Surface Modification of Pigments with Temperature-Responsive Polymer Grafted by Plasma-Induced Polymerization

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In order to develop temperature-responsive dispersing systems, we have grafted poly(N-isopropylacrylamide) (PNIPA), which is a temperature-responsive polymer having a lower critical solution temperature (LCST) at 32 °C, onto carbon black (CB) by plasma-induced graft polymerization technique. CB was treated with H₂O and/or O₂ plasma, to which aqueous solution of the monomer (NIPA) was introduced, resulted in simultaneous graft polymerization. The dispersibility of the PNIPA-grafted CB in water at 25 and 35 °C was investigated by the measurement of the transmittance of visible light (500 nm). The most of the PNIPA-grafted CB showed better dispersibility at 25 °C (below the LCST) than at 35 °C (above the LCST). In many graft polymerization conditions, CB grafted in 2 wt% of the monomer concentration with ultrasonic irradiation at room temperature showed the most clear temperature response of the dispersibility in water.

Keywords: temperature-sensitive polymer, poly(N-isopropylacrylamide), plasma-induced graft polymerization, carbon black, dispersion

1. Introduction

Since carbon black (CB) was first found to be grafted with polymers in the 1970s, many kinds of powders and particles have been reported to be grafted with various polymers as the surface modification. The most of the graftings onto powders were accomplished by the utilization of functional groups on the surface of powders. In the grafting onto CB, since CB does not have a large amount of functional groups and it is fairly hydrophobic, it is difficult to graft hydrophilic polymers on it.

In our laboratory, we have utilized low-temperature plasma to graft-polymerize vinyl monomers onto many types of solid surfaces including powders [1-3]. This method, called as plasma-induced graft polymerization, plasma is irradiated to solid surfaces in Stage 1, then liquid monomer solutions are introduced and contacted to the plasma-treated surfaces in Stage 2. Since polymerization-initiating species (radicals) are created in Stage 1, graft polymerization proceeds

simultaneously at room temperature in Stage 2. The most fascinating feature of plasma besides the radical formation may be the ability to alter surface property quickly and widely. For example, when hydrophilic plasma gas is used in Stage 1 for CB, the surface of CB becomes hydrophilic. Therefore, hydrophilic monomers can easily start graft polymerization from the CB surface as a good dispersion in a hydrophilic media such as water. When hydrophobic polymer is desired to be grafted, hydrophobic plasma gas ought to be selected. Regardless of the nature of powder surfaces, any kind of vinyl monomer can be graft polymerized by the use of plasma-induced graft polymerization technique.

Poly(N-isopropylacrylamide) (PNIPA) is known as a temperature-responsive or thermosensitive polymer in water [4]. The phase transition of PNIPA occurs at about 32 °C, of which temperature is called lower critical solution temperature, LCST. PNIPA exhibits a sensitive

and drastic and reversible soluble-insoluble change in water at below and above the LCST: At temperatures below the LCST, PNIPA is surrounded with water and hydrated, which makes clear aqueous solution, while at temperatures above the LCST, dehydration occurs and hydrophobic interaction increases, which makes the solution clouded. Because of this unique thermal property, PNIPA has been applied widely. For example, PNIPA-containing gel has been studied extensively for a new drug delivery system [5]. Immobilization of enzymes by PNIPA is another attractive field because its reactivity and solubility can be controlled easily by a slight change of temperature [6-8]. Microsphere of PNIPA has been also prepared [9].

Grafting of PNIPA on solid surfaces also opens more application fields [10]. There are quite a few reports on the application of PNIPA grafting on packing materials of chromatographies. By the grafting of PNIPA on packing materials, elution pattern changes dramatically at different temperatures [11-13].

There are some methods in grafting. Plasma is one of the easiest methods to graft polymers onto solid surfaces, and many researchers have been grafted many kinds of vinyl monomers onto various solid materials. Lee et al. grafted PNIPA onto porous polyamide membrane and used for a selective permeation [14].

In this study, we grafted PNIPA onto CB surface by plasma-induced graft polymerization and investigated the temperature dependence of the dispersibility of PNIPA-grafted CB in water.

2. Experimental

2.1. Materials

CB used in this study was high abrasion furnace CB for a rubber-reinforcement use. The specific surface area of the CB was 68 m²/g. As a grafting monomer, NIPA, purchased from Wako Chemical Co., was used after recrystallization. Water used in this study, as a solvent of NIPA, plasma gas, water-absorption test, and dispersion medium, was distilled and ion-exchanged before use. Water as a plasma gas and the monomer solution were put in ampules and degassed by a ultrasonic irradiation under vacuum before the plasma treatment, and connected to the reactor.

