



## Poly(lactic acid)/Graphene Oxide Nanocomposites: A Morphology Study and Mechanism of Reaction

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### ARTICLE INFO

#### Article history:

Received 23 June 2023

Received in revised form 27 October 2023

Accepted 8 November 2023

Available online 22 November 2023

#### Keywords:

Poly(lactic acid); graphene oxide;  
poly(ethylene glycol); melt blending

### ABSTRACT

Because of environmental concerns, the use of biopolymer poly(lactic acid) (PLA) as a matrix has gotten a lot of attention. The graphite (Gt) was modified to produce graphene oxide (GO) using an acid treatment prior to mixing. The modified GO was validated by Fourier Transform Infrared Spectroscopy (FT-IR) and Ultraviolet-Visible Spectroscopy (UV-Vis) tests. Melt mixing produced PLA nanocomposites with 1.5 wt.% loadings of two distinct carbon-based materials, Gt and GO. The effect of a plasticizer of 5 wt.% poly(ethylene glycol) (PEG) on nanocomposites was also investigated. The morphology study by Field Emission Scanning Electron Microscopy (FESEM) analysis showed the GO loading gave a smooth surface morphology as compared with PLA/Gt. These findings were identified by the presence of a smooth fracture surface, particularly when PEG was loaded, as an indication of good nanofiller spreading in the matrix. The mechanisms of reactions for Gt and GO dispersion in the PLA matrix were proposed to prove the morphology analysis.

## 1. Introduction

PLA is the best polymeric replacement for various petropolymers in the context of environmentally friendly processes and products due to its renewability, strong thermomechanical properties, ability to biodegrade, and biocompatibility. PLA has the potential to replace conservative petrochemical-based polymers for industrial applications as stated in previous study [1]. PLA has two features; biodegradable, which is appropriate for short-term packaging, and; biocompatible in contact with living tissues, making it suitable for medical applications, such as internal sutures, tissue scaffolds and implant devices. However, PLA has some shortcomings such as low solvent resistance, moderate barrier properties, brittleness and low thermal stability. Several tactics have been used to enhance PLA properties and to enlarge its applications recently.

Some of these improvements have been attained by the addition of fillers such as natural nanoclays or other carbon-based materials.

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<https://doi.org/10.37934/araset.33.3.384392>

Melt mixing is the most used process for manufacturing thermoplastic nanocomposites in the industry since it is quick, easy, and economical. A single, twin, or triple screw extruder, as well as a roll mixer or internal mixer, are used to melt the polymer at a high temperature and combine the graphene flakes, as discovered in Liu *et al.*, [2], Tiwari *et al.*, [3] and Rahmaoui *et al.*, [4], where numerous graphene-based nanomaterials have been prepared using this technique. In general, the findings revealed that the melt mixing technique produces composites with sufficient dispersion, but caution should be exercised when operating the mixing temperatures, as working at high temperatures will degrade the polymer. Furthermore, high shear forces are often needed for the effective mixing of the polymer with the flakes, which may even cause buckling or breaking of the graphene sheets. From the aforementioned details, the functionalization of graphene before incorporation into a polymer matrix is one of the most reliable and promising ways to prevent agglomeration. This aids in the formation of further chemical bonds with polymer functional groups, reducing the number of agglomerates. Besides, glass fiber is commonly used to improve the mechanical and thermal properties of composites as highlighted by Thanh *et al.*, in 2023 [5].

Due to its unique features such as miscibility, biodegradability, and food contactability, PEG is one of the most commonly used PLA plasticizers. PLA blends' properties are influenced by both molecular weight and the amount of plasticizer used, as reported by Li *et al.*, in 2018 [6] and their thermal characteristics are affected by PEG by disturbing the intermolecular forces as mentioned by Casalini *et al.*, [7]. Plasticized PLA normally has a single  $T_g$ , but adding PEG increases PLA chain mobility, allowing the chains to be arranged, lowering the  $T_g$  and improving crystallization. This finding has been also supported by Ozdemir and Hacaloglu in 2017 [8]. In a previous analysis, pyrolysis mass spectrometry studies of PLA-PEG blends revealed the existence of chains formed during the blending phase by interactions between PLA's -COOH groups and PEG's ether linkages [9]. As a result, the thermal stability of the mixture was reduced, and after prolonged mixing, an increase in both components was observed, which was related to the formation of a crosslinked structure.

