

Preparation and Characterization of Poly(vinyl alcohol)- and Cu(OH)₂-Poly(vinyl alcohol)-Intercalated Graphite Oxides

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Poly(vinyl alcohol)- (PVA) and Cu(OH)₂-PVA-intercalated graphite oxide (GO) were prepared and characterized in detail. The I_c values of PVA-intercalated GO varied widely in the range 1.32–2.24 nm. In the case of PVA-intercalated GO, a stepwise increase of the I_c value of ~0.5 nm was observed along with the increase of amount of intercalated PVA, which suggests that two types of orientation of PVA occur in GO layer, that is, PVA chains lie in the layer as a single layer or as double layers. In the case of Cu(OH)₂-PVA-intercalated GO, the I_c values changed in very wide range between 1.66 and 4.96 nm, strongly depending on the pH value of the solution. The formation of intercalation compound with about ~2.0 nm indicated that the PVA-Cu(OH)₂ complex that was observed only in aqueous solution was isolated in the form of solid by means of intercalation into the GO layer for the first time. The change of the I_c values over a wide range suggests that the Cu(OH)₂-PVA complex can take on various kinds of conformation in the layer of GO.

Introduction

In the last 10 years, many kinds of polymer-intercalated layered materials have been synthesized.^{1–16} The main interest in these materials was the ionic conductivity of co-intercalated Li⁺ ion or electronic conductivity of the intercalated polymers. One of the recent interests in application of these polymer-intercalated layered materials is the use of them for the cathode material of a Li secondary battery. It was reported that polyaniline-intercalated V₂O₅ showed good cycle performance compared with the pristine V₂O₅.¹⁴ The other interesting point on these materials is the structure of

the polymer in the interlayer spacing, because the conformation of polymer is highly restricted in two-dimensional space. For example, Wu et al.¹² reported that the intercalated polyaniline had “entotaxy” polymer ordering, on the basis of the structural data of the single-crystal polyaniline-intercalated FeOCl by synthesizing it via an in situ polymerization/intercalation reaction.

On the other hand, recently, Yokoi et al.^{17,18} have shown that hydrophilic polymers [poly(vinyl alcohol) (PVA) and polyacetic acid] and metal (copper and iron) hydroxides form clathrate complexes via hydrophobic interaction. In many cases, transition metal hydroxides are not soluble in water, however, in the presence of the polymers just mentioned, the transition metal hydroxides become soluble in water, forming a complex via hydrophobic interaction. Though they suggested that the structure of the polymer is a helical chain with its hydroxyl or amide groups bonded to the chain toward the outside and the metal hydroxides located in the center of the chain, their sizes are still ambiguous because the complex is stable in a limited pH range only in solution. This result would be because the hydrophobic interaction between PVA and metal hydroxides is so weak that in the absence of water, this complex is not stable. However, instead of a water molecule, a graphite oxide (GO) layer with many hydroxyl groups is expected to make the complex stable in the solid state.

In the previous papers,^{15,16} we reported the preparation of two types of poly(ethylene oxide) (PEO)-interca-

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lated GOs with different *c*-axis repeat distances. The X-ray data and infrared (IR) spectra of these two intercalation compounds suggested that the PEO chain did not take a helical but rather a zigzag conformation, and the difference in the *c*-axis repeat distances was not due to that in conformation of the intercalated polymer but was dependent on whether it was located as monolayer or double layer in the gallery of GO. In the case of a metal hydroxide containing PVA-intercalated GO, the conformation and the size of the polymer in the interlayer spacing are very interesting because hydrogen bonding between polymer chains is possible for PVA in contrast with PEO.

In this paper, PVA- and PVA-Cu(OH)₂-intercalated GOs were prepared and characterized in detail.

Experimental Section

All reagents were from commercial sources and were used without further purification.