2.2. Plasma-Induced Graft Polymerization

The plasma reactor system used in this study is shown in Figure 1. This reactor system was specially designed for plasma-induced graft polymerization for powdery materials, which equipped with a rotatable round-bottomed flask and plasma gas inlets and a liquid monomer inlet. The rotatable reactor enables uniform plasma treatment of powdery materials.

The plasma-induced graft polymerization of NIPA onto CB was carried out in the following manner.

Stage 1: CB (1 g) was put into the round-bottomed flask. The reactor system was evacuated by a rotary vacuum pump to the pressure of lower than 0.1 Pa. Then H₂O and/or O₂ was supplied to the reactor through a needle valve for the system pressure to be 67 Pa. When H₂O and O₂ was

Figure 1. Schematic illustration of plasma reactor system for plasma-induced graft polymerization for powdery materials.

mixed, the mixing ratio was 1:1, in which water was introduced first to be 33 Pa, then O_2 was added to be the total pressure of 67 Pa. Plasma was then generated in the reactor flask, which was surrounded by electrodes connected to a 13.56-MHz rf power supply. The plasma treatment of CB was done for 10 min. During the plasma treatment, the flask was kept rotating at about 10 rpm for the uniform treatment.

Stage 2: 30 mL of aqueous solution of NIPA (1-3 wt%), which was previously degassed, was introduced to the flask immediately after the plasma treatment. In this process, the monomer solution was easily sucked up and replaced to the reactor flask because the pressure of the system inside was much lower. After the monomer solution was replaced completely, the system pressure was raised to atmospheric pressure with Ar gas in order to prevent air (oxygen) to come in. Graft polymerization takes place simultaneously when CB surface contacts with the monomer since initiating species (radical) have been already created by the plasma treatment. Therefore, initiator or heating process is not necessary in plasma-induced graft polymerization. The graft polymerization was carried out at room temperature for 24 h unless otherwise specified. For the uniform grafting on CB, the reactor was irradiated by ultrasonic during the graft polymerization.

The products were washed with water for the removal of monomer and homopolymer. PNIPA-grafted CB was obtained after centrifugal separation, followed by vacuum drying.

2.3. Properties of PNIPA-Grafted CB

2.3.1. Water-Absorption Test

Water-absorption test was carried out for the evaluation of hydrophilicity of plasma-treated CB. 0.3 g of untreated and plasma-treated CB powders were reshaped to be a pellet (10-mm d.) by pressing at 290 MPa for 5 min. Ten microliters of water was placed on the CB pellet. Time the CB pellet required to absorb the water drop completely was measured by the captured image with a digital video camera (Sony DCR-VX 1000).

2.3.2. Thermal Analysis

Differential scanning calorimetry (DSC) was measured with a differential scanning calorimeter (Seiko Denshi DSC220C) for PNIPA polymerized with an initiator, H_2O_2 . The temperature was increased at a rate of 2 °C/min. The differential curve of DSC (DDSC) was also recorded.

2.3.3. Dispersibility and Its Temperature Response of CB in Water

Dispersibility of CB in water was evaluated by the measurement of the transmittance of its dispersion. In this experiment, we used water of pH 2 (prepared with HCl), in order to prevent the dissociation of acidic groups formed on the surface by the plasma treatment, which can keep good dispersibility even at higher temperature than the LCST. The dispersion was prepared in a sample bottle with 10 mL of water and 10 mg of CB by the irradiation of ultrasonic for 10 min. The dispersion was replaced into an optical cell and left still in an incubator at 25 or 35 °C (or given temperature) for 4 h, then transmittance of light (500 nm) was measured with a UV-vis absorption spectrometer (Shimadzu UV-1200).

In order to examine the temperature response of the CB dispersibility, we successively measured transmittance of CB dispersion in the following manner. First, CB dispersion in water was prepared at 35 °C in the same way as stated above, and transmittance was measured after 4 h. Then, the dispersion was irradiated again with ultrasonic at 25 °C, and transmittance was measured after 4 h. This ultrasonic dispersion-measurement at 25 °C was performed three times consecutively. We define the above four measurements, one at 35 °C and three at 25 °C, ONE sequence. After the first sequence, temperature was raised to 35 °C and the second sequence was started. For each sample, we repeated three sequences and finished with the measurement at 35 °C, altogether 13 measurements. In the figures exhibiting transmittance, the lower the transmittance is, the greater the dispersibility

Figure 2. DSC and DDSC curves of PNIPA.

Table 1. Time required for CB pellets to absorb a 10- μ L water droplet.

Treatment of CB	Time (s)
None	7 920
H ₂ O plasma	4.0
H ₂ O-O ₂ plasma	2.7
O ₂ plasma	0.1

is, because when CB disperses well, the whole dispersion looks dark, and transmittance becomes almost zero.

