

SYNTHESIS OF POLY(VINYL ACETATE)-INTERCALATED GRAPHITE OXIDE BY AN *IN SITU* INTERCALATIVE POLYMERIZATION*

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Abstract Graphite oxide, a pseudo-two-dimensional solid in bulk form, was synthesized from natural graphite powder by oxidization with KMnO_4 in concentrated H_2SO_4 . The poly(vinyl acetate)-intercalated graphite oxide nano-composite was prepared by an *in situ* intercalative polymerization reaction, in which *n*-octanol-graphite oxide intercalation compounds were first obtained, vinyl acetate monomer was then dispersed into the interlayer of modified graphite oxide, followed by thermal polymerization of the monomer. It was experimentally shown that the *c*-axis space of poly(vinyl acetate)-intercalated graphite oxide was increased to 0.115 nm, which suggested there existed a monolayer of poly(vinyl acetate) chain between the layers of graphite oxide. The nanocomposite was also characterized with thermal analysis and FT-IR spectrometry.

Keywords Graphite oxide, Poly(vinyl acetate), Intercalate

INTRODUCTION

Recently, studies on organic/inorganic nanocomposite materials have been attracting considerable research interest. In these nanocomposites, the inorganic components can be three-dimensional framework systems such as zeolites^[1], two-dimensional layered materials, such as metal oxides^[2-4], metal dichalcogenides^[5, 6], FeOCl ^[7], layered double hydroxides^[8], layered metal phosphate^[9, 10] and so on, while the organic components can be conjugated electroactive polymers or/and other polymers. These organic/inorganic nanocomposites have been proved to exhibit a variety of unique properties due to the synergies of the inorganic and organic component, such as electronic, mechanical, and structural properties.

It is well known that graphite oxide (GO) is a typical pseudo-two-dimensional solid in bulk form. Although there is still no consensus as to the precise structure of GO layer and structural model^[11, 12], some functional groups, such as hydroxyl, carbonyl and ether groups embedded in carbon sheets in GO lamellae make graphite oxide hydrophilic, and also enable GO to possess a richer intercalation chemistry. It has been reported that some polar organic molecules and polymers, such as alcohol^[13], poly(ethylene oxide) (PEO)^[13, 14], poly(vinyl alcohol) (PVA)^[15], poly(diallyldimethylammonium chloride) (PDAA)^[16], and even poly(furfuryl alcohol) (PFA)^[17] are easily inserted into GO lamellae to form intercalated GO nanocomposites by different methods with different *c*-axis repeat distances. It was suggested that in these nanocomposites there were some stronger molecular forces between GO and polymers, such as hydrogen bonding, coulombic electrostatic forces, and that the existence of these polymers enabled the physiochemical properties (electrical and thermal properties, etc) of graphite oxide to be greatly changed.

In the previous paper^[18], we reported the preparation of polyaniline(PAn)-intercalated GO by an

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exfoliation/absorption process via a stronger hydrogen bonding and a coulombic electrostatic interaction between GO and polyaniline due to the existence of polyaniline emeraldine salt. The X-ray data of the intercalation compound showed that monolayer and/or multilayers of polyaniline chains intercalated with GO layers. Similar to the other PAn-inorganic intercalated nanocomposites^[2-10], PAn-GO had also a higher electrical conductivity than the pristine GO. However, all polymers or their monomers mentioned above are water-soluble or hydrophilic. In contrast to these water-soluble/hydrophilic polymers or their monomers, oil-soluble or hydrophobic polymer's intercalating GO has never been reported. Here an *in situ* intercalative polymerization reaction is reported, which allows intercalation of poly(vinyl acetate), an oil-soluble polymer, into graphite oxide lamellae, and the characterization of the nanocomposite is also presented.

EXPERIMENTAL

Natural graphite powder (30–50 μm) was first treated twice with 5% HCl, then filtered, washed with water thoroughly, and dried at 110°C for 24 h. Azobisisobutyronitrile (AIBN) was purified by recrystallization before use. Vinyl acetate was redistilled according to usual procedure. All other reagents were obtained commercially and were used without further purification.

Preparation of Poly(vinyl acetate)-Intercalated Graphite Oxide

Graphite oxide (GO) was synthesized from natural graphite powder by graphite oxidization with KMnO_4 in concentrated H_2SO_4 according to Hummer's method^[19]. Graphite powder (10 g) was put into cold (0°C) concentrated H_2SO_4 (230 mL). KMnO_4 (30 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20°C. The mixture was then stirred at $35 \pm 3^\circ\text{C}$ for 30 min, and distilled water (460 mL) was slowly added to cause an increase in temperature to 98°C; this temperature was maintained for 15 min. After this, the reaction was terminated by addition of a large amount of distilled water (1.4 L) and 30% H_2O_2 solution (100 mL). The mixture was filtered and washed with 5% aqueous HCl solution thoroughly until the sulphate could not be detected with BaCl_2 . It was dried under vacuum at 50°C or in air.

