Hierarchical composites of conductivity controllable polyaniline layers on the exfoliated graphite for dielectric application

Li Yu, Yihe Zhang, Wangshu Tong, Jiwu Shang, Fengzhu Lv, Paul K. Chu, Wenmin Guo

Abstract

Hierarchical composites of polyaniline fibers on the surface of exfoliated graphite were synthesized by chemical oxidation method. The conductivity of polyaniline fibers was controlled by doping and dedoping procedures. The morphology, structure and chemical character of doped and dedoped hierarchical composites were systematically investigated by SEM, TEM, XRD, FT-IR, XPS and conductivity measurement. After dedoping procedure, polyaniline/exfoliated graphite composites were used to improve dielectric property of the electroactive polymer poly(vinylidene fluoride). The dielectric constant and loss tangent of composites were 17 and 0.06 (10³ Hz) when the polyaniline/exfoliated graphite loading was 3 wt%. Of great interest was that the dielectric loss tangent of composites showed inherent low loss of poly(vinylidene fluoride) because insulating polyaniline fibers on the surface of exfoliated graphite effectively prevented direct contact of exfoliated graphite flakes in poly(vinylidene fluoride) matrix.

1. Introduction

Polymeric composites with high dielectric constant have been attracted great attentions in capacitors and charge-storage applications due to their high dielectric strength and good processability [1]. However, the dielectric constant of general polymer is so low that limits their practical applications. Thus, extensive efforts have been focused on increasing dielectric constant of polymer.

Several strategies are developed to improve dielectric constant of polymer based materials. One method is combination of polymer with high dielectric constant ceramic particles such as BaTiO₃ [2], Pb(Mg₁/₃ Nb₂/₃)O₃–PbTiO₃ [3] and CaCu₃Ti₄O₁₂ [4]. Dielectric constant of polymeric materials can be greatly increased at the high ceramic loading over 50 vol% accompanying decrease of dielectric strength and high dielectric loss [5]. In order to maintain high dielectric strength and low dielectric loss, modifications of high dielectric constant ceramic particle surface, particularly producing an insulating layer on the surface of ceramic particle [6], are taken into consideration. However, high ceramic loading needed for enhancement of dielectric constant still impairs the flexibility of polymeric composites.

Recently, another promising method to fabricate percolative composites by using conductive particles as filler has been developed [7]. Dielectric constant of polymeric materials can be dramatically enhanced when volume fraction of conductive filler reaches percolation threshold [8]. Commonly selected conductive fillers include metal particles (Ag and Ni) [9,10], carbonaceous materials (carbon nanotube (CNT), exfoliated graphite (EG)) [11,12] and conductive polymeric materials (polyaniline (PANI)) [13]. The important parameter percolation threshold of this system is usually lower than 25 vol% and strongly dependents on the shape of conductive filler [14]. In order to increase dielectric constant of polymeric materials at the low loading, high aspect ratio fillers are often selected [15]. Although insulating polymer filled with conductive filler exhibits very high dielectric constant at very low loading, polymeric composites synthesized by this method suffer from very high dielectric losses and low breakdown strength attributed to high conductivity of fillers [16]. He et al. reported high dielectric constant composite films with ultra-low percolation threshold of 1.01 vol%. Although dielectric constant reached 200 as volume fraction near percolation threshold, dielectric loss also jumped to high value of 0.45 [12]. In comparison with dielectric constant, little attention has been paid to dielectric loss. To over this limitation, very promising work that produces stable dielectric shell on the surface of conductive filler has been carried out to prepare polymeric composites with inherent low dielectric loss of base polymer. Shen et al. achieved high dielectric constant composites through incorporation of core/shell hybrid particles into the epoxy [17]. The dielectric loss is about 0.05 almost the same as that of polymer matrix. Kofod et al. reported high permittivity polymeric composites based on well-defined spatial distribution of...
2.1. Materials

EG was purchased from Jinhua Company, Shandong, China. PVDF (average Mw ~530,000) was purchased from SIGMA-ALDRICH, USA. Aniline (≥99% pure), perchloric acid (HClO₄, 70%), ammonia (NH₃·H₂O, 25%), ammonium persulfate ((NH₄)₂S₂O₈, ≥99% pure), N,N-dimethylacetamide (DMAC, ≥99% pure), methanol, and ethanol were received as analytical grade and purchased from Beijing Reagent Co. (Beijing, China).

