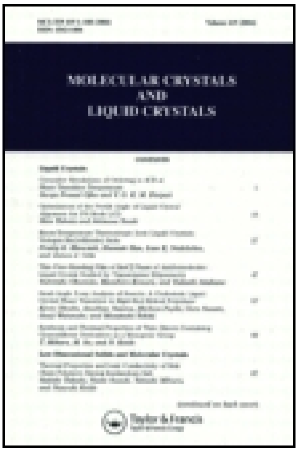

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Synthesis and Characterization of Graphene Oxide/Poly (2-ethyl-2-oxazoline) Composites

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Graphene oxide/poly (2-ethyl-2-oxazoline) (GO/PEOX) nanocomposites were fabricated via solution mixing technique. The chemical structure and morphology of the nanocomposites were investigated using FTIR, XRD, TGA, FESEM, EDX and HRTEM. Microscopic and XRD measurements demonstrated that the GO nanosheets were uniformly dispersed in the PEOX matrix. FTIR spectra revealed that the PEOX was non-covalently grafted to the GO surfaces. Furthermore, the incorporation of GO greatly improved the thermal stability of PEOX possibly due to the high aspect ratio and uniform dispersion of GO nanosheets in the PEOX matrix.

Keywords Graphene oxide; non-covalent functionalization; poly (2-ethyl-2-oxazoline); solution mixing technique

Introduction

Graphene, characterized by anatomically thin two-dimensional lattice of sp^2 atoms, has emerged in recent years as a novel class of carbon nanomaterials [1–3]. Its excellent electronic [4] and mechanical properties [5], unusual thermal conductivity [6], and large specific surface area [7] have made it promising for various applications. So far, graphene has been verified useful in variety of fundamental research and technological areas, such as electronics, sensors, electromechanics, solar cells, memory devices and hydrogen storage [8–10]. One of the most promising applications of this material is polymer matrix composites in which nanoscale filler materials are incorporated [11,12]. However, since graphene sheets are intrinsically stacked in graphite due to the high van der Waals forces of attraction between adjacent layers, the exfoliation and incorporation of it into polymer matrix to synthesize single-layer graphene reinforced polymer which has been considered as the best utilization of the excellent in-plane properties of graphene is rather difficult.

Among various strategies, which we have developed to address this obstacle, the most reliable and reproducible approach for preparing graphene based polymer composites was the employment of graphene oxide (GO) as a precursor [13–15]. In contrast to pristine graphene, there are plenty of oxygen-containing groups on the GO surface [16,17]. These

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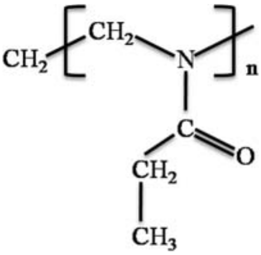
functional groups not only allow the good dispersion of GO in water, but also facilitate the interaction between the host polymer and GO via covalent or non-covalent bonds [18]. By taking the advantages of GO, several GO–water-soluble polymer composites with noticeably improved property have been obtained by simple mixing procedure in water [19–21]. However, further complex chemical modification of GO with different molecules or polymers is often required for preparation of water-insoluble polymer composites [22–24], since GO cannot be readily exfoliated in most organic solvents. The surface-modification process usually suffers from limited scalability, time-consuming and environmental problems. Therefore, it is highly desirable to find an easy approach for the exfoliation of GO to simplify the fabrication procedure of graphene–polymer composites.

Herein, we report the fabrication of GO/PEOX composites via solution mixing technique. The microstructure and morphology of the nanocomposites were characterized using FTIR, XRD, TGA, FESEM, EDX and HRTEM .



Scheme 1. PEOX.

Experimental

Materials

Graphite powder and poly (2-ethyl-2-oxazoline) ($M_n = 50,000$) were obtained from Sigma Aldrich (Korea). Conc. sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrazine monohydrate (85%) and hydrogen peroxide (H_2O_2) were purchased from Junsei (Japan) and used as received.

Preparation of Graphene Oxide

The GO was prepared from natural graphite using Hummers and Offeman [25]. About 1 g of graphite powder was added to 23 mL of cooled (0°C) concentrated H_2SO_4. About 3 g of $KMnO_4$ was added to the mixture gradually with stirring, so that the temperature of the mixture was maintained below 20°C. The mixture was then stirred at 35°C for 30 min. 46 mL of distilled water was slowly added and the temperature was increased to 98°C and the mixture was maintained at that temperature for 15 min. The reaction was terminated by adding 140 mL of distilled water followed by 10 ml of a 30% H_2O_2 aqueous solution. The solid product was separated by centrifugation, washed repeatedly with a 5% HCl aqueous solution, then washed 3–4 times with acetone and dried in an air oven at 65°C overnight.

