JOURNAL OF Materials CHEMISTRY

Preparation and characterization of poly(vinyl acetate)-intercalated graphite oxide nanocomposite

Pinggui Liu, Kecheng Gong,* Peng Xiao and Min Xiao

Polymer Structure & Modification Lab, South China University of Technology, Guangzhou 510640, China. E-mail: pskcgong@scut.edu.cn

Received 12th October 1999, Accepted 7th February 2000

Graphite oxide, a pseudo-two-dimensional solid in bulk form, was synthesized from natural graphite powder by graphite oxidation with $KMnO_4$ in concentrated H_2SO_4. Poly(vinyl acetate) intercalated graphite oxide nanocomposite was prepared by an *in situ* intercalative polymerization reaction, in which an n-octanol–graphite oxide intercalation compound was first obtained, vinyl acetate monomer was then dispersed into the interlayer of the modified graphite oxide, followed by thermally polymerizing the monomer. It was experimentally shown that the *c*-axis spacing increased to 1.152 nm when poly(vinyl acetate) was intercalated into the interlayer space of the graphite oxide. Thermal analysis and FT-IR spectrometry were also used to characterize the nanocomposite. The extractability of the intercalated poly(vinyl acetate) and the electrical properties of the nanocomposite were evaluated.

Introduction

Recently, organic/inorganic nanocomposite materials have been receiving considerable research interest. In these nanocomposites the inorganic material can be a three-dimensional framework system such as zeolites,[1] two-dimensional layered materials, such as metal oxides,[2–4] metal dichalcogenides,[5,6] FeOCl,[7] layered double hydroxides,[8] and layered metal phosphate,[9,10] *etc*. 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 on the precise structure of the GO layers and a structural model,[11,12] some functional groups, such as hydroxyl, carbonyl and ether groups embedded in carbon sheets in GO lamella make graphite oxide hydrophilic, and also enable GO to exhibit a rich intercalation chemistry. It has been reported that some polar organic molecules and polymers, such as alcohols,[13] poly(ethylene oxide) (PEO),[13,14] poly(vinyl alcohol)(PVA),[15] poly(diallyldimethylammonium chloride) (PDDA)[16] and even poly(furfuryl alcohol) (PFA)[17] and others[18] can easily be inserted by different methods into its lamellae to form intercalated GO nanocomposites with different *c*-axis repeat distances. It was suggested that in these nanocomposites there were strong molecular forces between GO and polymers, such as hydrogen bonding and Coulomb forces, and that the existence of these polymers allows the physicochemical properties (electrical and thermal properties, *etc.*) of graphite oxide to be greatly changed.

In a previous paper[19] we reported the preparation of polyaniline(PAn)-intercalated GO by an exfoliation/absorption process through a stronger hydrogen bonding and a Coulomb interaction between GO and PAn due to the existence of the PAn emeraldine salt. The X-ray data of the intercalation compound suggested that GO layers were intercalated by monolayers and/or bilayers of PAn chains. Similar to the other PAn-intercalated inorganic materials,[2–10] the PAn–GO intercalation composite had also a higher electrical conductivity than that of pristine GO. However, while all polymers or their monomers mentioned above are water-soluble or hydrophilic, intercalation of GO with oil-soluble or hydrophobic polymers 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 lamella to obtain poly(vinyl acetate) intercalated GO nanocomposite (PVAc–GO), and the characterization of the nanocomposite is also presented.

Experimental

Natural graphite powder (30–50 μμm) was first treated by 5% HCl twice, then filtered, washed with water thoroughly, and dried at 110 °C for 24 h. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization before usage. Vinyl acetate was redistilled according to the usual method. All other reagents were of analytical grade used without further purification.

Preparation of poly(vinyl acetate)-intercalated graphite oxide

Graphite oxide was synthesized from natural graphite powder by graphite oxidation with $KMnO_4$ in concentrated H_2SO_4 according to Hummers method.[20] Graphite powder (10 g) was placed in 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 ± 3 °C for 30 min, distilled water (460 ml) was slowly added to cause an increase in temperature to 98 °C, and this temperature was held 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, washed successively with 5% HCl aqueous solution completely until sulfate could not be detected with $BaCl_2$, and dried under vacuum at 50 °C or in air.