2.2. Preparation of EG/PANI composites and pure PANI fibers

The preparation method was illustrated in Fig. 1. First, EG was treated by ultrasonic method in order to be better exfoliated and with high aspect ratio [19]. EG cannot form homogeneous mixture in 1 M HClO₄ by ultrasonic treatment due to its hydrophobicity. The addition of ethanol in HClO₄ can easily make EG to form homogeneous suspension in the 1 M HClO₄ by ultrasonic treatment due to its hydrophobicity. The mixture was stirring for 4 h to finish the dedoping procedure. After washing with deionized water and ethanol several times, products were dried at 80 °C for 24 h. After dedoping procedure, composites and pure PANI fibers were represented as PANID-EG5, PANID-EG3, PANID-EG1 and PANID.

2.3. Dedoping procedure of composites and pure PANI fibers

Obtained composites and pure PANI fibers were adding into 1 M NH₃·H₂O. The mixture was stirring for 4 h to finish the dedoping procedure. After washing with deionized water and ethanol several times, products were dried at 80 °C for 24 h. After dedoping procedure, composites and pure PANI fibers were represented as PANID-EG5, PANID-EG3, PANID-EG1 and PANID.

2.4. Preparation of the PANID-EG1/PVDF composite

Aiming at investigating relationship between structure of composites and dielectric property, PANID-EG1/PVDF composites were synthesized by solution casting. Typical procedures were as follows: (i) fillers were firstly dispersed in DMAC by ultrasonic treatment and fiercely stirred with PVDF; and (ii) organic solution was removed to form composite films by solution casting on glasses.

2.5. Characterization

The morphology of sample was examined by scanning electron microscope (SEM, JSE-6301F, JEOL), atomic force microscope (Digital Instruments Dimension 3100 AFM) and transmission electron microscope (TEM, JEM-2010, JEOL). Chemical character and structure of samples were characterized by Fourier Transform Infrared Spectroscopy (FT-IR, 16 PC, Perkin Elmer), powder X-ray diffraction (XRD, BRUKER D8 ADVANCE, by Cu Kα radiation, 2θ range taken from 3° to 70°) measurement and ESCALAB 250 X-ray Photoelectron Spectroscopy (XPS)/ESCA equipment (XPS results were fitting by XPSpeak software). Thermogravimetric analysis (TGA) was used to investigate thermal stability of samples. Samples with about 4 mg were heated from room temperature to 800 °C at rate of 8 °C/min on a NETSCH STA449C thermogravimetric analyzer in nitrogen atmosphere. For electrical conductivity test, samples were pressed flake. The electrical conductivity test of EG, PANI, PANID-EG1, PANIN-EG3 and PANIN-EG5 was conducted by a four probe conductivity meter RST-5. Because electrical conductivities of PANID and PANID-EG1 were so low that were out of RST-5 measuring range. Electrical conductivities of PANID, PANID-EG1 were tested by megohmmeter ZC36. For dielectric measurements, top and bottom electrodes were made by coating silver paint on both sides of samples. The frequency dependence of the dielectric constant were measured under a frequency response analyzer (Novocontrol Alpha-analyzer) over a broad frequency range (10⁸ Hz–1 MHz).

3. Results and discussion

3.1. Morphology and structure

Fig. 2 showed morphology of EG flakes and pure PANI fiber. To achieve high aspect ratio, EG was treated by ultrasonic method.
As shown in Fig. 2a and b, EG had a lamellar structure of diameter 5–20 μm. The density of EG, 0.8 g/cm³, was lower than that of polymer which can maintain lightweight of polymeric composites reinforced by EG. Fig. 2c and d depicted morphology of pure PANI synthesized by chemical oxidation method using HClO₄ as dopant. Pure PANI was uniform nanofibers in shape with a diameter of about 50 nm and length of about 1 μm.