Preparation of GO/PEOX Composites

The procedures for preparing GO/PEOX composites are described as follows. GO (0.1 g) was dissolved in 20 mL of water and treated with ultrasound for 15 min at room temperature to yield a clear dispersion. PEOX (1 g) was dissolved in distilled water (10 mL) at 98°C for

1 h. The GO aqueous dispersion was gradually dropped into the PEOX solution, and stirred at 98°C for 30 min. No precipitate was observed in a few hours after magnetic stirring, it indicates that no GO aggregate was formed. The homogeneous GO/PEOX solution was filtered and washed repeatedly with water. The obtained product was then dried under vacuum at 60°C for 24 h.

Characterization

FT-IR spectroscopy is used to obtain the information about the interactions between GO and PEOX. FTIR spectra were measured on a Perkin-Elmer FT-IR spectrometer in the range 4000–400 cm^{-1} using KBr pellet method. Thermogravimetric analysis (TGA) was performed in nitrogen atmosphere at a heating rate of 10°C min^{-1} using a Perkin Elmer Pyris 1 TGA. XRD is an important tool for determining whether graphene-based sheets are indeed present as individual graphene sheets in the nanocomposites. The diffraction patterns were studied using a Rigaku diffractometer with CuKa ($\lambda = 0.15418$ nm) radiation at a generator voltage of 40 kV and a generator current of 40 mA. Field emission scanning electron microscopy (FESEM) images were obtained by using a JOEL 200 scanning electron microscope (Japan) with an accelerating voltage of 20 kV. High resolution transmission electron microscopy (HRTEM) analysis was taken with a JEOL-200EX (Japan) microscope.

Results and Discussion

The successful functionalization of GO with PEOX was confirmed using the FTIR spectroscopy. Fig. 1 shows the FTIR spectra of GO, GO/PEOX composites and neat PEOX. The GO spectrum showed a broad and intense peak centered at 3386 cm^{-1} and a peak at 1732 cm^{-1}, corresponding to the −OH groups and the carbonyl (C=O) stretching, respectively. The peaks at 1400, 1224 and 1057 cm^{-1} were assigned to the O–H deformation, epoxy (C–O–C) and the carboxyl (C–OH) groups, respectively. The strong band at 1600 cm^{-1} was associated with the remaining sp^2 character of graphite [26]. In the spectrum of PEOX (Fig. 1C), the sharp peaks at 1680 and 1110 cm^{-1} were assigned to the stretching of C=N and C–O groups, respectively. The characteristic band at 980 cm^{-1} could be attributed to the skeletal vibration of the pendant 2-oxazoline rings. The weak shoulders

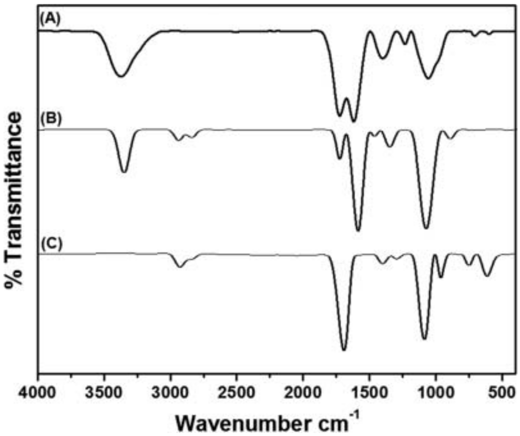


Figure 1. FTIR spectra of (A) GO (B) GO/PEOX composites (C) PEOX.

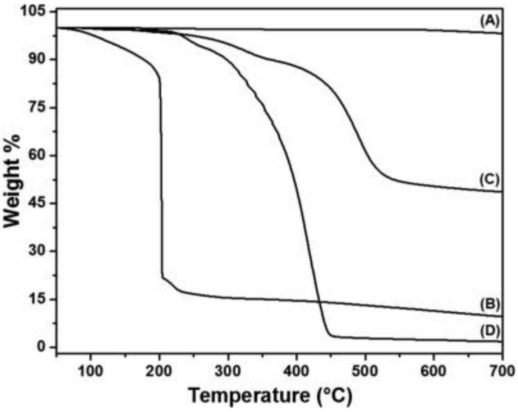


Figure 2. TGA of (A) pristine graphite (B) GO (C) GO/PEOX composites (D) PEOX.

at 2855 and 2962 cm^{-1} were associated with the symmetric and asymmetric vibrations of CH_2 [27]. The FTIR spectrum of GO/PEOX nanocomposites showed the characteristic peaks of PEOX chains at 1700 and 1110 cm^{-1}, corresponding to the C=N, C–O stretching vibration oxazoline ring. In addition to that, the nanocomposites exhibited a strong band at 1600 cm^{-1} was associated with the sp^2 character of carbon skeleton, indicating the presence of graphene structure in the composites.