A previous study reported the effect of PEG plasticizer on the degradation ability of PLA/carbon nanotubes (CNTs) nanocomposites prepared by melt blending [10]. It was discovered that adding CNTs and modified CNTs (m-CNTs) increases the weight loss and water absorption of nanocomposites by up to 2% for all samples, with and without PEG loading. Another study prepared PLA/GO using electrospinning to determine the possible placement of GO nano-sheets in the electrospun fiber mats [11]. Based on research that indicated that the position of GO sheets relies on their lateral size, they hypothesized three potential sites for them: (1) Thin GO sheets (less than 200 nm) wholly or partially inside the electrospun fibres. (2) Some larger ones roll around and on the surface of the fibre. (3) Parts of large sheets spanning between the fibres. Batakliiev *et al.*, (2019) studied the effect of graphene nanoplatelets and MWCNTs on the structure and mechanical properties of PLA composites. Higher tensile strength, Young's modulus and elongation at ultimate strength were obtained from PLA/MWCNTs [12].

The current study focused on the Gt modifications to produce GO. These carbon-based fillers were blended with PLA matrix and PEG plasticizer to examine the morphology behaviour of the nanocomposites. The mechanism of PLA nanocomposites was proposed.

## 2. Methodology

### 2.1 Modification of Graphite

1.0 g of graphite was added to 250 mL  $H_2SO_4$  and stirred for at least 30 min in the ice bath. Then, 20.0 g of  $KMnO_4$  was added to the mixture and the temperature was kept constant below 25 °C. The mixture was stirred for 24 hours. The mixture was then fed 50 mL of deionized water (DI) and agitated

for at least 30 min. The stirring speed was kept constant in all stages. After that, 100 mL H<sub>2</sub>O<sub>2</sub> (10%) was added to the mixture to reduce the KMnO<sub>4</sub> residue. To remove metal ions, the solid was filtered and washed with a 1.0 M HCl aqueous solution. The filtrate was washed with deionized water until neutral. The obtained graphite oxide was centrifuged several times at 2000 rpm for 20 minutes. After that, the graphite oxide was sonicated for 1 hour. The resulting GO was later filtered and dried in a vacuum oven at 60 °C for 24 hours.

## *2.2 Preparation of PLA Nanocomposites*

In an internal mixer, the nanocomposites were melt-blended using a twin screw rotator set to 180 °C. In an internal mixer, PLA was melted, then 1.5 wt.% Gt and GO were added until a homogenous mixture was obtained. Only one ratio of carbon-based material was used since the current research only focused on morphology study and the mechanism. For sample with the PEG, the 5 wt.% PEG was poured into the molten PLA before the fillers were added.

## *2.3 Analysis and Characterization*

The samples were characterized using Fourier Transmission Infrared Spectroscopy (FTIR), Perkin-Elmer Model, USA. The KBr method was applied. The transmission of IR spectra was obtained in the range between 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> at room temperature. The Shimadzu UV-1800 Model, USA with scanning speed at 200 nm/min and bandwidth of 0.1 nm was used in the Ultra-violet Visible Spectroscopy (UV-Vis) analysis. Visible wavelengths in the range of 200 to 500 nm were set up appropriately. Field Emission Scanning Electron Microscopy (FESEM), brand JEOL JSM-7800F, Belgium, was performed at a magnification of 10–300,000×. An extreme resolution of 0.8 nm at 15 kV and 1.2 nm at 1 kV with a gold coating was applied.