The intercalation of poly(vinyl acetate) (PVAc) into the GO layers was performed in the following way. 5 g of air-dried GO were placed in 100 ml n-octanol in a closed vessel, and the mixture was kept stirring at ambient temperature. After 3 days the octanol–GO intercalation complex was isolated by centrifugation, and then dispersed in 100 g of the vinyl acetate monomer containing 0.5% (w/w) AIBN as initiator, with stirring for 24 h. After slight centrifugation and removing most of the supernatant vinyl acetate, the crude product containing

DOI: 10.1039/a908179h

monomer was subsequently heated to 50 °C under flowing N_2 for 24 h to cause polymerization according to a procedure similar to that used by Sugahara.[21] The as-prepared powder was stirred in n-hexane solution for 30 min to remove residual vinyl acetate, centrifuged and dried at 50 °C overnight.

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 hours at room temperature were mixed with a 20% (w/v) solution of n-dodecanol or n-octadecanol in benzene at 40 °C for 2–3 days with stirring. Filtration while hot and washing with warm benzene solution gave the modified GO which was dried at 50 °C for 1–2 hours. It was then dispersed in vinyl acetate solution containing AIBN, and the subsequent procedure was the same as with octanol modified GO.

Characterization of intercalation compounds

X-Ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX- diffractometer with a Cu-Kα/graphite monochromator. Data were collected at room temperature over the range $2 \leqslant 2\theta \leqslant 45°$ 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) was used to conduct the thermogravimetric (TG) and differential scan calorimetric (DSC) analysis respectively. Programmed heating at 5 °C min^{-1} and a dynamic air atmosphere were employed; the flow rate of air was 45 ml min^{-1}. The extent of the graphite oxidation was determined by an ISIS-300 elemental analyzer (Shimadzu Co.).

Results and discussion

The XRD pattern of vacuum-dried GO prepared here reveals a sharp reflection peak at $2\theta = 11.61°$, which corresponds to a *c*-axis spacing (I_C) of 7.62 Å; this suggests there exists intercalated water in the lamella of GO, because the GO interlayer distance depends strongly on the GO : H_2O ratio. No (002) diffraction peak from unreacted graphite is observable in the XRD pattern. The GO prepared had the following atomic composition (wt%): C, 47.24; H, 2.19. From these, 50.57% O could be estimated when other elements were neglected. The calculated ratio of C : O : H is 4 : 3.21 : 2.23.

Different from the cases of PEO, PVA, PDDA, PFA, and PAn,[13–17,19] the method of direct intercalation of polymers or their monomers is not adaptable to synthesizing PVAc intercalated GO, because the existence of polar groups in GO prevents GO from dispersing in oil-soluble vinyl acetate (VAc) monomer and its polymer. However, these polar groups enable GO easily to absorb polar molecules, such as alcohols[13] and n-alkylammonium[22] compounds, to form intercalation compounds with an increased *c*-axis distance (I_C). Such modified GO had a good adsorptivity to towards organic compounds.[22] In the present study, some longer-chain aliphatic alcohols (n-octanol, n-dodecanol or n-octadecanol) were chosen to modify GO.

Fig. 1 shows the X-ray diffraction patterns of the octanol–GO and the PVAc–GO intercalation compounds, together with that of pristine GO. Clearly, when octanol was inserted into the GO layers the I_C greatly increased to 24.84 Å from 7.62 Å for pristine GO (Fig. 1b). The driving force for the reaction between octanol and GO should be hydrogen-bond formation between the hydroxy (OH) groups of octanol and the polar groups on the internal layers of GO. However, this I_C value was much larger than that estimated for a pseudo-three-layered alkyl chain arrangement between the GO layers. Apparently, the octanol–GO is swollen by excess of octanol according to the absorbing/swelling theory of Dekany *et al.*[22] After the VAc monomer was dispersed a broad diffraction peak centered near 5° (2θ) was observed (Fig. 1c), and the I_C (17.74 Å) was smaller than that of the octanol–GO composite due to VAc replacing octanol used for swelling. 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 11.52 Å due to the monomer's polymerization within the lamellae of GO. This is similar to polymerization of aniline in the lamellae of α-M(HOPO$_3$)$_2$ (M = Zr or Ti)[10] and δ-MnO$_2$,[2] where I_C decreased when aniline was polymerized.

