Piezoelectric β-polymorph enhancement in graphene oxide - PLA nanocomposite films

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Abstract: The flexible piezoelectric nanocomposite films have attracted considerable interest for use in autonomous nanosystems, sensors and portable electronics. The effect of graphene oxide (GO) nanoparticles on the crystal structure, unique crystallization, mechanical behavior and significant improvement in piezoelectricity of polylactic acid (PLA) has been reported. Polylactic acid/graphene oxide (PLA/GO) nanocomposite films were prepared by the solvent casting technique using different percentages of GO. The different samples were characterized by Polarized optical microscope (POM), Fourier transformed infrared (FTIR) and X-ray diffraction analysis. The presence of β phase in nanocomposites and the enhancement of their piezoelectric properties were confirmed by FTIR and XRD analysis. These electroactive and biodegradable polymer nanocomposite thin films may be a potential candidate for the piezoelectric nanogenerators, energy storage devices and energy harvesting applications.

Keywords: PLA; Graphene oxide; piezoelectric properties; β-phase

1. Introduction
The use of mechanical energy wasted as a useful source of energy was honored. In the recent years, several studies have focused on the themes of harvesting energy [1-6]. There is a growing demand for the recovery of the mechanical energy west from our daily life for autonomous sensors and implantable energy devices [7, 8]. The electroactive polymers are one of the most important materials that have received considerable attention as electronic systems, thermal and mechanical detectors and sensors [9].

The piezoelectric nanocomposite films have attracted a growing amount of interest that its energy can be valuable for sensing and energy harvesting application.

In this paper, different amounts of graphene oxide nanosheet (GO) were added into the polylactic acid (PLA) matrix in order to enhance the crystalline β-phase and to improve the piezoelectric properties of the PLA/GO nanocomposite. The nanosheets of graphene oxide (GO) can also be used as a nucleating agent for the PVDF to produce high-performance nanocomposite. GO is a single layer of graphite oxide (GO) obtained by a process of oxidation/exfoliation natural graphite [10]. GO are essentially graphene sheets on which oxygen-containing functional groups are thought to be present in the form of carboxyl, hydroxyl and epoxy groups [11-13].
The graphene oxide was prepared by the Hummers method and the nanocomposite films were made by the solvent casting-evaporation technique. The characterization of graphene oxide are observed by Fourier transform infrared and X-ray diffraction studies, and the nanocomposite films were characterized by polarized optical microscope (POM), Fourier transform infrared and X-ray diffraction analysis, to confirm the enhancement of piezoelectric crystalline $\beta$-phase and barrier properties of the nanocomposite to can be valuable for energy harvesting application.

2. Experimental section:

2.1. Materials
The PLA (pellets) used has a density of $\rho = 1.78 \text{ g/cm}^3$, $\text{Mn} = 130,000 \text{ g/mol}$ and $\text{Mw} = 400,000 \text{ g/mol}$, was obtained from Sigma Aldrich. Tetrahydrofuran (THF) is used as the organic polar solvent often used to dissolve PLA. It has a density of $0.949 \text{ g/cm}^3$ at 20 °C and boiling temperature of 163 to 165 °C, was obtained from LabChem.

2.2. Graphene oxide synthesis
The synthesis of graphene oxide was made by the method of Hummers change. This method of synthesis involves both oxidation and exfoliation of graphite sheets due to the heat treatment of the solution.

An amount of 2 g of graphite powder with 2 g of sodium nitrate ($\text{NaNO}_3$) dissolved in 90 ml of $\text{H}_2\text{SO}_4$ (98%) and maintained under an ice bath (0-5 °C) with continuous stirring. After 4 hours of stirring, 12 g of potassium permanganate ($\text{KMnO}_4$) was added to the suspension very slowly. The rate of addition is carefully controlled to keep the reaction temperature below 15 °C. The solution was diluted with a large amount of distilled water and kept stirring for 2 hours. The ice bath was then removed, and the mixture was stirred at 35 °C for 2 hours. The mixture is maintained in a reflux system at 98 °C for 10-15 min. After 10 min, the temperature was changed to 30 °C which gives the solution a brown color. Again after 10 min, the temperature was lowered to 25 °C and held for 2 hours. The solution is finally treated with 40 ml of $\text{H}_2\text{O}_2$ to reduce the residual permanganate to soluble manganese ions until the gas evolution ceases, giving a yellow color. 200 ml of water was added to the prepared solution and stirred for 1 hour. It is then maintained without agitation for 3-4 hours. The latter was washed several times with HCl (10 %) and then with deionized water several times until neutralization (neutral pH). After centrifugation, the gel-like substance was dried under vacuum at 60 °C overnight to obtain graphene oxide (Figure 1).

![Figure 1. Photograph of graphene oxide nanosheets](image)

2.3. PLA/GO based nanocomposite synthesis
The nanocomposite PLA / GO films were developed by the solution-mixing technique (Figure 2).