## **3. Results**

### *3.1 FT-IR Characterization*

Figure 1 shows the FTIR peaks of graphite (Gt) and graphene oxide (GO). The result is in line with other researches [13,14]. The low intensity of O-H peak in graphite and graphene is believed from moisture absorbed from the surrounding. The conjugated C=C ring stretching that appeared around 1580 cm<sup>-1</sup> in these materials is related to aromatic vibrations of graphite nature. The presence of different types of oxygen functionalities in GO confirmed at the broad and sharp peak of 3431 cm<sup>-1</sup> can be attributed to the O-H stretching vibrations of the C-OH groups and water. The absorption bands at 1740 cm<sup>-1</sup> can be attributed to carbonyl groups and the intense peak at 1410 cm<sup>-1</sup> can be attributed to CO-carboxylic acid. The C-O (epoxy) stretching vibration is around 1227 cm<sup>-1</sup> wavenumber, while C-OH (alkoxy) stretching vibration is at 1049 cm<sup>-1</sup>. The presence of oxygen or –OH means that the initial extended conjugated  $\eta$ -orbital system of graphite was broken and oxygen-containing functional groups were introduced into the carbon skeleton during the oxidation phase of the graphite powder with KMnO<sub>4</sub> in concentrated sulphuric acid. The existence of these vibrations indicates that epoxide and hydroxyl groups have been attached.

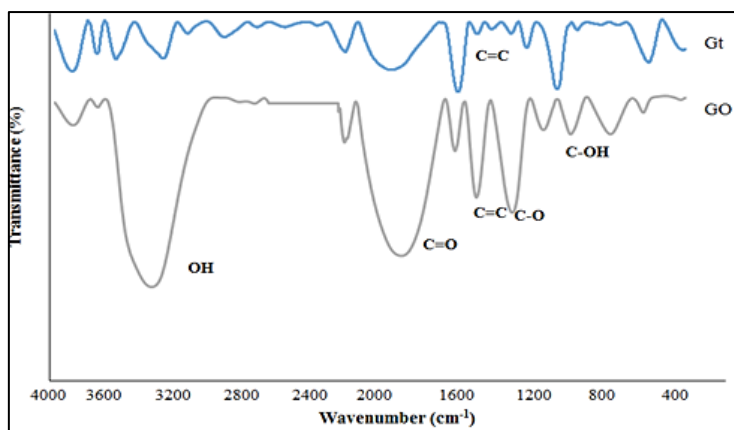


Fig. 1. FT-IR analysis of graphite and graphene oxide

### 3.2 UV-Vis Analysis

Figure 2 presents the UV-Vis spectra of Gt and GO nanofillers and depicts some variations in the absorption at a wavelength range between 200 and 500 nm. It is well recognized that the absorption around 230 nm in graphite is attributed to a  $\pi$ -electron Plasmon excitation of graphitic carbon ( $\pi \rightarrow \pi^*$  transition) of the C=C bond. In the GO peak, the same absorption peak is shown at 230 nm and an additional shoulder around 300 nm in GO was assigned to the  $n-\pi^*$  transition of the C=O bond. The appearance of absorption of these bands in oxidized graphite is a characteristic feature of GO which is consistent with the earlier reports [14,15]. While the shifted absorption peak in the spectra to 272 nm confirmed the Gr nanofiller due to the restoration of electronic conjugation within graphene nanosheets.