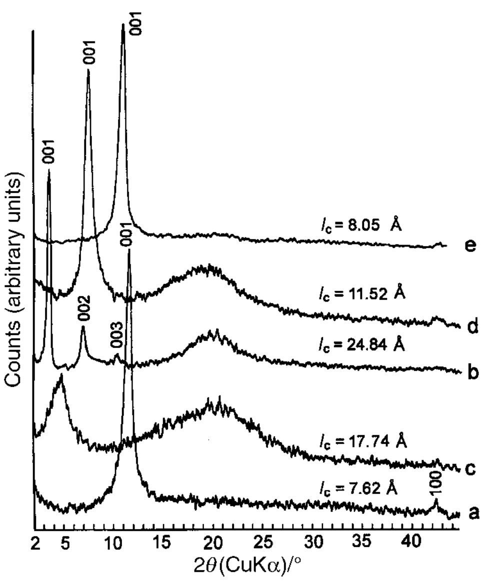

Fig. 1 X-Ray diffraction patterns of (a) GO and its composites, (b) GO–octanol, (c) GO–VAc, (d) PVAc intercalated GO and (e) GO–octanol after heating at 50 °C for 24 h.

To confirm the existence of PVAc in the lamellae of GO, PVAc–GO and n-octanol–GO composites were thermally treated at 50 °C for 24 h in air. It was shown that the latter was not thermally stable; its I_C decreased to 8.05 Å, very close to that of pristine GO, *i.e.* complete deintercalation occurred due to heating (Fig. 1e). However, no deintercalation occurred for the former compound.

Similarly, when n-dodecanol and n-octadecanol were used, similar results for PVAc–GO could be obtained (the I_C values of PVAc–GO were 11.25 and 11.44 Å respectively).

In FTIR spectra of the above intercalation composite, together with that of pristine GO, bands near 3400 and 1715, 1630, 1398, 1068 cm^{-1} are obtained, and wide and strong peaks at 1743, 1250, 1082 cm^{-1}, in addition to those at 2973, 2938, 1018, and a strong 1377 cm^{-1} peak were observed. This suggests the existence of intercalated water in pristine GO, especially the coexistence of PVAc with GO in the nanocomposite, and also that the (001) peak in Fig. 1d is due to the polymerization of VAc in the interlayers of GO.

Extraction experiments were done in order to evaluate the extractability of the intercalated PVAc. It was shown when PVAc–GO was extracted by benzene for 30 and 90 h a less than 10% reduction in weight of the composite after extraction was obtained. The weight reduction of the nanocomposite should be ascribed to the PVAc on the surface of GO being dissolved by the solvent. However, the interlayer PVAc had a higher stability against extraction by the solvent. This was confirmed by XRD and FT-IR analysis of the samples before and after extraction. The XRD patterns show that the crystalline structure of the nanocomposite has changed little except for a slight decrease of I_C values to 10.32 Å after extraction, very likely due to PVAc chains reorienting in GO lamellae. The FT-IR data of the extracted samples also show the existence of PVAc. Based on this, it is difficult to obtain detailed information on PVAc in the GO lamellae, such as molecular weight, polydispersity.

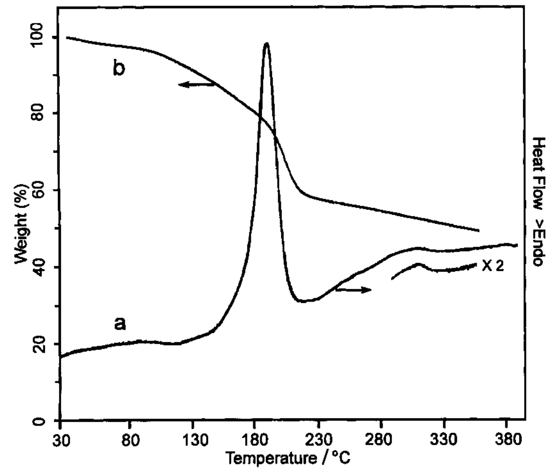

Fig. 2 DSC (a) and TGA (b) curves of PVAc intercalated GO.

Fig. 2 shows the TG and DSC curves of the PVAc–GO sample obtained under an air flow at 5 °C min^{-1}. In the DSC curve of the PVAc–GO nanocomposite two exothermic peaks were observed, as shown in Fig. 2a. Considering that GO was converted into carbon when heated to 180 °C[22] (also seen in Fig. 2b), the higher and larger peak at 193 °C seems to be caused by the destruction of the carbon skeleton of GO to some extent, and also the formation of some stable compounds, *i.e.* CO, CO_2, H_2O, and carbon, very likely accompanied by deintercalation of PVAc from the GO by breaking of the van der Waals or/and other forces between PVAc and GO. Concerning PVAc's decomposition at 300 °C,[23] the second broad and weak DSC peak at 311 °C in Fig. 2a could be ascribed to such decomposition. Clearly, the decomposition temperature of PVAc in PVAc–GO nanocomposite was 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 were formed from the GO's decomposition, then absorbed on PVAc surfaces, thus preventing decomposition of PVAc.

