Novel Preparation of Electrically Conductive Poly(4,4′-oxybis(benzene)disulfide)/Graphite Exfoliated Nanocomposite*

XIAO Min[1], DU Xu-sheng[2], MENG Yue-zhong[1,3], TJONG Sie Chin[3]
(1. *School of Physics Science and Engineering, Sun Yat-sen Unversity, Guangzhou* 510275, *China*;
2. *Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou* 510650, *China*;
3. *Department of Physics & Materials Sciences, City University of Hong Kong, Kowloon, Hong Kong, China*)

Abstract: An exfoliated poly(4,4′-oxybis(benzene)disulfide)/graphite nanocomposite was prepared by using cyclo(4,4′-oxybis(benzene)disulfide) oligomers and hexadecyltrimethylammonium bromide exchanged graphite oxide. The nanocomposites were fabricated in two steps. First, the cyclo(4,4′-oxybis(benzene)disulfide) oligomer was used to swell and exfoliate organo-VMT to afford cyclo(4,4′-oxybis(benzene)disulfide)/graphite oxide nanocomposite precursor. Subsequently, the exfoliated POBDS/graphite nanocomposite can be made via in situ and instant melt ring opening polymerization of the precursor. The nano scale dispersion of graphite layers within the polymer was confirmed by both the X-ray diffraction patterns and TEM examinations. According to the conductivity test, the conductivity of the final poly(arylene disulfide)/graphite nanocomposite was increased by about 5 orders of magnitude compared with GO.

Key words: graphite oxide; nanocomposite; transmission electron microscopy
CLC number: TM242 **Document code**: A **Article ID**: 0529-6579(2003)S1-0047-03

In the past few years, much attention has been paid to polymer/layered silicate nanocomposites. Layered silicates usually exhibit very high aspect ratios (length-to-thickness). Once some silicate layers are individually dispersed in a polymer matrix, properties of the polymer matrix can be significantly improved, and some of them may not be shared with the conventional macro-composite counterparts.

Like layered silicates, graphite is also composed of layered carbon nano-sheets although the gallery (0.335 nm) between the carbon nano-sheets is much smaller than that (~1.0 nm) of layered silicates. Because of this structure, graphite is a good electrical conductor. Although certain atoms, molecules and ions can be intercalated into the galleries of the graphite, it is difficult for organic molecules and polymers to intercalate directly into it to form nanocomposites. Graphite oxide (GO) is an oxidation product of graphite. It also exhibits a layered structure, in which some functional groups such as hydroxyl, carbonyl and ether groups embedded in carbon sheets in GO lamellae. These functional groups make GO more hydrophilic, and therefore endow GO a rich intercalation chemistry. It have been reported that some polar organic molecules and polymers, such as alcohols[1], cationic surfactants[2], poly(ethylene oxide)[1,3], poly(vinyl alcohol)[4], poly(diallyldimethylammonium chloride)[5], poly(furfuryl alcohol)[6] and polyaniline[7-9] can be inserted into the GO lamellae by different methods to form intercalated GO nanocomposites with different *c*-axis repeat distances. Intercalation of hydrophobic polymer such as poly(vinyl acetate) into GO has also been achieved by in situ polymerization of the vinyl acetate monomer in GO intercalated with long-chain aliphatic alcohols that make GO more hydrophobic due to the interaction between GO and alcohol[10]. GO was also reported to restore graphene sheet structure when subjected to thermal treatment[11]. So it is possible to use polymer/GO intercalation nanocomposites as a precursor to prepare polymer/graphite nanocomposites.

More recently, a series of cyclic(arylene disulfide) oligomers have been synthesized in Hay's research group[12-15]. The typical structure can be depicted in Fig.1(a).

These cyclic oligomers exhibit low melt viscosity and can undergo ring-opening polymerization upon heating to form high-performance poly(arylene disulfide)s via a radical reaction mechanism. For instance, cyclic(4,4′-oxybis(benzene) disulfide) (Fig.1b) has a melting point

* Received 10 December 2002; Accepted 18 April 2003
Corresponding author: mengyz@yahoo.com(Meng Y Z)

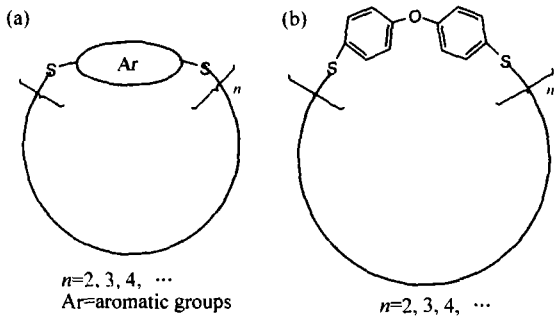

Fig. 1 Cyclic(arylene disulfide) oligomers

of about 110 ~ 115 ℃, and therefore, can carry out ring-opening polymerization at temperatures as low as 150 ℃. Combined with their high resistance to environmental degradation, good low temperature properties, low water-vapor transmission, excellent resistance to organic solvent, acid and bases, and good adhesion to metal, glass and concrete, these cyclic(arylene disulfide)s show potential practical applications as hot-melt adhesives used at high temperature, conductive adhesives, coatings and for high-performance matrices for polymeric composites.