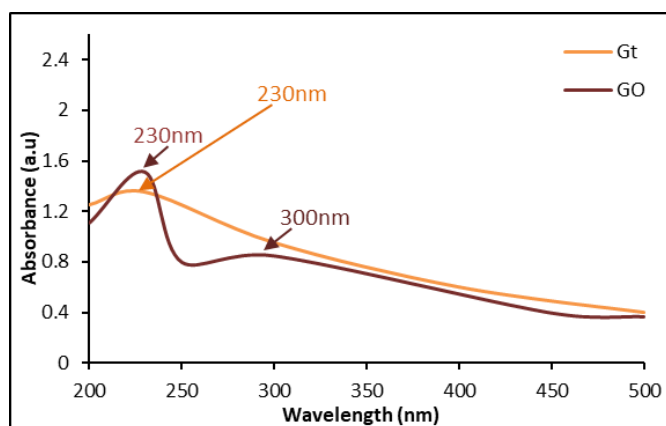
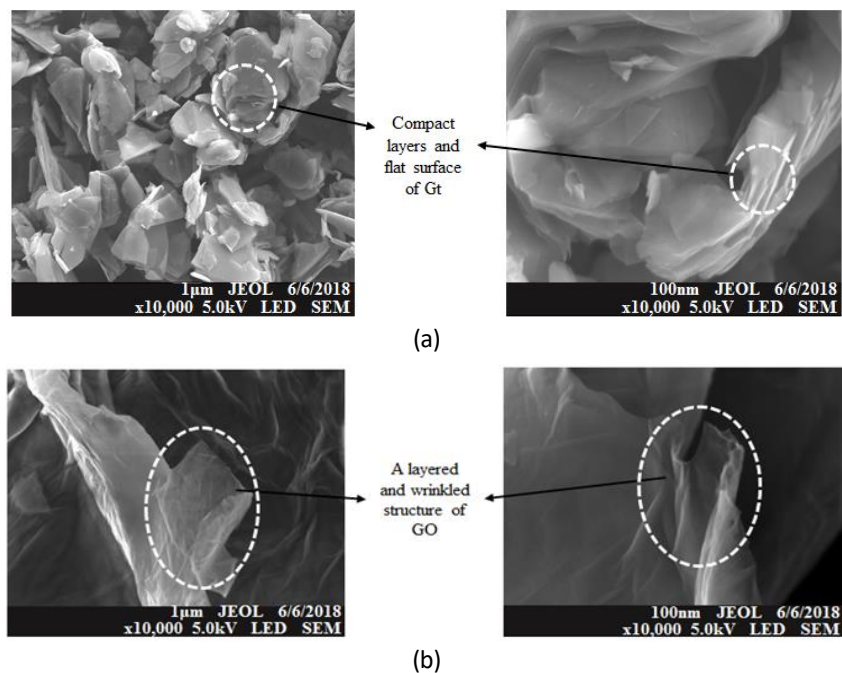


Fig. 2. UV-Visible analysis of Gt and GO materials

### 3.3 Morphology Study

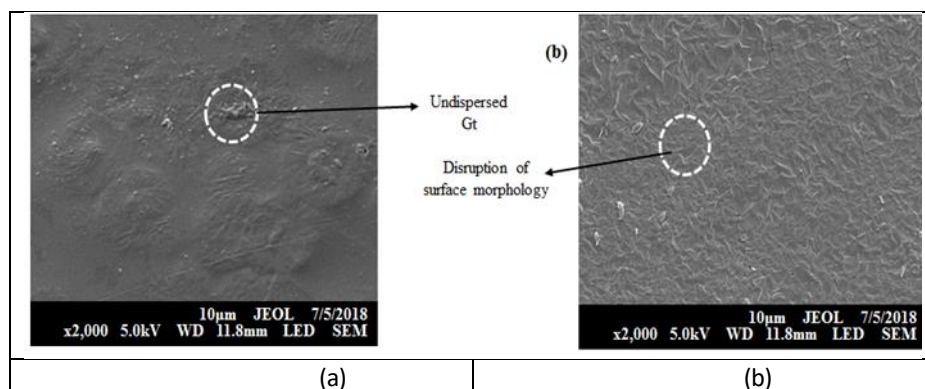
The surface of pristine graphite was exceedingly flat and smooth, and each layer was closely connected, as shown in Figure 3 (a). This was due to strong inter-layer Van der Waals interactions. It had compact, rigidly bound graphitic sheets. The images for GO showed a more disordered structure than the ordered graphite flakes as shown in Figure 3 (b), which was due to the existence of various oxygen functional groups on the surfaces and edges as also supported by a previous study [14]. The surface of GO had a layered structure and was not smooth. There were wrinkles on the surface of the GO sheets, which were stacked. The open structure of GO, as well as the outer layers, can exfoliate into the matrices, resulting in improved dispersion.