Finally, when the PVAc–GO was chemically reduced by hydrazine hydrate, good electrical conductivity (0.14 S cm^{-1} at ambient temperature detected by a four-probe method) was observed, similar to those of PDDA/GO[16] and PAn/GO[19] nanocomposites.

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 the vinyl acetate monomer in GO intercalated with long-chain aliphatic alcohols because the interaction between GO and alcohol makes GO more hydrophobic. XRD measurements indicate the I_C value of PVAc-intercalated GO increases from 7.62 of GO to 11.52 Å. FT-IR measurements indicate the coexistence of GO and PVAc in the polymer intercalated GO nanocomposite. Thermal analysis also shows that the intercalated PVAc decomposes at a somewhat higher temperature than pure that of PVAc due to protection by the GO matrix.

The intercalated nanocomposite has a higher stability against extraction by organic solvent due to a strong interaction between the GO layers and PVAc chains.

Finally, when the PVAc intercalated GO synthesized in this way was chemically reduced good electrical conductivity could be obtained. The structures and properties of reduced GO and its polymer composite will be studied in the future.

Acknowledgements

Financial support from the Key Project of the National Science Foundation of China (No. 59836230) is gratefully acknowledged.

References

1 P. Enzel and T. Bein, *J. Phys. Chem.*, 1989, **93**, 6270.
2 K. C. Gong and W. Zhang, *Abstract Fall Meeting of the Materials Research Society*, Boston, 1997, N3.9.
3 F. Leroux, B. E. Koene and L. F. Nazar, *J. Electrochem. Soc.*, 1996, **143**, L181.
4 T. A. Kerr, H. Wu and L. F. Nazar, *Chem. Mater.*, 1996, **8**, 2005.
5 M. G. Kanatzidis, R. Bissessur, D. C. DeGroot, J. L. Schindler and C. R. Kannewurf, *Chem. Mater.*, 1993, **5**, 595.
6 L. Wang, J. Schindler, J. A. Thomas, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1995, **7**, 1753.
7 C.-G. Wu, D. C. DeGroot, H. O. Marcy, J. L. Schindler, C. R. Kannewurf, T. Bakas, V. Papaefthymiou, W. Hiopo, J. P. Yesinowski, Y.-J. Liu and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1995, **117**, 9229.
8 T. Challier and R. C. T. Slade, *J. Mater. Chem.*, 1994, **4**, 367.
9 R. Backov, B. Bonnet, D. J. Jones and J. Roziere, *Chem. Mater.*, 1997, **9**, 1812.
10 Y.-J. Liu and M. G. Kanatzidis, *Chem. Mater.*, 1995, **7**, 1525.
11 T. Nakajima, A. Mabuchi and R. Hagiwara, *Carbon*, 1988, **26**, 357.
12 A. Lerf, H. He, M. Forster and J. Klinowski, *J. Phys. Chem. B*, 1998, **102**, 4477.
13 Y. Matsuo, K. Tahara and Y. Sugie, *Carbon*, 1997, **35**, 113.
14 Y. Matsuo, K. Tahara and Y. Sugie, *Carbon*, 1996, **34**, 672.
15 Y. Matsuo, K. Hatase and Y. Sugie, *Chem. Mater.*, 1998, **10**, 2266.
16 N. A. Kotov, I. Dekany and J. H. Fendler, *Adv. Mater.*, 1996, **8**, 637.
17 T. Kyotani, H. Moriyama and A. Tomita, *Carbon*, 1997, **35**, 1185.
18 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **3**, 771.
19 P. Liu and K. Gong, *Carbon*, 1999, **37**, 706.
20 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
21 Y. Sugahara, S. Satokawa, K. Kuroda and C. Kato, *Clay Clay Min.*, 1988, **36**, 343.
22 I. Dekany, R. Kruger-Grasser and A. Weiss, *Colloid Polym. Sci.*, 1998, **276**, 570, and references therein.
23 N. Sonobe, T. Kyotani and A. Tomita, *Carbon*, 1990, **28**, 483.

Paper a908179h