Enhanced Physical Properties of PEO /GRAPHENE Composites

Lei Hua

Department of Materials science and Engineering, Tong Ji Zhejiang College, Jia Xing, 314051
hualei@tjzj.edu.cn; Fud No :LGF21E030001

Abstract. PEO/graphene composites were prepared by a simple and green method in presence of graphite oxide (GO) reduced by Vitamin C (VC) in aqueous. The resultant PEO/RG-VC composites exhibited excellent thermal and outstanding mechanical properties. When loading about 7 wt.% RG-VC graphene sheets, the Youngs modulus of PEO/RG-VC 7 was improved as two times as that of the neat PEO. However, the crystallization behaviour of the composites could not be improved as expected.

1. Introduction

Graphene, the basal plane of graphite, is an atomically thick, two-dimensional (2-D) sheet composed of sp2 carbon atoms arranged in a honeycomb structure and aroused much interest for the unique electrical conductivity, [1] outstanding thermal, [2] and mechanical [3] properties. Because of the extraordinary properties of graphene, it could be looked as great potential nanofillers for improving mechanical, electrical, and thermal properties of polymers. The resultant nanocomposites utilizing graphene as nanofillers are offering opportunities to enhance the physical and mechanical properties to the polymers at the lower loading [4]. However, the preparation of polymer/ graphene is a challenging research work because graphene produced from mechanical cleavage method is lack of the functionalized and modification surface. Vitamin C (VC) is an ideal substitute for hydrazine in reduction of GO. [5] It is noted that the reduction and deoxygenation of GO by VC could be prepared not only in water but also in common organic solvents such as N, N-dimethylformamide (DMF) or N-methyl-apyrrolidone(NMP). It becomes feasible to incorporate graphene sheets into polymer matrix by simply blending them in solution.

Poly(ethylene oxide) (PEO) is a water soluble polymer. It could be always applied as a kind of capsule for medicinal powders or granules for lack of toxicity. [6] Hence, PEO is considered as a suitable medical material for biomedical and biotechnological applications. In recent years, PEO has been wildly developed in the polymer-based nanocomposite area. For instance, Song et al. reported that the mechanical properties could be improved as double-C60-end-capped PEO composites [7]. Chatterjee et al. prepared PEO/ carbon nanotube composites through blending PEO with modified carbon nanotube. Although the mechanical and electrical properties of PEO/ organic fillers composites could be enhanced in these approaches, these methods are toxicity and hazardous [8]. Thus, the applications of PEO would be unfeasible in the biomedical field.

In this study, PEO/graphene composites were prepared by a green and simple method. The extraordinary mechanical properties and thermal properties of PEO/ graphene composites could be rendered with addition of lower content graphene sheets.
2. Experimental and Characterization

2.1. Materials
Graphite (Lot: M4P3193) and the potassium permanganate (Lot: M5E9617) were purchased from Nacalai Tesque, Inc and used as received. Sulfuric acid (>96 %), nitric acid, hydrogen peroxide, were purchased from Kanto Chemical Co. Inc. and used also as received. VC and PEO (average Mv=300,000) was purchased from Sigma-Aldrich Co. Inc

2.2. Preparation of PEO/RG-VC Composites
PEO was used as polymeric matrix to prepare PEO/RG-VC nanocomposite using a solution blending method. In brief, an aqueous GO dispersion was prepared firstly. An exfoliated GO dispersion in water was achieved by strongly sonicating for 30 min. After sonication, PEO was mixed within GO suspension stirring for 60 min at 80°C in oil bath. The presence of small amount of PEO in solution during the reduction step might assist to depressing agglomeration degree of the graphene sheets. The reduction was started by addition of VC and then stirred mechanically for 24 h at 80°C. The obtained graphene dispersion was washed with water before addition of PEO. The solid of PEO/RG-VC composite was obtained through mechanically stirring at 80°C for one day to evaporate water. The resultant nanocomposites at varying compositions of RG-VC are summarized in Table 1. The resultant nanocomposites at varying compositions of RG-VC are summarized in Table 1.

| Sample Code | GO g | PEO g | RG-VC % |
|-------------|------|-------|---------|
| PEO/RG-VC 0.5 | 0.01 | 2     | 0.5     |
| PEO/RG-VC 1   | 0.02 | 2     | 1       |
| PEO/RG-VC 3   | 0.06 | 2     | 3       |
| PEO/RG-VC 5   | 0.1  | 2     | 5       |
| PEO/RG-VC 7   | 0.14 | 2     | 7       |

2.3. Characterization
Wide-angle X ray Diffraction (WAXD) patterns of the sample films were recorded in an angle range of 0~40° at scanning speed of 2°/min on a RU-200 X-ray diffractometer (Rigaku) at 40 KV and 200 mA at room temperature. Nickel-filtered Cu Kα X-ray radiation (λ=0.15418 nm) was used as source. The process of nonisothermal crystallization was monitored by using a Pyris Diamond Differential Scanning Calorimetry (DSC) (Perkin-Elmer) equipped with a Perkin-Elmer intracooler 2P cooling accessory. Tensile properties were investigated with the EZ test machine (Shimadzu) at a cross head speed of 5 mm/min. All film samples have a gauge length of 22.5 mm, a width of 4.76 mm, and a thickness of about 0.3 mm. Each value of mechanical properties reported here was an average of more than six specimens.