The intercalation of poly(vinyl acetate) (PVAc) into GO layers was performed in the following way. 5 g of air-dried GO was added to 100 mL *n*-octanol in a closed vessel, and the mixture was stirred at ambient temperature. After 3 days, the octanol-GO intercalation complex was obtained by centrifugation, and then dispersed in 100 g vinyl acetate monomer containing 0.5% (W/W) AIBN as initiator with stirring for 24 hr. After slight centrifugation to remove most of the surplus vinyl acetate, the crude product was subsequently heated at 50°C under flowing N_2 for 24 h to induce the polymerization according to a similar procedure devised by Sugahara^[20]. The as-prepared powder was stirred in *n*-hexane solution for 30 min to remove residual vinyl acetate, centrifuged, dried at 50°C overnight, and the product was obtained.

When PVAc-GO was prepared with *n*-dodecanol or *n*-octadecanol modified GO, the modified GO was first synthesized as follows. 5 g GO pretreated with 100 mL ethanol for 12 h at room temperature was mixed with a 20% (W/V) solution of *n*-dodecanol or *n*-octadecanol in benzene at 40°C for 2–3 days with stirring. After warm-up, filtering and washing with warm benzene solution, the modified GO was obtained after drying at 50°C for 1–2 h. Then the modified GO was dispersed in vinyl acetate solution containing AIBN, and the same treatment was done as for octanol modified GO.

Characterization of Intercalation Compounds

X-ray powder diffraction (XRD) patterns of the samples were recorded on a Rigaku D/MAX-III diffractometer with $\text{CuK}\alpha$ /graphite radiation. Data were collected at ambient temperature over the range $2^\circ \leq 2\theta \leq 45^\circ$ in increments of 0.2° . Infrared (FT-IR) spectra were collected from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} on a Nicolet 5DX FT-IR spectrometer using pressed KBr pellets. A TGS-2 and DTA1700 (Perkin-Elmer) were used to conduct the thermogravimetric (TG) and differential scanning calorimetric analysis (DSC) respectively in an air atmosphere with a programmed heating rate of 5 K/min, the flow rate of air was 45 mL/min. An ISIS-300 elemental analyzer (Shimadzu) was used to determine the extent of the graphite oxidation.

RESULTS AND DISCUSSION

The XRD pattern of vacuum-dried GO prepared here reveals a sharp reflection peak at $2\theta = 11.61^\circ$, which corresponds to a c -axis spacing (I_c) of 0.76 nm. This suggests that there exists intercalated water in the lamellae of GO, because the GO interlayer distance depends strongly on the GO:H₂O ratio^[11, 21]. No (002) diffraction peak from unreacted graphite is observable in the XRD pattern. In addition, GO prepared here gave the following atomic composition (wt%): C, 47.24; H, 2.19. From these, O, 50.57% could be obtained when other elements were neglected. The calculated ratio C:O:H = 4:3.21:2.23 is richer in O and H than that of the ideal formula C₈O₂(OH)₂ for GO^[11], which corresponds to the presence of intercalated/absorbed water and carboxyl groups^[21].

In the previously reported papers^[13–18] about PEO, PVA, PDDA, PFA, and PAn intercalating into GO lamellae, a stronger polarity or/and good water-solubility of these polymers or their monomers made them easily disperse in GO aqueous suspension or into GO lamellae to form intercalation compounds. However, it is experimentally shown that this method is not adaptable to synthesis of PVAc intercalated GO, because GO could not disperse in either oil-soluble vinyl acetate (VAc) or its polymer solution. This should be attributed to the existence of polar groups in the interlayers of GO. But, on the other hand, the existence of these polar groups enables GO to absorb polar molecules easily, such as alcohol^[13] and n -alkylammonium^[22] compounds, to form intercalation compounds with c -axis distance (I_c) increment. And these intercalation compounds made the modified GO hydrophobic, and also gave a good adsorptivity to organic compounds^[22]. To obtain PVAc intercalated GO, here some longer chain aliphatic alcohol compounds (n -octanol, n -dodecanol or n -octadecanol) were chosen to modify GO.