The objective of the present work is to firstly synthesize cyclic(4,4′-oxybis(benzene) disulfide)/GO nanocomposite, and then thermally treat the nanocomposites to obtain poly(4,4′-oxybis(benzene) disulfide)/graphite nanocomposites with good electrical conductivity.

GO was synthesized from natural graphite powder by the method of Hummers and Offeman[16]. Cyclic(4,4′-oxybis(benzene) disulfide) was fabricated according to the previous work[15]. Because of the relative larger size for hydrophobic cyclic(4,4′-oxybis(benzene) disulfide), it is rather difficult for the cyclic oligomers to intercalate directly into the interlayer of hydrophilic GO with a *c*-axes repeat distance of only 0.7 ~ 0.8 nm. In this sense, hexadecyltrimethylammonium bromide (C-16 TMA) is employed to intercalate GO and to improve the hydrophobic property of GO. C-16 TMA-intercalated GO was prepared as follows: To 100 mL 0.05 mol/L NaOH was dissolved 0.5 g GO with sonicating stirring for 30 min. Subsequently, C-16 TMA 300 mg dissolved in 50 mL water was introduced into this solution while stirring, and then the dispersed GO polyanions were readily precipitated out from the solution. These precipitates were filtered off and washed with 1∶1 alcohol/water solution followed by drying at 333 K overnight.

To a 20 mL benzene solution containing 1.0 g cyclic (4,4′-oxybis(benzene) disulfide) oligomer, 0.2 g of C-16 TMA-intercalated GO was added. The resulting suspension was kept stirring in a sealed flask at ambient temperature for 48 hours followed by sonicating for 30 min. Thereafter, the flask was unsealed and benzene evaporated at room temperature, the residue was subsequently dried at 333 K overnight to obtain cyclic(4,4′-oxybis(benzene) disulfide)/GO compound.

In order to obtain poly(4,4′-oxybis(benzene) disulfide)/graphite nanocomposites with good electrical conductivity, cyclic(4,4′-oxybis(benzene) disulfide)/GO nanocomposite was then heated under N_2 at 200 ℃ to allow cyclic (4,4′-oxybis(benzene) disulfide) to undergo ring-opening polymerization to afford high molecular weight polymer, and at the same time to facilitate GO to in-situ restore graphite sheet structure. The increasing temperature profiles were 2℃/min from room temperature to 110 ℃, 0.25 ℃/min from 110 to 200 ℃.

Fig.2 shows the X-ray diffraction patterns (XRD) of the cyclic(4,4′-oxybis(benzene) disulfide)/GO nanocomposite together with that of C-16 TMA-GO intercalated compound and pristine GO. XRD analysis of the C-16 TMA-GO intercalated compound reveals a stacking height of 1.113 nm(Fig. 2b), an expansion of 0.0342 nm relative to the pristine GO This indicates the formation of (C-16 TMA)-intercalated GO nano structured compound and the orientation of alkyl chains is parallel to the layer of GO. Quaternary alklammonium-GO intercalated compounds have been reported to swell in organic solvents, and the swelling extent increase with decreasing the polarity of the solvent[17]. Similar to above behavior, the C-16 TMA-GO intercalated compound showed larger interlayer spacing when subjecting to stirred in benzene solution of cyclic(4,4′-oxybis(benzene) disulfide). In this process, benzene was absorbed into the interlayer spacing of C-16 TMA-GO, making an extended interlayer spacing. Furthermore, the GO layers can be exfoliated or delaminated with the aid of the ultrasonic force, resulting in the formation of cyclic (4,4′-oxybis(benzene) disulfide)/GO nano structured compound upon benzene evaporating. This is confirmed by the absence of XRD diffraction peaks shown in Fig.2(c).

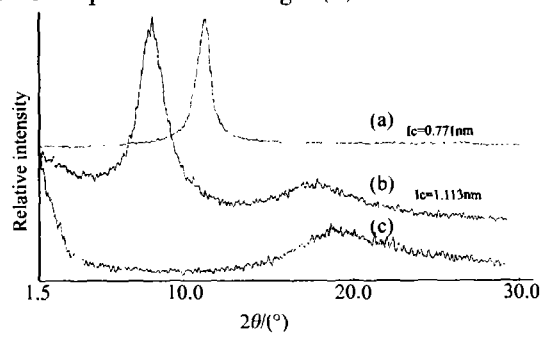

Fig.2 XRD patterns of (a) pristine GO, (b) C-16 TMA-GO intercalated compound, (c) cyclic(4,4′-oxybis(benzene) disulfide)/GO nanoc structured compound

The exfoliation of the GO layers within the polymer matrix was further confirmed by the obervation of TEM. Fig. 3 shows the TEM micrograph of poly(4,4′-oxybis (benzene) disulfide)/graphite nanocomposite. The dark lines in the picture correspond to the exfoliated graphite nanolayers. The graphite nanolayers individually dispersed in the polymer matrix with a thickness of less than 3 nm.