From Fig. 3, it cannot clarify thickness, layer number of graphene sheets in EG after ultrasonic treatment. More detailed information concerned about EG can be obtained from AFM analysis. In Fig. 3, it can be seen that diameter of EG thickness was around 5 μm in accordance with Fig. 2a and b. Thickness of EG was about 20 nm containing approximately 57 layers graphene sheets. Thus, EG with large aspect ratio can be gained by ultrasonic treatment.

Hierarchical composites of PANI fibers on surface of EG were synthesized by in situ polymerization. In Fig. 4a and b, composites with regular lamellar structure the same as pure EG can be obviously seen. In higher magnification, in Fig. 4d and e, uniform PANI fibers were produced on surface of EG flakes. In Fig. 4c and f, composites exhibited irregular morphology including lamellar structure and PANI agglomeration. The distinction of morphology was due to different concentration of aniline monomer. As concentration of aniline monomer was low, aniline monomer was almost adsorbed on surface of EG flakes and polymerization of PANI only occurred on surface of EG flakes. As concentration of aniline monomer was high, self-nucleation of PANI was unavoidable between EG flakes [20]. TEM confirmed morphology of EG and composites. In Fig. 4i, it can be seen that EG flakes were almost transparent whereas composites were obscure indicating PANI fibers covered on surface of EG flakes. For dielectric application, hierarchical composite was treated by ammonia. Morphology of subsequent composite was not influenced by ammonia treatment (see in Fig. 4g and h).

The structure of EG, PANI, PANID and composites were investigated by XRD. XRD patterns of EG, PANI, PANID, PANI-EG1, PANID-EG1, PANI-EG3 and EG PANID-EG5 were shown in Fig. 5. A sharp diffraction peak centered at 2θ = 26.6° accompanied by other low intensity peaks with their positions around 44.3°, 54.5° and 77.4° can be seen in XRD pattern of EG. It indicated graphic structure of EG. Although ultrasonic treatment can make EG nano-graphite sheets, EG cannot fully be exfoliated by ultrasonic treatment. PANI exhibited three typical broad diffraction peaks at 2θ = 9.6°, 19° and 25.1° indicating some crystalline order in PANI [22]. The PANID only exhibited a broad diffraction peak at 2θ = 19° demonstrating the conversion of PANI from partial crystal to amorphous by dedoping procedure [23]. Compared to PANI-EG1, peak at 2θ = 25.1° of PANID-EG1 almost disappeared attributed to dedoping procedure. For composites, peak centered at 2θ = 26.6° of EG overlapped with peak at 2θ = 25.1° corresponding to periodicity perpendicular to PANI chain [21]. Moreover, peak at 2θ = 44.3° of EG cannot be seen in composites indicating EG flakes were completely covered by PANI fibers [24].

3.2. Chemical characters

Fig. 6 showed FTIR spectra of EG, PANI, PANID and composites. A broad peak centered at 3690 cm⁻¹ in EG assigned to O–H stretching vibration. PANI exhibited four main peaks at 1137, 1298, 1495, and 1576 cm⁻¹ attributed to stretching vibration C=N, stretching vibration of C=N secondary aromatic amine, stretching vibration of C=C in benzenoid ring and stretching vibration of C=C in quinoid ring [21]. In PANID spectra, four main peaks of PANI exhibited. However, peak corresponding to stretching vibration C=N shifted from 1137 to 1166 cm⁻¹ due to lower extent of electron delocalization in PANID [25]. The shift conformed dedoping procedure for PANID that was in agreement with XRD result. In comparison with PANI-EG1, PANID-EG1 showed the same shift of peak corresponding to stretching vibration C=N. For composites, typical peaks of PANI were included. Moreover, some differences between composites and PANI were observed. The peak centered
Fig. 3. Typical tapping mode AFM images of EG. (For interpretation to colours in this figure, the reader is referred to the web version of this paper.)

Fig. 4. Low-magnification SEM images of (a) PANI-EG1, (b) PANI-EG3, (c) PANI-EG5, and (g) PANI-EG1 and high-magnification SEM images of (d) PANI-EG1, (e) PANI-EG3, (f) PANI-EG5, and (h) PANID-EG1; TEM image of (i) PANI-EG1 and inset exhibited TEM image of the EG.