3. Results and Discussion

3.1. Thermal Analysis of PNIPA

DSC and DDSC of PNIPA, polymerized in an aqueous solution with H₂O₂ as an initiator, in the temperature range between 20 and 45 °C with temperature-increasing rate of 2 °C/min are shown in Figure 2. In DSC curve, a small and broad endothermic peak can be found at about 32 °C resulted from the phase transfer of PNIPA, as many literatures have described. From a closer analysis of the DDSC curve, the endothermic phase transfer of PNIPA was found to start at 29.3 °C and end at 37.0 °C and to have the endothermic peak, LCST, at 32.3 °C. The enthalpy, ΔH , of the phase transfer obtained from the endothermic peak area of the DSC curve was 15 J/g. In general, ΔH of phase transfer for organic polymers is small, but that of PNIPA can be said one of the smallest.

3.2. Property of Plasma-Treated CB Surface

After the plasma treatment with H₂O and/or O₂, the surface of CB became hydrophilic because those plasma gases are hydrophilic or effective to create hydrophilic groups. For the evaluation of hydrophilicity, the absorbability of water was measured. Table 1 shows the time that CB pellet required to absorb a 10-mL water drop. Without plasma treatment, it took more than two hours. With plasma treatments with H₂O, H₂O-O₂, and O₂, the time dramatically shortened to 4.0, 0.3, and 0.1 s, respectively. It was very effective for those plasma to alter the CB surface to hydrophilic. In addition to radical formation, this hydrophilic surface modification enables effective and uniform graft polymerization of aqueous monomers. In the comparison between H₂O and O₂ plasmas, O₂ plasma was more effective in hydrophilic modification probably because hydrophilic groups created were effective.

Figure 3. Transmittance of the dispersion of PNIPA-grafted CB in water for three consecutive sequences of temperature change.

Open symbols, 35 °C; closed symbols, 25 °C. Δ , $\blacktriangle$, Grafted without ultrasonic irradiation at room temperature; $\circ$, $\bullet$, with ultrasonic irradiation at room temperature; $\square$, $\blacksquare$, with ultrasonic irradiation at 60 °C. Plasma, H₂O-O₂; monomer concn, 2 wt%.

3.3. Dispersibility of PNIPA-Grafted CB

In order to evaluate of the dispersibility of CB, we measured the transmittance of light (500 nm) passed through an optical cell containing dispersion of CB in water. Figure 3 shows transmittance of the dispersion of PNIPA-grafted CB in water for three consecutive sequences of temperature change as stated in the experimental section: Each sequence consists of a measurement at 35 °C, followed by three measurements at 25 °C. In this figure, three kinds of CB are compared. All three CB were treated with H₂O-O₂ mixture plasma in Stage 1, but the condition of graft polymerization in Stage 2 was different as follows: (1) without ultrasonic irradiation at room temperature; (2) with ultrasonic irradiation at room temperature; (3) with ultrasonic irradiation at 60 °C. At the beginning of the first sequence, all three samples at 35 °C (open symbols) showed transmittance about 40%, which implies poor dispersibility. Next, when the temperature was lowered to 25 °C (closed symbols), transmittance for all three decreased. Among them, that of CB grafted with ultrasonic at room temperature showed the lowest transmittance, zero, which indicates excellent dispersibility. In the comparison between 25 and 35 °C, PNIPA-grafted CB showed better dispersibility at 25 °C than 35 °C. The reason is that, as we stated repeatedly, PNIPA has an LCST at 32 °C. At above the LCST, grafted PNIPA on CB shrinks because of

hydrophobic interaction, which results in poor dispersibility.

In the 2nd sequence in Fig. 3, when the temperature was raised to 35 °C again, the transmittance for all CB showed almost the same transmittance as at the beginning of the 1st sequence. When temperature was lowered to 25 °C again and measured three times in the 2nd sequence, although the transmittance for CB grafted with ultrasonic at room temperature, which is the lowest among the three, did not fall to as low as in the 1st sequence, the pattern of the transmittance for all CB was very similar to the 1st sequence.

The 3rd sequence was also very much similar to the 2nd sequence. The similarity of the transmittance pattern, or dispersibility change, proved the reversible temperature response in the phase transfer of grafted PNIPA on CB. Without ultrasonic, probably NIPA did not grafted on CB uniformly and there were many CB particles which had not been grafted. With ultrasonic at 60 °C, NIPA may have been grafted uniformly, but since the temperature was above the LCST, CB particles might have aggregated because of the hydrophobic interaction of PNIPA and aggregated gradually during the polymerization process.

