP-adsorbed carbon black particles were not filtered out due to their high viscosity by excess PVP (Figure 1(b)). Consequently, we could not progress to the next step (the synthesis of silica) with the excess PVP-adsorbed carbon black.

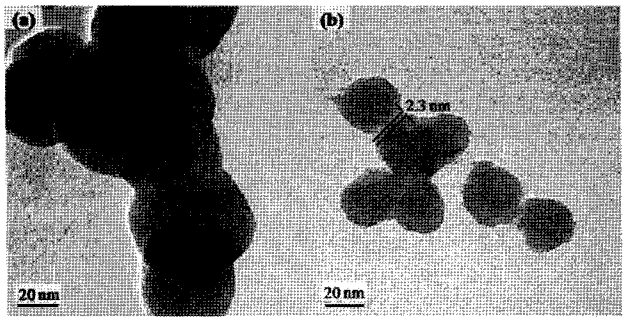


Figure 1. TEM photographs of (a) raw and (b) PVP-adsorbed carbon black at 0.8 wt% PVP relative to medium (water).

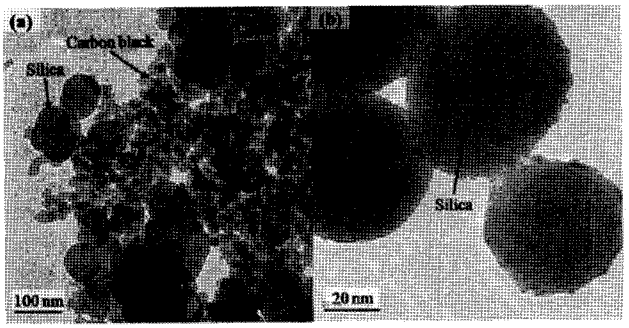


Figure 2. TEM micrographs of carbon black/silica composites prepared by sol-gel reaction of TEOS at different concentrations of PVP relative to medium (water): (a) 0.4 and (b) 0.6 wt%.

Since we confirmed that silica particles were successfully synthesized on the surface of carbon black at 0.6 wt% PVP (Figure 2(b)), the concentration of PVP was fixed at 0.6 wt%, while the amount of TEOS was changed. The carbon black/silica composite particles were produced by the polycondensation of TEOS under ammonia conditions in the presence of PVP-adsorbed carbon black.

After the completion of the reaction, the solution was washed with ethanol and then centrifuged repeatedly to remove free silica. The resultant was redispersed using an ultrasonicator (200 W, Sonics, USA) to check out the binding strength between carbon black and silica. Although the composites were ultrasonicated for 10 min, their morphology of composite particles did not change. It means that silica particles were mechanically interlocked into the pores of carbon black as they were synthesized.

Figure 3 shows the TEM microphotographs of the carbon black/silica composite particles with various TEOS concentrations. As the TEOS concentration increases, the size and quantity of silica particles tend to increase. At 3 and 4 wt% TEOS relative to medium (ethanol), the shape of carbon black/silica composite particles has a raspberry form because the concentration of TEOS was relatively lower to another. The surface of carbon blacks was covered by silica particles about 2.90 (at 3 wt% TEOS) and 8.62 % (at 4 wt% TEOS), repectively. On the contrary, at 5 wt% TEOS relative to the medium, the shape of composite particles shows a core-shell type. It is noted that the surface coverage was simply

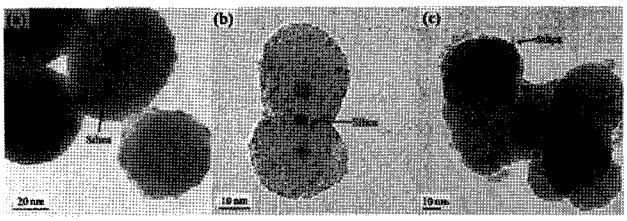


Figure 3. TEM micrographs of carbon black/silica composites prepared by sol-gel reaction of TEOS at different concentrations of TEOS relative to medium (ethanol): (a) 3, (b) 4, and (c) 5 wt%.

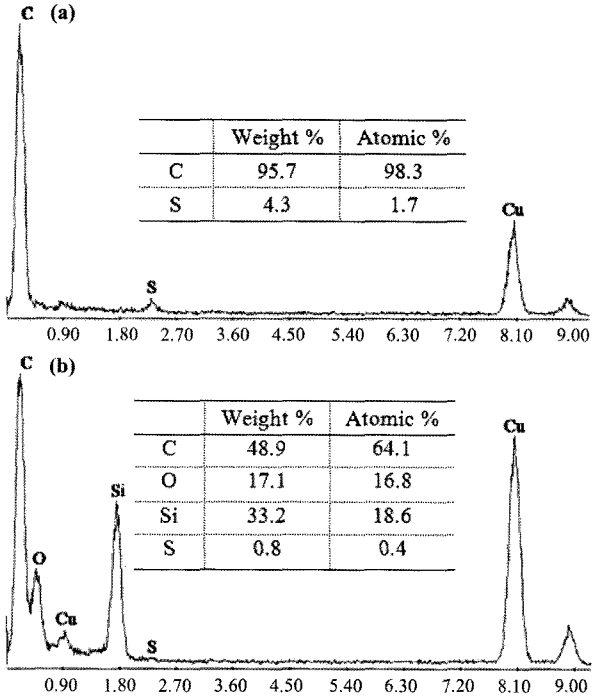


Figure 4. The energy dispersive X-ray spectroscopy (EDAX) spectra of (a) raw carbon black and (b) carbon black/silica composite prepared with 0.6 wt% PVP and 5 wt% TEOS.

measured by taking the projection area of silica particles on carbon black on Scion Image Analyzer®.

Energy dispersive X-ray (EDX) was used to confirm the existence of silica in the composites. The Cu atom detected in spectra was resulted from a TEM grid. Figure 4(b) is the EDX spectrum of carbon black/silica composite prepared with 0.6 wt% PVP and 5 wt% TEOS. In the spectrum of the composites, the O (17.1 wt%) and Si (33.2 wt%) atoms originated from PVP and silica, respectively. Through the existence of O and Si, one can confirm that silica is well synthesized from TEOS onto PVP-adsorbed carbon black by the interaction with PVP molecules.

Conclusions

Silica particles were successfully introduced onto surface of carbon black by sol-gel reaction of TEOS. Carbon black was stable in water and ethanol due to the adsorbed PVP. The PVP-adsorbed carbon black could be directly covered with silica particles of variable size and quantity by different concentrations of TEOS by interaction of PVP with the hydroxyl-rich silica through the hydrogen bond or by electrical attraction.

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