Effect of graphene nanoplatelet addition on the electrical conductivity of poly(hydroxybutyrate-co-hydroxyvalerate) biocomposites

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Abstract. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) is one of the most promising biodegradable polymers used in many applications due to its biodegradability and non-toxicity. However, the usage of PHBV in electronic, biomedical, and biosensor applications has been limited due to its poor electrical properties. This study shows a simple method of producing and enhancing the electrical conductivity of PHBV-based biocomposites by adding graphene nanoplatelet (GNP) as a conductive filler. The biocomposite films were prepared using the solvent casting method, consist of five GNP loading (0-5 wt. %). The prepared PHBV/GNP biocomposites show enhanced electrical conductivity compared to neat PHBV. PHBV/GNP biocomposite with 5 wt. % filler loading exhibits the highest electrical conductivity at 3.83 × 10^{-3} S/cm. Higher crystalline regions in the PHBV/GNP biocomposites have facilitated the transfer of electrons between PHBV, resulting in the formation of conductive biocomposites, as evident from X-ray diffraction (XRD) characterization.

1 Introduction

The development of polymer composites with enhanced electrical conductivity is currently in the surge in academic and industrial communities due to their great potential in electronic, biomedical, and biosensor applications. Conductive polymer composites have advantages over metal conductors. They can be easily processed when mixed with thermoplastics using low-cost techniques; they are lightweight and corrosion-resistant [1]. However, polymer composites that are made from petroleum-based polymer are less environmentally friendly.

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) is one of the biopolymers that can potentially replace existing conventional polymers due to its exceptional properties such as

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biocompatibility, biodegradability and high strength. However, it also has few drawbacks that have restricted PHBV application in broader areas, such as brittleness, low impact resistance, and poor electrical properties [2].

As a novel carbon particle, graphene has attracted tremendous attention for its potential in modifying polymers with multifunctional properties [3,4]. Graphene nanoplatelets (GNPs) are two-dimensional disk-shaped particles with high electrical conductivity (1460 Scm⁻¹) and good compatibility with most polymers, making them an excellent conductive filler [5]. The use of GNPs as conductive fillers in polymer composites has been extensively studied [6-8]. Ravindran et al. [9] developed epoxy/graphene nanoplatelets nanocomposites with significantly improved electrical conductivity and excellent dielectric properties. For instance, by adding 10 wt % of 25 μm GNP, the electrical conductivity was increased to 2.80 × 10⁻⁴ S/cm. To date, no articles have reported the electrical conductivity properties of GNP-based PHBV biocomposites. In this study, GNP was investigated as a conductive filler in PHBV biopolymer. The PHBV/GNP biocomposites were then characterized for their electrical conductivity properties, crystalline and chemical structures.

2 Materials and Method

2.1 Materials

PHBV powder (ENMAT Y1000) as the polymer matrix was supplied by Tianan Biologic Materials Co., LTD. GNP (25 μm particle size) was provided by Sigma Aldrich. Polyethylene glycol (PEG) and chloroform were supplied by Merck KGaA and HmbG Chemicals, respectively.

2.2 Preparation of PHBV/GNP biocomposites

PHBV/GNP biocomposites were prepared via the solvent casting method. First, PHBV powder was dissolved in chloroform solution (5 wt./v) for 1 hour at 55 °C. 4 droplets of PEG solution were added to the mixture and stirred for about 3 minutes. The PHBV solution was filled with GNP filler (0, 1, 2, 3, 4, 5) wt.%. The formulation for the PHBV/GNP biocomposites is shown in Table 1. The solution mixture was then further agitated for 30 minutes to ensure complete filler dispersion throughout the matrix. The polymer biocomposite solution was then poured into a glass casting plate. The casting plate was left at room temperature for 24 hours to allow the solvent to evaporate completely.
Table 1. PHBV/GNP biocomposites formulation

| Sample     | PHBV (wt. %) | GNP (wt. %) |
|------------|--------------|-------------|
| PHBV       | 100          | 0           |
| PHBV/GNP1  | 99           | 1           |
| PHBV/GNP2  | 98           | 2           |
| PHBV/GNP3  | 97           | 3           |
| PHBV/GNP4  | 96           | 4           |
| PHBV/GNP5  | 95           | 5           |