3. Results and Discussion

3.1. WAXD Analysis
Fig. 1(a) shows WAXD patterns of graphite, GO, and RG-VC graphene sheets. According to Fig. 1(a), the diffraction peak of graphite appears at 2θ = 26.45°, which is corresponding to the interlayer spacing of the natural graphite was about 3.35 Å.\textsuperscript{[9]} The interlayer distance was markedly expended to 2θ = 11.25° after oxidation to form the layered structure of GO. The larger interlayer space was due to the existence of oxygen-rich groups on both sides of sheets and a large number of water molecules trapped into between the layers.\textsuperscript{[10]} However, after reduction by VC, the peak appearing at 2θ = 11.25° of GO completely disappears, a broad and small bump appearing around 24~26° became visible relative to native graphite. This demonstrates that a large amount of RG-VC graphene sheets shows an exfoliated structure after chemical reduction. However, small amount of RG-VC graphene sheets
forms a little coagulation, which might be caused by reconstructed and interbedded structure of graphene sheets.

WAXD patterns of neat PEO and its blends with different weight loading RG-VC graphene are also shown in Fig. 1(b). The diffraction peaks of the composites correspond to the characteristic crystalline peaks of PEO. Based on the analysis of Fig. 1(a), a broad and small bump appearing around 24–26 °corresponding to a little agglomerates of graphene nanosheets could not be observed in the composites regardless of graphene content, which might indicate that the graphene sheets exfoliate in PEO matrix.

3.2. DSC Analysis
As the graphite are reported as a nucleating agent on the crystallization for polymer crystallization,[11] The crystallization behavior of dispersed RG-VC sheets on PEO matrix are studied shown in Fig. 2. Melting enthalpy of PEO ($\Delta H_m$) from the first heating curves and the sequence crystallization temperature ($T_c$) of PEO from the cooling curves are summarized and shown in Fig. 2. It is observed that with addition about 0.5 wt. % RG-VC sheets, the $T_c$ shows a little improvement as compared with neat PEO. However, with further increasing the weight content of RG-VC graphene, the crystallization of PEO could not be improved. On the other hand, $\Delta H_m$ of all the samples also behaves the similar phenomenon as that of $T_c$. The initial increased in the $T_c$ and $\Delta H_m$ might be attributing to the fact that graphene sheets acted as nucleating centres and favored crystallization by providing a relatively higher nucleation density. The depressed $T_c$ and $\Delta H_m$ observed with further addition of graphene sheets might be relative to that, as the excessive graphene sheets of RG-VC limited the segmental mobility of PEO resulting in inhibiting the growing crystalline lamella to spread in size and particular direction. Although RG-VC graphene sheets could accelerate the formation of crystal nucleus with the lower graphene loading at about 0.5 wt.%, the crystallinity of PEO decreases as RG-VC graphene sheets increase.

![Fig. 1. WAXD spectra of (a) graphite, GO and RG-VC. (b) PEO/RG-VC composites with different graphene loading 0.5, 1, 3, 5, 7 wt.%.

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3.3. Mechanical Properties

Incorporation of RG-VC graphene sheets into PEO matrix affords outstanding improvement of mechanical properties of the composites. The effect of RG-VC graphene sheets on the mechanical properties of PEO in the composites has been studied by tensile tests and summarized in Fig. 3. The relationship between elongation at break and RG-VC sheets content are shown in Fig. 3 (a). With increasing the weight content of RG-VC graphene sheets into PEO matrix, obvious decrease of elongation at break could be observed. About 450±80% of the neat PEO was depressed to 100±20% of PEO/RG-VC 7. This decrease might be due to the aggregated and less efficiently dispersed graphene sheets in PEO matrix.

However, the remarkable improvement of yield stress and young's modulus of the composites could be observed with increasing the weight loading of graphene sheets in Fig. 3(b) and (c). The yield stress of PEO is about 8.1 MPa. With further increasing content of graphene sheets in PEO matrix, the yield stress of the composites is increased gradually. When loading about 7 wt. % graphene sheets, the yield stress of PEO/RG-VC 7 is increased to 15.07 MPa. On the other hand, the Young’s modulus of neat PEO is also significantly increased from 334 MPa of pure PEO to 731 MPa of the PEO/RG-VC 7. Namely, loading 7 wt.% RG-VC graphene sheets, Young's modulus of PEO/RG-VC 7 is improved remarkably as two times as that of neat PEO. The reason for the significant enhancement of mechanical properties (yield stress and Young’s modulus) with composites should be due to the graphene sheets with higher aspect ratio and higher mechanical properties. Furthermore, the improvement was attributed to the presence of immobilized or partially mobilized polymer phase as a consequence of interaction of polymer chain with the graphene sheets. However, the outstanding enhancement of the mechanical properties of the composites cannot be relative to the degree of crystallinity of PEO because the crystallinity of PEO in the composites could not be increased with increasing the graphene sheets in the composites.
Fig. 3. Stress-strain curves of PEO and PEO/RG-VC composites. (a) Elongation at break, (b) Tensile yield stress and (c) Young’s modulus of PEO/RG-VC composites as a function of RG-VC graphene weight fraction.
4. Conclusions
In this study, PEO/RG-VC composites were prepared by simple and green method. The resultant PEO/graphene composites exhibited the outstanding mechanical and thermal properties. When loading about 7 wt.% RG-VC graphene sheets, Young's modulus of PEO/RG-VC 7 was improved as two times as that of the neat PEO. However, the crystallization behavior of PEO/RG-VC composites showed a little improvement at loading 0.5 wt.% RG-VC graphene sheets. With further increasing the weight content of RG-VC graphene, the crystallization of PEO could not be improved. In view of the improved thermal, mechanical properties of PEO/graphene composites fabricated by this green method, such PEO/RG-VC composites might widen the applications in the biomedical and biotechnological fields.

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