1 g of PLA was dissolved in 20 ml of THF using the mechanical stirring at 71 °C for 2 hours, as soon as a dissolution of the known GO masses (0.1, 0.3, 0.5, 0.8, 1 and 2 wt.%) in 5 ml of THF by ultrasonication. Then the solution of the sonified nanosheet is added in order to prepare a premixed PLA-GO-THF which the mixture is brought to ultrasonication for 5 min followed by stirring for 1 hour. Then the PLA-GO solution is left to dry in the oven at 66 °C for 15 min to form a nanocomposite film.
3. Results and discussions

3.1. Structural analysis of graphene oxide:

Graphite was used as the starting material in the process of preparing graphene oxide. Graphene oxide powder was examined by XRD and the result obtained was compared with that of natural graphite (Figure 3 (a)). The X-ray spectrum of graphite powder shows the hexagonal structure by the single peak at $2\theta = 26.23^\circ$ according to the orientation (200), which corresponds to a spacing of ~ 0.34 nm between the graphite planes [14]. In the graphene oxide spectrum, we observe the disappearance of this structure which confirms the formation of graphene oxide.

The infrared analysis (FTIR) revealed that the mixture of potassium permanganate, sulfuric acid and sodium nitrate, used during the chemical oxidation of graphite, results in the formation of groups of epoxide, carboxyl, carbonyl and also of hydroxide [15]. The FTIR spectra obtained for graphite and graphene oxide are shown in (Figure 3 (b)). The existence of several transmission bands confirms the presence of a variety of oxygen groups on the surfaces and edges of each plane of graphene oxide. The bands at 3410 and 1410 cm$^{-1}$ are attributed to the O-H hydroxyl groups. The band at 1720 cm$^{-1}$ is attributed to the elongation vibration of the carbonyl group (= O), the band at 1612 cm$^{-1}$ is attributed to the bond C = C, and the vibrations at 1036 cm$^{-1}$ are attributed to epoxy group (> O). In addition, several vibration bands of the C-H bond can be observed around 2000-3340 cm$^{-1}$ [16], which confirms the formation of graphene oxide.

Figure 2. PLA/GO based nanocomposite preparation steps.
3.2. PLA/GO based nanocomposite

3.2.1. Polarized optical microscope

Figure 4 presents POM images showing the state of dispersion of the GO nanoparticles in terms of different quantities of nanoparticles (0.1 and 1% by weight) within the PLA matrix. The neat PLA matrix shows a porous surface. It can generally be seen in the POM images that the GO layers have been dispersed homogeneously in the matrix (Figure 4(b)). In Figure 4(c) i.e. when 1wt.% of graphene oxide is added, the appearance of a few agglomerations is observed, which is probably linked to the rheological aspects which explain the percolation phenomenon [17].

3.2.2. Fourier transform infrared spectroscopy

Figure 5 show the FTIR spectroscopy of different PLA phases (α, β and γ) which identified by excitation of the molecular bonds of the PLA/GO samples. At 1384 cm⁻¹, we observe a weak presence of polymorphs of the α phase which hardly changes with the increase in the fraction of GO nanofillers in the PLA matrix and which disappears under the effect of the addition of nanofillers [17]. The β phase is strongly identified by the absorption bands 872 and 1212 cm⁻¹ [18] and becomes more dominant by the addition of only a small amount of GO (0.1wt.%). Thus, bands 1130 cm⁻¹ show the presence of the semi-polar γ phase which remains insignificant compared to the strong dominance of the β phase. This shows the influence of the incorporation of a small amount of GO on the enhancement of the β phase of PLA and all the di-/piezo-/pyro-electric properties that this phase can bring to the nanocomposite.
3.2.3. X-ray diffraction spectroscopy

Figure 6 show the X-ray diffraction spectroscopy of neat PLA and its nanocomposites. According to the spectra of the PLA/GO nanocomposite series with different mass fractions of graphene oxide (0.1; 0.5 and 1 wt.%) and in comparison with those of neat PLA, no peak corresponds to the graphitic structure was not detected. This indicates that the graphene oxide nanosheets are well dispersed in the PLA matrix without the formation of stacked structures. From this figure, it can be inferred that PLA exhibits a strong reflection at $2\theta = 16.6^\circ$ and $22.5^\circ$ corresponding to the piezoelectric $\beta$-phase [13] which becomes more and more intense with the increase in GO percentage.

Figure 6. X-ray diffraction spectra of PLA/GO nanocomposite films with 0.1; 0.5; and 1 wt.% of GO
4. Conclusion

In this work, the crystallization of PLA/GO as a potential smart piezoelectric nanocomposite, was investigated. The GO nanoparticles were prepared by modified Hummers method and the nanocomposite samples were prepared through the casting-evaporation technic using different amounts of GO. The nanocomposites obtained were analyzed by polarized optical microscope, Fourier transform infrared and X-ray diffraction analysis. The morphological results show that GO is well dispersed and distributed within the PLA matrix. The crystalline structures of samples were studied by FTIR and XRD analysis, and the results showed that the presence of 0.1 wt% of GO nanoparticles enhances the piezoelectric $\beta$-phase of PLA than the enhancement in piezoelectric properties of the nanocomposite.

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