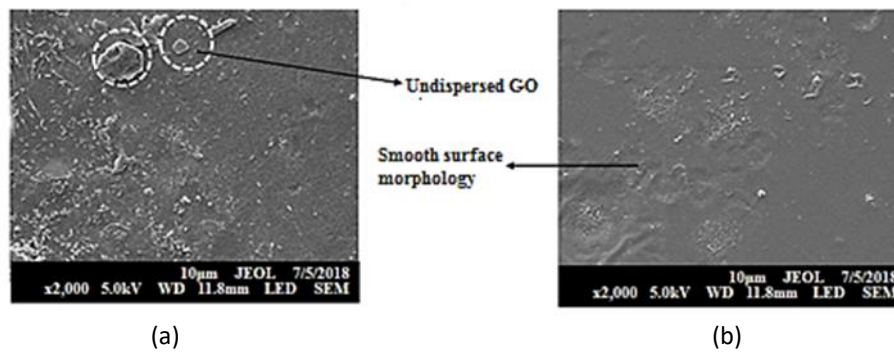
**Fig. 3.** FESEM images with different magnifications of (a) Gt and (b) GO materials

### 3.4 Morphology Study of PLA Nanocomposites

According to Figure 4, the loading of 5 wt.% of PEG affected the surface morphology of nanocomposites. Figures 4 (a) and (b) show the smooth surface of PLA nanocomposites with less undispersed pristine graphite. Surprisingly, with the same resolution, the surface morphology of PLA/PEG/Gt seems to be disrupted by the existence of cracks due to thermal penetration during analysis. Figure 5 (a) and (b) show the phase separation between PLA and nanofiller. After the filler spots were discovered, the GO was not well-distributed in the PLA matrix. Figure 5 (b) shows that adding PEG increased the dispersion between PLA and nanofiller, resulting in a smooth surface. This showed a stronger interfacial interaction between the GO sheets and the polymer matrix. The PLA matrix was wrapped around a wrinkled sheet of GO, as a result, there was no discernible boundary between the nanofiller and the matrix. The finding proves the good distribution of nanofiller in the matrix was established.



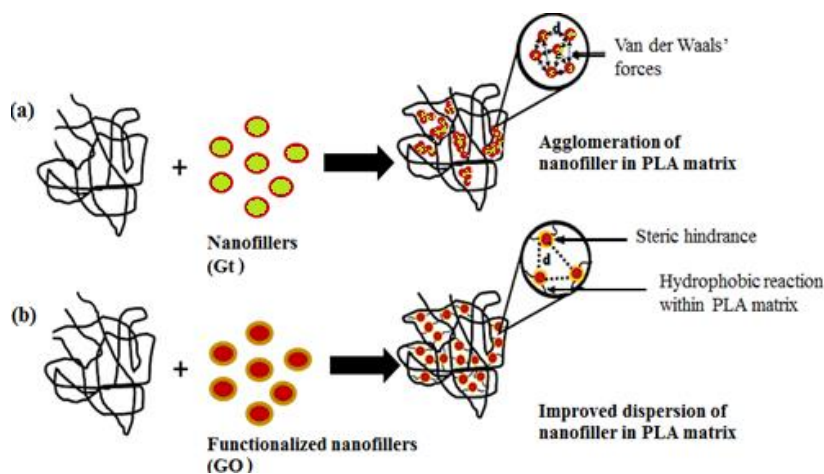
**Fig. 4.** Fracture surface of (a) PLA/Gt; and (b) PLA/PEG/Gt obtained from FESEM analysis



**Fig. 5.** Fracture surface of (a) PLA/GO; and (b) PLA/PEG/GO obtained from FESEM analysis

### 3.5 Dispersion Ability of PLA Nanocomposites

Figure 6 depicts the distribution of nanofiller in the polymer matrix. Modified nanofiller with functional groups has a higher spreading capacity than unmodified nanofiller as was stated in previous study [16]. Particle loading, filler size, and the polymer-filler interfacial interaction, as well as the structures of the fillers and polymers, all influence the reinforcement effect of nanofillers on nanocomposite characteristics. The majority of polymers are hydrophobic, making them unsuitable for use with hydrophilic nanofillers. Agglomeration and a lack of particle-polymer affinity may have a negative impact on mechanical performance. Interfacial debonding is always the first sign of failure. Phase separation and early material failure will occur if there is a lack of adhesion between the two phases and was discussed in a study by Jana and Jain in 2001 [17].