2.3 Characterization and testing

2.3.1 Electrical Conductivity

The electrical conductivity of the PHBV/GNP biocomposites was measured using two I-V probe measurement systems (Model: Keithley Model 4200 Semiconductor Characterization System). The samples were cut to the desired size (15 × 20 × 1 mm). A series of range voltage values (from 0 to 10 V) with step size 1 V was used to measure the electrical conductivity of the samples [11]. Equation (1) shows the formulation for the resistance of the samples, while Equation (2) shows the formulation for the conductivity of the samples.

\[
\rho = \frac{R \cdot w \cdot t}{l} \tag{1}
\]

\[
\sigma = \frac{1}{\rho} \tag{2}
\]

Where, \(\rho\) represents the resistivity of the samples; \(R\) stands for resistance; \(w\) is the width of the sample; \(l\) is the length of the sample; \(t\) represents the thickness of the samples and the \(\sigma\) stands for the electrical conductivity of the samples.

2.3.2 X-Ray Diffraction

XRD (Shimadzu XRD-6000 Analyzer) was used to characterize the crystalline structure of PHBV/GNP biocomposites. A voltage of 35 kV and 25 mA with CuKα (\(\lambda = 1.5406\) nm) radiation source, in the scale of 10-60 (2θ) were used.
2.3.3 *Fourier Transform Infrared (FTIR) Analysis*

FTIR spectrometer (Perkin-Elmer Spectrum 400 Series) was used to characterize the chemical structure of PHBV/GNP biocomposites. The spectrum resolution and scanning range used were 4 cm\(^{-1}\) and 650-4000 cm\(^{-1}\), respectively.

3 Results and Discussion

3.1 Electrical conductivity

Based on Fig. 1, the electrical conductivity of PHBV/GNP biocomposites increased when the graphene nanoplatelet filler loading increases. It can be seen that the addition of GNP below 2 wt.% scarcely shows any effect on the electrical conductivity of the PHBV/GNP biocomposites. However, the addition of 2 wt.% GNP loading has tremendously increased the electrical conductivity of the biocomposite by several orders of magnitude. The PHBV/GNP biocomposite prepared with the highest loading of GNP (5 wt.%), gives the highest electrical conductivity with 3.83×10\(^{-3}\) S/cm. Meanwhile, neat PHBV, an insulator material, possesses the lowest electrical conductivity with 4.36×10\(^{-12}\) S/cm.

This increasing trend of electrical conductivity with the increment of GNP loading had shown that as more GNP conductive nanofiller particles incorporated into PHBV matrix, the flow movement of electrons in the PHBV/GNP biocomposite is enhanced by the formation conductive path, resulting in electrical conductivity intensifying in the PHBV/GNP biocomposites. The electrical conductivity improvement of the biocomposites was attributed to the formation of a continuous conductive network, which allows efficient electron transfer through the matrix, increasing conductivity [10]. For example, Khamlich uses solvent-assisted dispersion method during the production of polypyrrole/graphene nanosheet biocomposite, and they achieved a low percolation threshold at only 0.1 vol.% filler content [11]. Generally, the variation in the electrical conductivity of polymer biocomposites as a function of the conductive filler content displays an S-shaped curve for the transition from insulating to the conductive system [12]. Therefore, it is evident in this study the PHBV/GNP biocomposites exhibited a typical transition curve.

![Fig. 1. Electrical conductivity of PHBV/GNP biocomposites with different GNP loading](image)
3.2 XRD Characterization

As shown in Fig. 2, neat PHBV showed an intense diffraction peak at 22.87° corresponding to the (111) crystalline plane, and small peaks at 13.32° and 16.98°, which were assigned to the reflections of the (020) and (110) crystalline planes. XRD pattern for Fig. 2 (b) and Figure 4.2 (c) biocomposites also showed similar diffraction peaks at 13.32°, 16.98° and 22.87°, respectively. These peaks are in agreement with the previously observed PHBV structure [13].