Figure 1 shows the X-ray diffraction patterns of n -octanol-GO, PVAc-GO intercalation compound, together with that of pristine GO. Clearly, when octanol was inserted into GO layers, the I_c was greatly increased to 2.48 nm from 0.76 nm of that of pristine GO (Fig. 1b), which was much larger than that of Dekany's lateral pseudo-three-layered alkyl chain arrangement between GO layers^[22]. Taking into account the interaction between GO and alcohol, the driving force for the reaction between octanol and GO there should be hydrogen-bond formation between the hydroxyl (OH) groups of octanol and the polar groups on the internal layers of GO. And it could also be concluded according to Dekany^[22] here that the intercalated octanol very likely forms a lateral monolayer- or bilayer-structure between the GO layers; the octanol-GO is then swollen by excess n -octanol

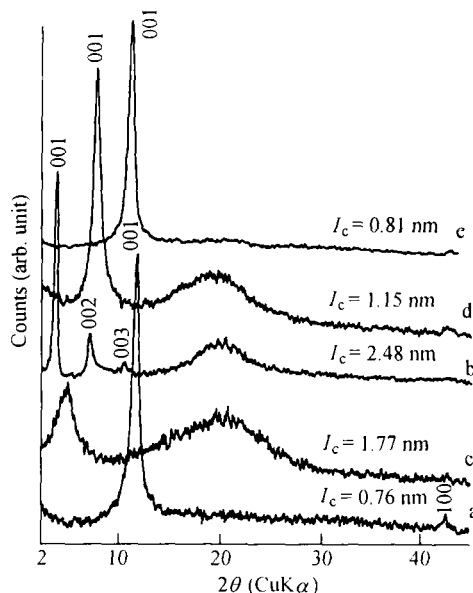


Fig. 1 X-ray diffraction patterns of (a) GO, (b) GO-octanol, (c) GO-PVAc, (d) GO-PVAc and (e) GO-octanol after heating at 50°C for 24 h

resulting in an increase of its I_C like organics swelling *n*-alkylammonium GO intercalation compounds^[22]. However, after VAc monomer was dispersed, a broad diffraction peak centered near 5° (2θ) was observed (Fig. 1c), the I_C (1.774 nm) was smaller than that of octanol-GO composite due to the replacement of octanol for VAc in swelling. And when the composite was heated at 50°C for 24 h, the diffraction peak shifted to a higher angle as shown in Fig. 1d, its I_C value was calculated to be 1.15 nm due to the monomer's polymerization in the lamellae of GO. This is similar to the polymerization of aniline in the lamellae of $\alpha\text{-M}(\text{HOPO}_3)_2$ ($\text{M} = \text{Zr}, \text{Ti}$)^[10] and $\delta\text{-MnO}_2$ ^[2], where the I_C value decreased when aniline was polymerized.

To determine the precise structure of the PVAc-GO intercalation compound, it is necessary to know the size of the GO monolayer. However, it is difficult to determine the ideal structure of GO, because its I_C value varies widely between 0.61 and 1.1 nm depending on the content of hydroxyl groups on its basal planes and the amount of water adsorbed according to Nakajima's structural model^[11]. By considering the pre-treatment with hydrophobic long-chain aliphatic alcohol, and assuming the absorbed water was completely extracted by alcohol, a thickness of 0.61 nm for the individual GO lamellae was assumed. By subtracting the size from that of PVAc-intercalated GO, a 0.54 nm increase of I_C value was obtained. This value is close to that of PVAc-intercalated montmorillonite (0.40 nm)^[23], and suggests that there exists a single layer of PVAc chain in the layer of GO.

Similar to solvent extraction experiments^[24], a thermal treatment also confirms the existence of PVAc in the lamellae of GO. When PVAc-GO and *n*-octanol-GO were thermally treated at 50°C for 24 h in air, the I_C value of the latter decreased to 0.81 nm, very close to that of pristine GO (Fig. 1e), but little change occurred for the former. These results suggest that octanol-GO was not thermally stable, complete deintercalation of organic molecules from GO lamella occurring due to heating^[14], also that no deintercalation occurred for the former compound due to a stronger interaction between GO and PVAc chain^[24].

Similarly, when *n*-dodecanol and *n*-octadecanol were used, similar results for PVAc intercalated GO could be obtained (here, I_C value of PVAc-GO was 1.13 nm, 1.14 nm, respectively).

In FTIR spectra of the above PVAc-GO intercalation composite and the pristine GO, the band peaks at ~ 3400 , 1715, 1630, 1398 and 1068 cm^{-1} , as shown in Fig. 2(a), and the broad and strong 1743, 1250, 1082 cm^{-1} peaks in addition to those at 2973, 2938, 1018 cm^{-1} and a strong 1377 cm^{-1} peak in Fig. 2(b) were observed. This result suggests the existence of intercalated water in pristine GO, especially the co-existence of PVAc with GO in the nanocomposite, and also that the position of the (001) peak in Fig. 1(d) is due to the polymerization of VAc in the interlayer of GO.