The weight loss curves for the pristine graphite, GO, GO/PEOX composites and neat PEOX are presented in Fig. 2. The pristine graphite showed a weight loss at 650°C due to combustion to carbon dioxide. On the contrary, the GO powders exhibited two steps of mass loss at 200 and 550°C, which are attributed to the removal of oxygen-containing groups and carbon oxidation, respectively. For neat PEOX, the first major weight loss occurred at 250°C and the second at 350°C. However, the nanocomposites showed a similar decomposition profile to that of neat PEOX. The GO/PEOX composites showed a major weight loss between 280 and 350°C, associated with the decomposition of PEOX chains grafted on the GO surfaces. The TGA results revealed that the GO/PEOX composite showed superior thermal stability than GO and neat PEOX.

Figure 3 shows the XRD patterns of pristine graphite, GO, GO/PEOX and the neat PEOX. Pristine graphite exhibits a sharp peak (0 0 2) at 26.46° with an interlayer spacing

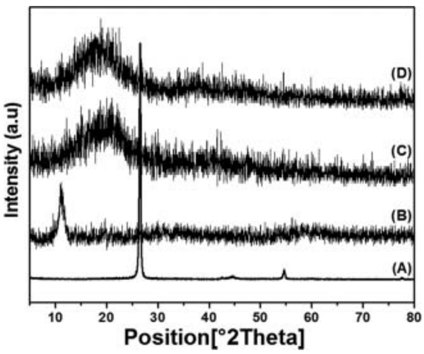


Figure 3. XRD patterns of (A) pristine graphite (B) GO (C) GO/PEOX composites (D) PEOX.

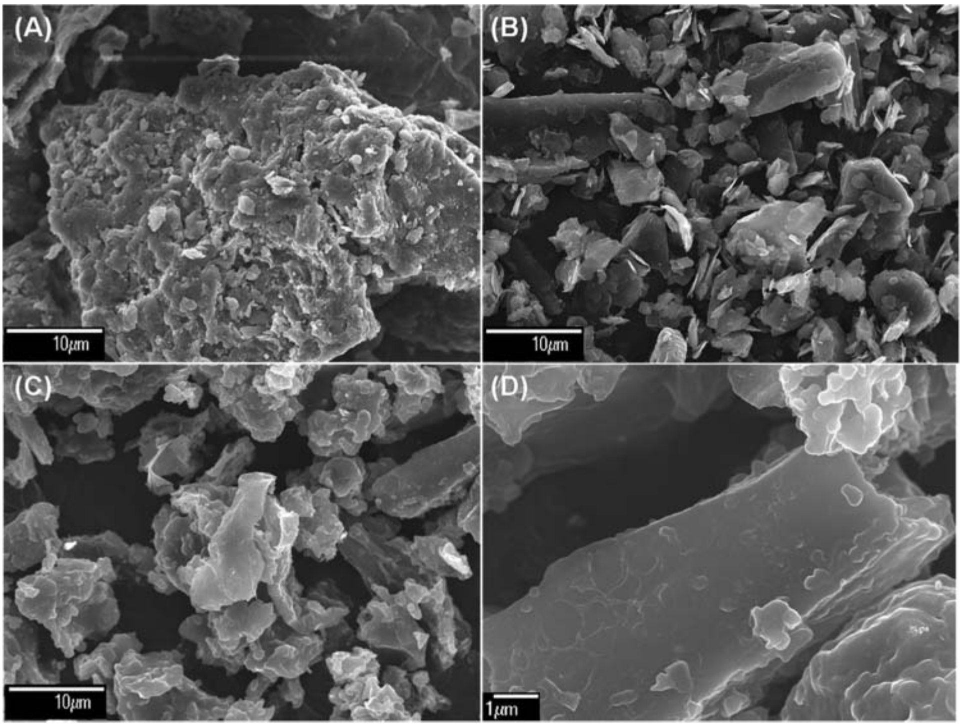


Figure 4. FE-SEM images of (A) pristine graphite (B) GO (C) & (D) GO/PEOX composites under high magnifications.

of 0.337 nm. The pattern of GO reveals an intense, sharp peak centered at $2\theta = 12.1°$, corresponding to the (001) interplanar spacing of 0.73 nm. After oxidation, the characteristic XRD peak of neat GO sheets appears at $2\theta = 10.5°$. The neat PEOX did not show any clear peaks in XRD, indicating its amorphous structure. However, the XRD pattern of the GO/PEOX composites was nearly same as the neat PEOX, implying that GO sheets were well exfoliated in the PEOX matrix and the amorphous structure of PEOX was not affected by the incorporation of GO.