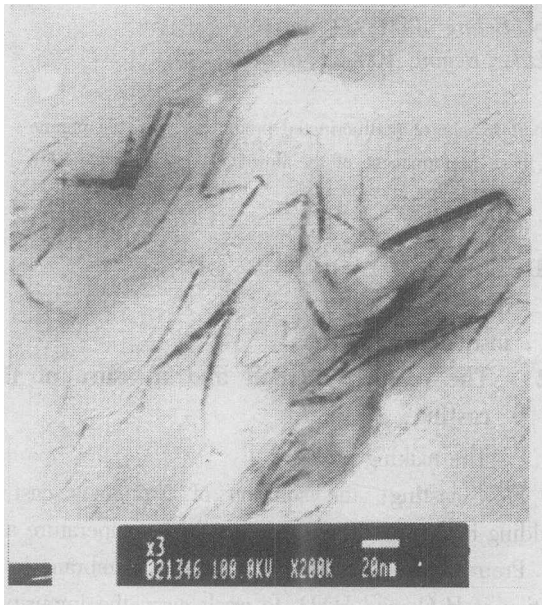

Fig. 3 TEM micrograph of poly(4,4′-oxybis(benzene) disulfide)/graphite nanocomposite

Pristine GO exhibits low electrical conductivity due to the cyclohexane-like zigzag array structure of its carbon sheets. In the heating treatment process, the cyclohexane-like zigzag array structure of GO changes into a planar graphene sheet structure that behaviors good electrical conductivity. Therefore, the resulting poly(4,4′-oxybis (benzene) disulfide)/graphite nanocomposite has a high conductivity of 1.1×10^{-2} S·cm^{-1} at ambient temperature measured by a four-probe method. The conductive graphite nanocomposite shows potential applications in fuel cell bipolar plates.

Acknowledgements: Financial support from the Natural Science Foundation of Guangzhou Province of China (Project Grant No. 000941; Key Project Grant No. 010525; Team Project Grant No. 015007) and the Guangdong Province Sci&Tech Bureau (Key Strategic Project Grant No. A1100402) is gratefully acknowledged.

References:

[1] Matsuo Y, Tahara K, Sugie Y. *Carbon*, 1997, 35:113.
[2] Matsuo Y, Niwa T, Sugie Y. *Carbon*, 1999, 37:897 - 901.
[3] Matsuo Y, Tahara K, Sugie Y. *Carbon*, 1996, 1996, 34:672.
[4] Matsuo Y, Hatasa K, Sugie Y. *Chem Mater*, 1998, 10:2266.
[5] Kotov N A, Dekany I, Fendler J H. *Adv Mater*, 1996, 8: 637.
[6] Kyotani T, Moriyama H, Tomita A. *Carbon*, 1997, 35:1185.
[7] Higashika S, Kimura K, Matsuo Y, et al. *Carbon*, 1999, 37: 354.
[8] Liu P, Gong K. *Carbon*, 1999, 37:706.
[9] Xiao P, Xiao M, Liu P, et al. *Carbon*, 2000, 38:626.
[10] Liu P, Xiao P, Gong K. *J Mater Chem*, 2000, 10:933.
[11] Matsuo Y, Sugie Y. *Carbon*, 1998, 36:301.
[12] Ding Y, Hay A S. *Macromolecules*, 1996, 29: 3090.
[13] Ding Y, Hay A S. *Macromolecules*, 1996, 29: 6386.
[14] Meng Y Z, Hay A S. *J Appl Polym Sci*, 1999, 74:3069 - 3077.
[15] Meng Y Z, Tjong S C, Hay A S. *Polymer*, 2001, 42: 5215.
[16] Hummers W S, Offeman R E. *J Am Chem Soc*, 1958, 80: 1339.
[17] Dékány I, Krüger-Grasser R. *Colloid & Polymer Science*, 1998, 276: 570.

新方法合成导电聚芳双硫醚/石墨剥离纳米复合材料

肖 敏[1], 杜续生[2], 孟跃中[1,3], 张世震[3]
(1. 中山大学理工学院, 广东 广州 510275;
2. 中国科学院广州化学研究所, 广东 广州 510650;
3. 香港城市大学物理与材料科学系, 香港)

摘 要: 利用季胺盐对氧化石墨进行有机化来改善氧化石墨层间的化学环境和扩大其层间距离。再将环状芳香双硫醚化合物插层到其层间。后经层间的环状芳香双硫醚化合物原位热开环聚合, 合成了石墨片层剥离分散于聚合物基体中的聚芳双硫醚/石墨纳米复合材料。XRD 及 TEM 均证明了无机片层在聚合物基体中呈剥离分散状态。电导率测试表明所合成的纳米复合材料的电导率较氧化石墨提高了近 5 个数量级。

关键词: 氧化石墨; 纳米复合材料; 透射电镜
中图分类号: TM242 **文献标识码**: A