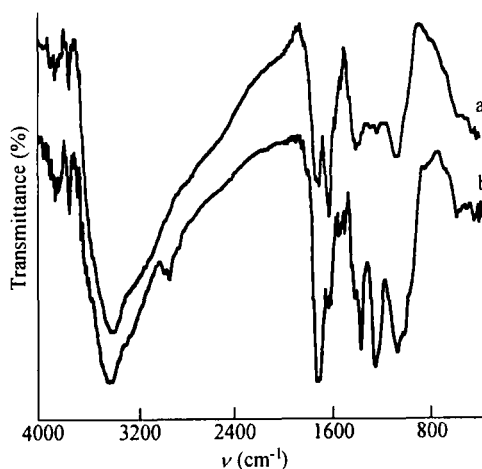


Fig. 2 FT-IR spectra of (a) pristine GO and (b) PVAc intercalated GO obtained from *n*-octanol modified GO

Figure 3 shows the TG and DSC curves of the PVAc intercalated GO sample obtained under air flow at 5 K/min. In the DSC curve of the PVAc-intercalated GO nanocomposite, two exothermic peaks were observed,

as shown in Fig. 3a. Considering that GO was converted into carbon when it was heated to 180°C ^[22] (also seen in Fig. 3b), the higher and larger peak at 193°C should be due to the destruction of the carbon skeleton of GO to some extent, and also the formation of some stable compounds, i.e. CO, CO₂, H₂O, and carbon. But this phenomenon is very likely accompanied by the deintercalation of PVAc from the GO by breaking of the van der Waal or/and other forces between PVAc and GO. Considering that the decomposition of PVAc occurred at 300°C ^[23], the second broad and weak DSC peak at 311°C in Fig. 3(a) could be ascribed to the decomposition of PVAc. Clearly, the decomposition temperature of PVAc in PVAc-GO nanocomposite is somewhat higher than that of pure PVAc. The difference in the thermal behavior could arise from a situation in which PVAc intercalated into the GO layers was very likely protected by the thin crumpled carbon sheets, which are formed from the decomposition of GO and then absorbed on PVAc surfaces, thus preventing the decomposition of PVAc.

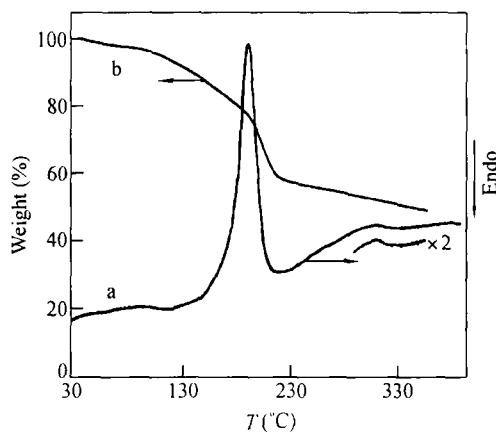


Fig. 3 (a) DSC and (b) TGA thermograms of PVAc-intercalated GO

GO can be chemically and/or electrochemically reduced, resulting in an increase of the electrical conductivity of its composite^[16, 18]. Similarly, when PVAc intercalated GO was chemically reduced by hydrazine hydrate, good electrical conductivity (0.14 S/cm at ambient temperature as detected by the four-probe method) was also observed.

CONCLUSION

Hydrophilic graphite oxide of lamellar structure was prepared by oxidation of natural graphite. Intercalation of PVAc into GO was achieved by *in situ* polymerization of vinyl acetate monomer into long chain aliphatic alcohol-modified GOs because the interaction between GO and alcohol makes GO hydrophobic. Contrary to alcohol-GO, PVAc-GO has good thermal stability because there is a stronger interaction between GO and polymer chain. X-ray diffraction measurements indicate that the I_C value of PVAc-intercalated GO increases from 0.762 for GO to 1.15 nm, which suggests that there exists a single layer of PVAc chain in the GO layer. Thermal treatment and FT-IR measurement indicate the co-existence of GO and PVAc in the polymer intercalated GO nanocomposite. Thermal analysis also shows that the intercalated PVAc decomposes at higher temperature than pure PVAc due to the protection of carbon sheets.

When the intercalation compound synthesized in this way is chemically reduced, good electrical conductivity can be obtained. The structure and properties of the reduced GO and its polymer composite will be studied in the future.

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