Fig. 5. XRD patterns of samples: (a) PANID, (b) PANI, (c) PANI-EG5, (d) PANI-EG3, (e) PANID-EG1, and (f) PANI-EG1 and inset exhibited the XRD pattern of the EG. (For interpretation to colours in this figure, the reader is referred to the web version of this paper.)

Fig. 6. FTIR of samples: (a) EG, (b) PANI-EG5, (c) PANI-EG3, (d) PANID-EG1 (e) PANI-EG1, (f) PANID (g) PANI. (For interpretation to colours in this figure, the reader is referred to the web version of this paper.)
at 832 cm⁻¹ assigned to out-of-plane bending vibration of C–H in aromatic ring. It became weaken in composites because PANI chains were anchored by EG plane attributed to π–π interaction between graphite lamellar structure and PANI backbone [21].

More information about chemical character of EG, PANI and composites were obtained through XPS. The C1s XPS spectrum of EG with peak-fitting curves was presented in Fig. 7a. Peaks centered at 284.5, 285.8 and 290.0 eV were assigned to C=C, C=O and O=C=O [26]. Compared to C=C, intensity of other two peaks was weak suggesting that few functional groups were on surface of EG. In Fig. 7b, N1s XPS spectrum of PANI doped by HClO₄ showed that it displayed three different electronic states: benzenoid amine with binding energy (BE) at 399.7 eV, quinoid amine with BE at 398.5 eV and nitrogen cationic radical (N⁺) with BE > 400.0 eV [27]. Doping level usually represented by [N⁺]/[N] ratio is a primary factor that controls electrical conductivity of PANI [27]. The doping level of PANI doped by HClO₄ was around 0.48 the same as the report [21]. For composite PANI-EG1, one more peak centered at 408.9 eV was observed in Fig. 7c. It caused by N1s shake-up satellite of ionized nitrogen in PANI chains [28]. The doping level of PANI-EG1 was 0.43 smaller than that of PANI. In comparison with PANI-EG1, N1s XPS spectrum of PANID-EG1 showed that intensity of peak at 398.5 eV corresponding to quinoid amine dramatically increased and intensity of peak with BE > 400.0 eV corresponding to nitrogen cationic radical apparently decreased indicating dedoping procedure almost completed (Fig. 7d) in agreement with XRD and FTIR results.

Functional groups on graphene sheets and π–π stacking force between phenyl and basal planes of EG play a core role for the link between EG and PANI [20]. In this paper, EG has few functional groups demonstrated by FT-IR and XPS results. Thus, π–π stacking force between phenyl and basal planes of EG is beneficial for PANI growth on the surface of EG.

### 3.3. Electrical conductivity

EG, PANI, PANID and composites were pressed into pellets for electrical conductivity measurement. Table 1 showed electrical conductivity of all samples. It can be seen that EG exhibited highest electrical conductivity of 11.5 S/cm. The electrical conductivity of PANI was 7 × 10⁻³ S/cm showed semiconductor behavior in agreement with the doping level of 0.5 [21]. Moreover, electrical conductivity of PANI rapidly decreased to 3.51 × 10⁻¹³ S/cm confirming complete dedoping procedure. For composites PANI-EG5, PANI-EG3 and PANI-EG1, electrical conductivity of composites raised with the increasing concentration of EG. It can be simply explained by higher electrical conductivity of EG than semiconductive PANI [29]. Additionally, it was notable that electrical conductivity of PANID-EG1 fast decreased to 6.02 × 10⁻¹³ S/cm that was much lower than that of PANI-EG1 4.2 S/cm and similar to that of PANIN 3.51 × 10⁻¹³ S/cm. As many researchers reported that

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (S/cm)</th>
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<tbody>
<tr>
<td>EG</td>
<td>11.5</td>
</tr>
<tr>
<td>PANI</td>
<td>7 × 10⁻³</td>
</tr>
<tr>
<td>PANID</td>
<td>3.51 × 10⁻¹³</td>
</tr>
<tr>
<td>PANI-EG1</td>
<td>6.02 × 10⁻¹³</td>
</tr>
<tr>
<td>PANI-EG3</td>
<td>0.68</td>
</tr>
<tr>
<td>PANI-EG5</td>
<td>0.185</td>
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*Measured by four probe conductivity meter RST-5.*