Preparation of Polymer-Intercalated GO. Graphite oxide as host material was synthesized from natural graphite powder by Brodie method.¹⁹ Graphite powder (57–74 μm, 2 g) was oxidized by KClO₃ (16 g) in fuming nitric acid (30 mL) for 3 h at 60 °C. The preparation method of PVA-intercalated GO was similar to that reported for PEO-intercalated GO in a previous paper.^{15,16} A colloidal solution of GO was obtained by neutralizing GO (100 mg) with 0.1 M NaOH aqueous solution (10 mL) and sonicating for 30 min. The obtained colloidal GO solution and 15–100 mL of PVA (MW, 88 000) aqueous solution (0.5 g of PVA/100 mL of water) were mixed, and the resulting solution was stirred for 3 days. Filtration of the precipitate allowed one to obtain an amorphous PVA-GO composite. After the composite was dried at 60 °C overnight, a layered structure was reconstructed as was the case of the preparation of PEO-intercalated GO,¹⁵ and then PVA-intercalated GO was obtained.

Preparation of Cu(OH)₂-PVA-Intercalated GO. The preparation method for copper species containing PVA-intercalated GO was rather complicated and is shown as follows. After adding 20 mL of PVA (0.1 g) aqueous solution into copper acetate monohydrate (0.045 g) aqueous solution (230 mL) (Cu/PVA unit ratio: 1:8), 1.0–6.0 mL of 0.1 M NaOH aqueous solution was dropped in the resulting solution to obtain the solution of Cu(OH)₂-PVA complex. The pH value during the reaction was controlled by the amount of the added 0.1 M NaOH solution at this step. The color of the solution changed from blue to green by adding NaOH solution. This color change indicated that hydrated Cu²⁺ cation changed to the Cu(OH)₂-PVA complex in this solution. This solution was mixed with 4 mL of the colloidal solution of GO (50 mg) obtained by the same operation as described in previous section, and after measuring pH value, the mixture was stirred for 1 day. After aging this solution at room temperature for 3 days, a precipitate was formed. The precipitate was filtered, washed with water, and then dried at 60 °C overnight. The contents of the complex in GO were calculated from the weight increase during the reaction.

Characterization of Intercalation Compounds. X-ray powder diffraction patterns were recorded on a Rigaku Rint-2100 diffractometer with Ni-filtered Cu Kα radiation. Infrared (IR) spectra were obtained on a JASCO FT/IR-5M spectrometer using KBr pellets. A Seiko Instruments SSC/5200 was used to conduct the differential thermal and thermogravimetric analyses (TG/DTA) in N₂ atm. The temperature increase rate was 1 °C/min and the flow rate of N₂ was 50 cm³/min.

Results and Discussion

Preparation and Characterization of PVA-Intercalated GO. In Figure 1, the relationship between

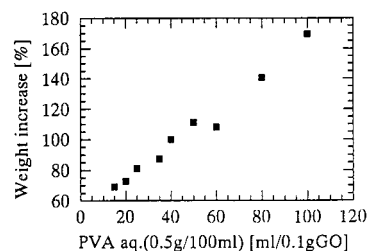


Figure 1. The relationship between the amount of added PVA and weight increase.

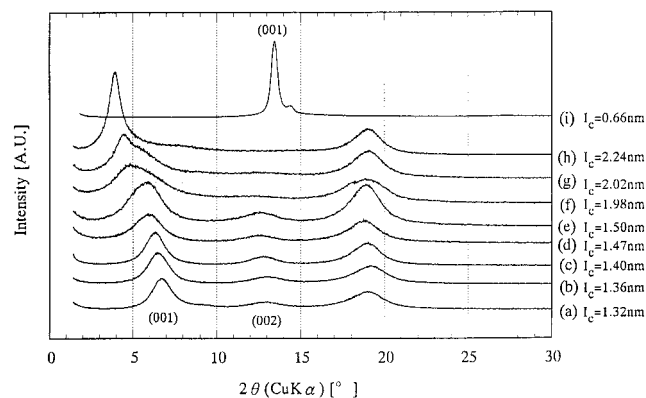


Figure 2. X-ray diffraction patterns of PVA-intercalated GOs synthesized by adding PVA solution (a) 15 mL; (b) 20 mL; (c) 25 mL; (d) 35 mL; (e) 40 mL; (f) 50 mL; (g) 60 mL; (h) 80 mL; and (i) GO.