The microstructure of GO/PEOX composites was characterized by FESEM. Fig. 4 shows the FESEM images of pristine graphite, GO, GO/PEOX composites. The SEM image of the GO/PEOX (Fig. 4c) composites revealed the typical crumpled and wrinkled graphene sheet structure. It could be observed (Fig. 4b) that the GO nanosheets were

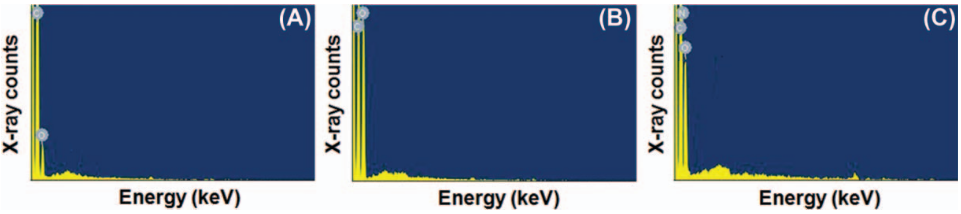


Figure 5. EDX spectra of (A) pristine graphite (B) GO (C) GO/PEOX composites.

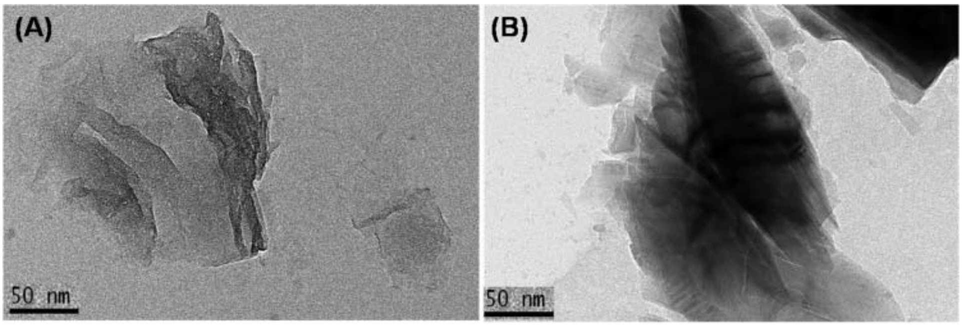


Figure 6. HR-TEM images of (A) GO (B) GO/PEOX composites.

homogeneously dispersed in PEOX matrix and there were almost no large agglomerates. The good dispersion of GO sheets should be due to the good interaction between the oxygen and hydroxyl functional groups on the surface of GO and the PEOX matrix.

The EDX spectra of the pristine graphite, GO and its nanocomposites are shown in Fig. 5. The EDX characterization revealed that the pristine graphite were partially oxidized and contained hydroxyl, carboxyl, and carbonyl groups. After modification with PEOX, the peak representing nitrogen atoms was observed, indicating successful functionalization of GO nanosheets with PEOX matrix.

Figure 6 shows the TEM images of GO nanosheets and its nanocomposites. It is evident that GO nanosheets showed a curled and paper-like structure. However, after incorporation with PEOX, the TEM image of the GO/PEOX confirmed that the GO nanosheets were dispersed homogeneously in the PEOX matrix. The good dispersion of graphene sheets should be due to the good interfacial interaction between the modified graphene and polymer matrix. However, the TEM image also showed the presence of a few layers of graphene in the composite.

Conclusions

An exfoliated PEOX grafted GO composites were prepared via the solution mixing technique. The formation of GO/PEOX composites was confirmed by FTIR, XRD, TGA, FESEM, EDX and HRTEM analyses. FTIR spectra showed that the PEOX was noncovalently grafted to the GO surface. Morphological analysis indicated that the GO nanosheets exhibited a uniform dispersion in the PEOX matrix. The thermal stability of the GO/PEOX nanocomposites was increased compared with neat PEOX. The improvement in thermal stability of the nanocomposites can be ascribed mainly to the homogeneous dispersion and alignment of GO nanosheets in the PEOX matrix. Therefore, this method provides an easy and effective way to prepare graphene-based polymer composites.

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