*Measured by the megohmmeter ZC36.*

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**Fig. 6.** FTIR of samples: (a) EG, (b) PANI-EG5, (c) PANI-EG3, (d) PANID-EG1, (e) PANI-EG1, (f) PANID, (g) PANI. (For interpretation to colours in this figure, the reader is referred to the web version of this paper.)
electrical conductivity of composites based on EG/PANI fast increased to high values (>0.01 S/cm) by adding small content of EG (<8 wt%) in which PANI was insulator. The ultra-low electrical conductivity of PAEN50 can be explained by two reasons. Firstly, PANI in PANID-EG1 was almost dedoped by ammonia proved by XPS. Secondly, PANID-EG1 possessed “core–shell” structure that EG flakes completely were covered by insulative PANI (see in Fig. 3g and h). It was very different from composites reinforced by EG that electrical conductivity of composites fast jumped to high values at low loading due to formation of conductive path [30]. The conductive path cannot form in PANID-EG1 due to insulative PANI layer on the surface of EG that resulted in ultra-low electrical conductivity.

3.4. Thermal property

The composition and structure of EG, PANI and composites were further investigated by TGA. As shown in Fig. 8, EG exhibited no mass loss over measured temperature demonstrating it possessed few oxygen-containing groups [31]. Pure PANI showed obviously three weight loss stages corresponding to deintercalation of water around 100 °C, elimination of dopant from 100 °C to 215 °C and decomposition of PANI over 215 °C [29]. Composites displayed the same TGA feature as PANI but they showed better thermal stability than PANI. They showed little mass loss over 250 °C that was much higher than processing temperature of many polymer matrices indicating their wide applicability.

3.5. Dielectric application

The frequency dependence of room temperature dielectric constant, dielectric loss tangent and ac conductivity for PANID-EG1/PVDF composites was shown in the Fig. 9. In Fig. 9a, it can be observed that dielectric constant of composites enhanced with increasing PANID-EG1 content over measured frequency. The dielectric constant was 17 for composites with PANID-EG1 3 wt% and 9 for pure PVDF at 10^3 Hz. Of great interest was that dielectric loss tangent of composites with PANID-EG1 3 wt% was 0.06 and 0.2 with 3 wt%.
showed inherent low loss of polymer matrix (see in Fig. 9b). These features were inconsistent with dielectric loss tangent result reported in literature in which dielectric loss tangent of polymer composite dramatically increased with EG loading [12]. The low dielectric loss tangent was attributed to insulating PANI layers on the surface of EG that prevented direct contact of EG flakes within polymer matrix [32]. From Fig. 9c, ac conductivity of composites slightly increased with increasing PANID-EG1 content and was only 6.6 x 10^{-10} S/cm as PANID-EG1 content was 3 wt%. Moreover, ac conductivity of composites increased linearly with increasing frequency over the whole frequency. The ac conductivity of composites was evaluated by “Universal law” which was used to describe conductive behavior of disordered materials [33].

\[ \sigma(\omega) = \sigma_0 + A\omega^s \]  
(1)

where \( \sigma_0 \) was DC conductivity of composites, \( \omega \) the angular frequency and \( u \) the critical component. The best fitting result was shown in the Fig. 9d. The \( \sigma_0 \) were 8.4 x 10^{-13} and 8.5 x 10^{-10} S/cm for pure PVDF and composites with PANID-EG1 loading 3 wt%. For both of them, critical component \( u \) was 1.32. The fitting result apparently confirmed that composites were inherent insulating.

4. Conclusion

In conclusion, hierarchical composites of conductivity controllable PANI fibers on the surface of EG were successful synthesized by simple chemical oxidation. SEM, TEM and conductivity measurement results confirmed that EG flakes were completely covered by PANI fibers. XRD, FTIR and XPS investigations showed that doping and dedoping procedures of hierarchical composites were the same as those of pure PANI fibers. The dielectric analysis of composites based on hierarchical composites with insulating PANI layer and PVDF revealed that hierarchical composites can be used to enhance the dielectric constant of the polymer as well as maintain inherent low loss of the polymer matrix.

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References