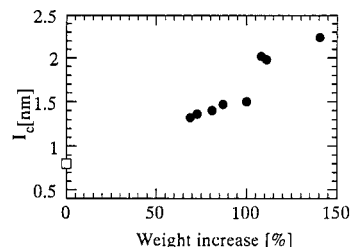


Figure 3. The relationship between weight increase and *I_c* values of PVA-intercalated GOs.

the amount of added PVA aqueous solution and the weight increase of GO is shown. Almost one-half of added PVA in the solution reacted with GO, and the weight of GO increased linearly with the increase of the amount of added PVA solution. Figure 2 shows the X-ray diffraction patterns of PVA-intercalated GOs with various weight increases. In all cases, one to three peaks of (001) lines were observed and, from these diffraction lines, *I_c* values were calculated. The peak at around $\sim 2\theta = 19^\circ$ would be due to the PVA existing at the surface of the intercalation compound. The *I_c* values varied widely in the range 1.32–2.24 nm, depending on the amount of intercalated PVA. Figure 3 shows the relationship between the weight change and *I_c* value of the PVA-intercalated GOs. A steep increase of the *I_c* value from 1.50 to 1.98 nm was observed. This large change of *I_c* value suggested that there exist two types of PVA-intercalated GOs exist: one is that with a single layer of PVA chain (0.47–0.65 nm) in the layer of GO, and the other is with a double layer of PVA chain (1.13–1.39 nm), considering that the size of intercalated PVA is calculated by the subtraction of the interlayer spacing of hydrated GO (0.85 nm) from their *I_c* values.¹⁵ The small difference in two types of intercalation

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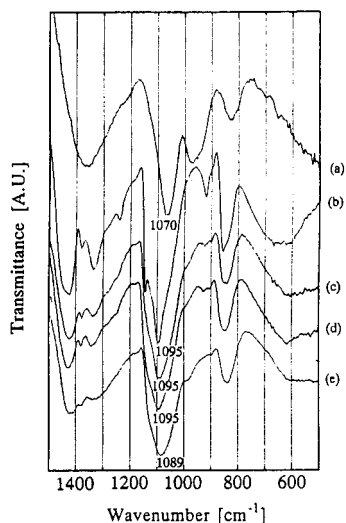


Figure 4. The IR spectra of (a) GO; (b) PVA; and PVA-intercalated GO with (c) $I_c = 1.32$ nm; (d) $I_c = 1.50$ nm; (e) $I_c = 2.02$ nm; and (f) $I_c = 1.32$ nm.

compound would be due to the slight change of conformation of polymer chain in the layer of GO. As reported in the previous paper,¹⁵ only one I_c value (~ 1.25 nm) was observed for PEO-intercalated GO that was independent of the amount of added PEO, and most of the oxygen atoms in PEO chain were bonded to hydroxyl groups of GO via hydrogen bonding. A double layer of the PEO chain was observed only when the copper ion was coexisted. However, in case of PVA with the same unit composition as that of PEO (C_2H_4O), the wide variety of the weight change and I_c values was observed. This result would be because of the existence of hydrogen bonding not only between the polymer chain of PVA, but also between each polymer chain of PVA and the hydroxyl group of the GO layer. This fact results in the wide variety of the conformation of the polymer chain in the GO layer and intercalated compounds with many I_c values.

Figure 4 shows the IR spectra of GO, PVA, and PVA-intercalated GOs with various I_c values. Most of the peaks observed for pristine GO and PVA appeared in the spectra of PVA-intercalated GOs. Among these peaks, that due to the C–OH group of PVA at 1095 cm^{-1} shifted to a lower wavenumber and became similar to that of the C–OH group of GO when the I_c value became smaller. Because hydroxyl groups of PVA with $I_c = 1.32$ nm are bonded to only that of GO, this shift would be due to the decrease of hydrogen bonding between the hydroxyl groups of polymer chains of PVA and only of that remaining between GO and polymer.