Next, we compared the effect of the monomer concentration in the graft polymerization on the dispersibility. Figure 4, looks similar to Fig. 3, shows transmittance of the dispersion of PNIPA-grafted CB for three sequences of the temperature

Figure 4. Transmittance of the dispersion of PNIPA-grafted CB in water for three consecutive sequences of temperature change.

Open symbols, 35 °C; closed symbols, 25 °C. Grafted with ultrasonic irradiation at room temperature in monomer concentration of 3 wt% (Δ), 2 wt% ($\bullet$), 1 wt% ($\square$). Plasma: $\text{H}_2\text{O}-\text{O}_2$.

change for CB grafted with different concentrations of NIPA with ultrasonic irradiation at room temperature. Plasma treatment gas in Stage 1 was $\text{H}_2\text{O}-\text{O}_2$ mixture. In this figure, CB grafted in NIPA concentration of 2 wt% showed the most clear reversible temperature response, while those in 1 and 3 wt% did not achieve good dispersibility. CB grafted in 1 wt% NIPA seems to have too little grafted polymer on to maintain good dispersion. That grafted in 3 wt% seems to have been aggregated during the graft polymerization because of a little too long or dense polymer chains.

Figure 5 shows transmittance of the dispersion of PNIPA-grafted CB at various temperatures from 20 to 40 °C along with the DSC curve of PNIPA (same as Fig. 2). The all measurements were done 4 h after the ultrasonic dispersion. The CB used in this figure was plasma-treated with $\text{H}_2\text{O}-\text{O}_2$ and grafted in 2 wt% of NIPA with ultrasonic at room temperature. The transmittance was almost zero, or dispersibility was excellent, at 20 and 25 °C, but it started increasing at 28 °C, then it reached the maximum at 34 °C and was constant after that. In the DSC curve, the endothermic peak can be observed from 29 to 35 °C, which indicate the phase change of grafted PNIPA. The temperatures for the two property changes coincided each other.

Figure 6 shows the transmittance of the dispersion of PNIPA-grafted CB for three sequences in the comparison between $\text{H}_2\text{O}-\text{O}_2$ and O_2 plasmas. Both the CB were grafted in 2 wt% of NIPA with

Figure 5. Transmittance of the dispersion of PNIPA-grafted CB at temperatures between 20 and 40 °C and its comparison with DSC and DDSC curves.

Grafted in monomer concn. of 2 wt% with ultrasonic irradiation at room temperature. Plasma: $\text{H}_2\text{O}-\text{O}_2$.

Figure 6. Transmittance of the dispersion of PNIPA-grafted CB in water for three consecutive sequences of temperature change.

Open symbols, 35 °C; closed symbols, 25 °C.
 ○●, H₂O-O₂ plasma treated in Stage 1; □■, O₂ plasma treated in Stage 1.
 Grafted in monomer concentration of 2 wt% with ultrasonic irradiation at room temperature.

ultrasonic at room temperature. O₂ plasma-treated CB, similar to H₂O-O₂ treated one, showed temperature dependence on the transmittance: It dispersed poorly at 35 °C while it dispersed excellent at 25 °C. The transmittance of O₂ treated CB was lower than that of H₂O-O₂ treated one at 35 °C, and those of all O₂ treated one at 25 °C were zero. We can say the transmittance for O₂ treated CB shifted a little lower than that for H₂O-O₂ treated one. The reason for this difference probably comes from the difference in the hydrophilicity of CB just after the plasma treatment described in Table 1. That is, O₂ treated CB was more hydrophilic than that treated with H₂O-O₂ plasma. Therefore, even after the graft polymerization, the surface of O₂ treated CB may be relatively hydrophilic. We do not have complete results for H₂O plasma-treated CB correspond to Fig. 6, but its dispersibility at 25 °C was not as good as the others, as expected from the results in Table 1.

4. Conclusion

PNIPA was grafted onto CB by plasma-induced graft polymerization. In the plasma treatment of CB in Stage 1, H₂O and/or O₂ plasma was used, which altered the CB surface drastically to hydrophilic in addition to the radical formation. Therefore, aqueous solution of NIPA was easy to contact with CB in Stage 2 and graft polymerization

proceeded uniformly in water. The most PNIPA-grafted CB showed temperature dependence of its dispersibility in water, evaluated by the transmittance of light: The dispersibility was better at 25 °C (below the LCST of PNIPA) than at 35 °C (above the LCST). The most clear temperature response was observed in the PNIPA-grafted CB polymerized in 2 wt% NIPA with ultrasonic irradiation at room temperature. Between plasma treatments with H₂O-O₂ and O₂, PNIPA-grafted CB treated with the latter in Stage 1 showed a little better dispersibility at both 25 and 35 °C.

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