![XRD Pattern](image)

Fig. 2. XRD pattern of the (a) neat PHBV, (b) PHBV/GNP 2 wt. % biocomposite, (c) PHBV/GNP 5 wt. % biocomposite.

Increased intensity of the peak corresponding to (111) crystal plane was observed in the PHBV/GNP biocomposites, notably in PHBV/GNP 5 biocomposites (Figure 4.1 (c)), suggesting an increased crystallinity in the biocomposite samples. The emergence of a new peak was observed at 22.87° in the biocomposites’ XRD patterns, indicating a new crystalline phase (002) that originated from GNP filler. This sharper defined crystalline structure observed in the biocomposites suggest an overall increase in the crystallinity of the PHBV/GNP biocomposites upon the incorporation of GNP filler in the PHBV matrix. As previously reported [14], the efficiency of electron transfers in an insulating polymer, such as PHBV, depends on the polymer chains’ orientation. Ordered packing of crystalline regions will facilitate the transfer of electrons more favourably than disordered amorphous regions. Higher electrical conductivity of the PHBV/GNP biocomposites is expected because the crystalline order at the PHBV/GNP interface will reduce contact resistance and result in less electron scattering. A similar observation was observed by Sullivan et al., who prepared exfoliated graphite nanoplatelet/polylactic acid biocomposite films and reported an enhancement of electrical conductivity by three orders of magnitude when the crystallinity increased by 40% [15].

3.3 FTIR Analysis

Fig. 3 illustrates the FTIR spectra of neat PHBV and PHBV/GNP biocomposites at 2 wt. % and 5wt. % GNP loading. Four prominent peaks are observed in the neat PHBV sample. Neat PHBV (Fig. 3 (a)) shows a broad peak at 3290 cm⁻¹, corresponding to the O-H stretching vibration [15]. The sharp peak at 1720 cm⁻¹ is linked to the presence of C=O stretching
vibration of the PHBV matrix [16], whereas C-O asymmetrical stretching bands were observed at 1272 cm\(^{-1}\) and 1058 cm\(^{-1}\), respectively.

As shown for PHBV/GNP biocomposites samples in Fig. 3 (b) and Fig. 3 (c), the adsorption peaks at 1720 cm\(^{-1}\) which corresponds to C=O vibration, and at 1272 cm\(^{-1}\) and 1058 cm\(^{-1}\), which correspond to the C-O asymmetrical stretching vibrations, are present in both neat PHBV and PHBV/GNP biocomposite samples. It can be observed that upon the addition of GNP (Fig. 3 (b) and Fig. 3 (c)), the O-H stretching vibration shifted slightly from 3290 cm\(^{-1}\) to 3400 cm\(^{-1}\), corresponding to the occurrence of a strong O-H group originated from the GNP filler [16]. Nevertheless, no additional significant changes were observed in the PHBV/GNP biocomposite samples, indicating that the incorporation of GNP does not induce any chemical interaction with the polymer matrix [17]. Hence, it is postulated that only physical interaction occurs between the PHBV matrix and GNP filler in this study.

4 Conclusion

PHBV/GNP biocomposites were successfully prepared via solvent casting with 0-5 wt. % of GNPs. With the increase of GNP filler loading, the electrical conductivity of PHBV/GNP biocomposites increased significantly up to 3.83 × 10\(^{-3}\) S/cm (5 wt. % GNP). X-ray diffraction results showed that GNPs had a significant effect on the crystalline structure of PHBV, hence aided the transfer of electrons between PHBV, resulting in the formation of conductive biocomposites. Based on the FTIR spectra, no significant changes were observed upon the addition of GNPs, suggesting only physical interaction occurred between the GNPs and the PHBV matrix.
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