Preparation and Characterization of $Cu(OH)_2$ -PVA-Intercalated GO. When the green aqueous solution containing $Cu(OH)_2$ -PVA complex was mixed with the colloidal solution of GO, a precipitate was formed and the color of the solution changed to pale green or almost disappeared. This result suggested that not only PVA, but also $Cu(OH)_2$ was absorbed by GO, forming $Cu(OH)_2$ -PVA-intercalated GO. The I_c values of the precipitate after being dried at 60°C for 2 days and calculated from X-ray diffraction patterns, shown in Figure 5, were between 1.66 and 4.96 nm. These values depended strongly on the pH value just after mixing the GO colloid and PVA- $Cu(OH)_2$ complex solutions. The

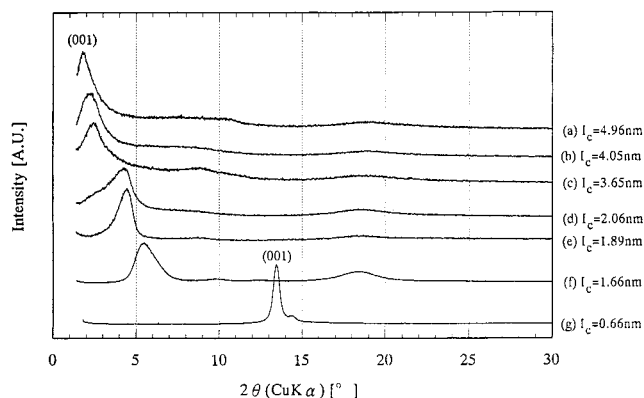


Figure 5. X-ray diffraction patterns of $Cu(OH)_2$ -PVA-intercalated GOs synthesized in the solution with (a) pH = 7.6; (b) pH = 7.2; (c) pH = 6.1; (d) pH = 8.5; (e) pH = 9.9; (f) pH = 10.7; and (g) GO.

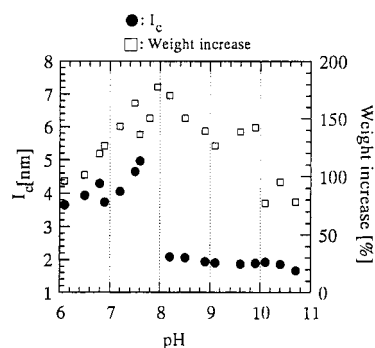


Figure 6. The relationships between pH and I_c value (filled circle), and between pH and weight increase (open circle) of $Cu(OH)_2$ -PVA-intercalated GOs.

relationship between pH value and weight increase during reaction, together with that between pH and I_c values are summarized in Figure 6. As the pH value increased up to ~ 8 , weight change and I_c values increased vigorously from 98 to 180% and 3.65 to 4.96 nm, respectively. At pH = 8.2, the I_c value decreased drastically to 2.1 nm and was almost constant between pH 8.2 and 10. Then, above pH = 10, the weight change decreased from 140 to 80% and the I_c value decreased slightly and became 1.66 nm at pH = 10.7.

The structure of the $Cu(OH)_2$ -PVA complex is ambiguous because it was not possible to obtain it as a solid form by the same procedure as used for the preparation of PVA- $Cu(OH)_2$ -intercalated GO. Moreover, evaporation of water from the solution containing PVA- $Cu(OH)_2$ complex provided an amorphous compound. However, based on the model for this compound with the ratio of $Cu(OH)_2$:PVA unit = 1:8 reported by Yokoi et al.,^{17,18} PVA would locate in the layer of GO as a helical chain surrounding a $Cu(OH)_2$ cluster via hydrophobic interaction in the intercalation compound obtained in the range pH = 8–10 with an I_c value of ~ 2.0 nm, as shown in Figure 7. On the other hand, the intercalation compounds with large I_c values obtained at pH = 6–8 are difficult to be explained at this moment. However, considering that the susceptibility of $Cu(II)$ -PVA complex in aqueous solution starts to decrease above pH = 6 and becomes almost zero at around pH = 8,¹⁷ which suggests that the size of $Cu(OH)_2$ -PVA complex is rather small in the range pH = 6–8, one explanation for large I_c values is that they locate both

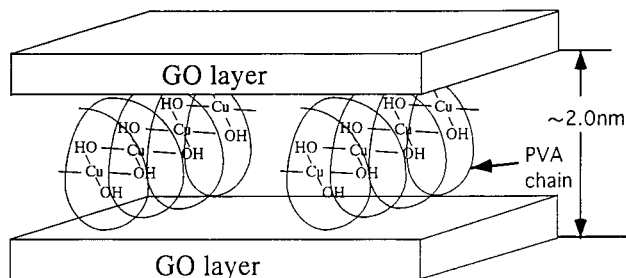


Figure 7. Possible structure models for $\text{Cu}(\text{OH})_2$ -PVA-intercalated GO with $I_c \approx 2.0$ nm.

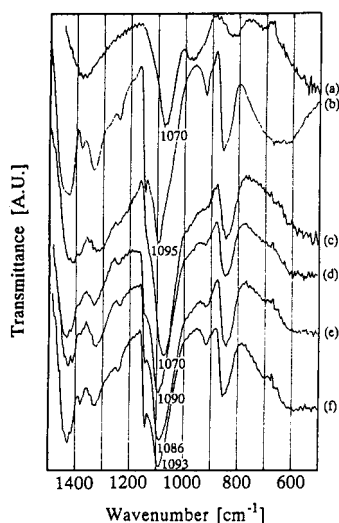


Figure 8. The IR spectra of (a) GO; (b) PVA; and $\text{Cu}(\text{OH})_2$ -PVA-intercalated GO with (c) $I_c = 4.65$ nm; (d) $I_c = 2.06$ nm; and (e) $I_c = 1.66$ nm.

parallel and perpendicular to c -axis. Above $\text{pH} = 10$, a chelate complex occurring between the Cu^{2+} ion and the partially ionized PVA chain is dominant, and a compound similar to Cu^{2+} -PEO-intercalated GO with a double layer of zigzag polymer chain¹⁵ would be obtained. Figure 8 shows the IR spectra of GO, PVA, and $\text{Cu}(\text{OH})_2$ -PVA-intercalated GOs with various I_c values. The spectra were similar to those observed for PVA-intercalated GO with larger I_c values, apart from slight shift in the absorption peak at 1096 cm^{-1} to lower wavenumber for the sample with small I_c value of 1.66 nm.

Figure 9 shows the TG/DTA curve of $\text{Cu}(\text{OH})_2$ -PVA-intercalated GO with an I_c value of 4.26 nm. The decomposition of it occurred at 178°C under nitrogen gas flow showing an exothermic peak and vigorous weight decrease, which was the same behavior as that

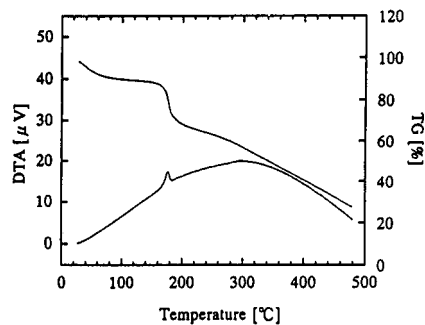


Figure 9. The TG/DTA curve of $\text{Cu}(\text{OH})_2$ -PVA-intercalated GO with $I_c = 4.26$ nm.

observed for Cu^{2+} -PEO-intercalated GO.¹⁶ This result shows that the decomposition temperature of the polymer-intercalated GO mainly depends on the stability of the hydrogen bonding between polymer and GO.

Conclusion

Intercalation of PVA and $\text{Cu}(\text{OH})_2$ -PVA complex into GO was achieved by mixing aqueous PVA or $\text{Cu}(\text{OH})_2$ -PVA solution with colloidal GO solution. The I_c values of PVA-intercalated GO varied widely between 1.32 and 2.21 nm depending on the amount of intercalated PVA. A stepwise increase of I_c value of ~ 0.5 nm was observed as the amount of intercalated PVA increased, which would be caused by single and double layers of PVA chains in the GO layer. In the case of $\text{Cu}(\text{OH})_2$ -PVA-intercalated GO, the weight increase during reaction and I_c values changed drastically, depending on the pH value of the solution. When the pH value was below 8, the I_c values were very large between 3.65 and 4.96 nm. These values were almost constant at ~ 2.1 nm up to $\text{pH} = 10$, and then decreased to 1.66 nm. The $\text{Cu}(\text{OH})_2$ -PVA complex that was observed only in aqueous solution previously was isolated in the form of a solid for the first time by means of the intercalation into GO layer. These results suggest that the structure of $\text{Cu}(\text{OH})_2$ -PVA complex changes depending on pH value of solution.

Finally, the intercalation compounds synthesized in this study possess a wide variety of interlayer spacings, which indicates that by changing the synthetic conditions, it is possible to control the size of space occurring between polymer chains in the layer of GO and they would be applied to selective absorption of small molecules.

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