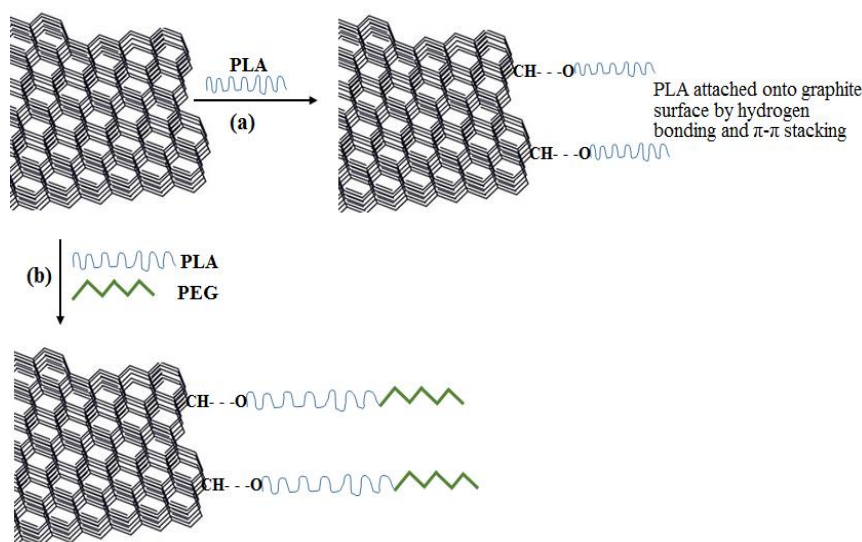


**Fig. 6.** Diagram of (a) agglomerates of graphite and; (b) smooth GO dispersion in the PLA matrix

### 3.6 Mechanism Study of PLA Nanocomposites

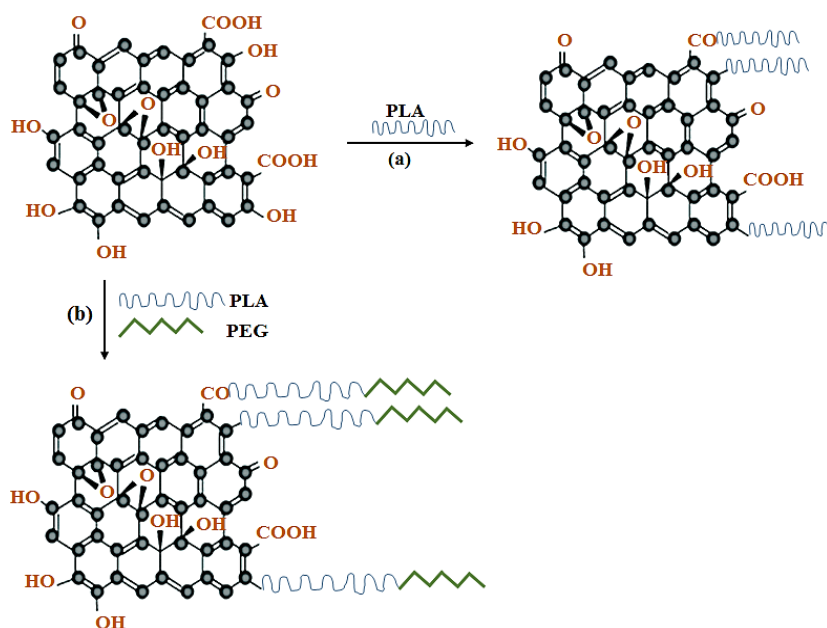
In general, one of the most important parameters in deciding the efficacy of the fillers added as well as the final characteristics obtained is filler dispersion inside the host polymer matrices. The interfacial adhesion between the filler and the host matrix is critical to the overall performance of carbon-based composites. Although physical bonding is the strongest possible interaction between carbon-based materials and polymers, various studies have used oxygen functional groups, which are responsible for hydrogen bond formation, to react with polymeric molecules, as illustrated and summarized in the following figures.

Graphite is arranged in hexagonal planar rings with no visible functional groups. Figure 7 shows how naturally hydrophobic nanofillers dispersed readily inside a hydrophobic polymer matrix using  $\eta$ - $\eta$  stacking. However, some polymers have unusual surface properties that prevent nanofiller from dispersing uniformly inside the matrix, resulting in the agglomeration of nanofiller sheets and poor mechanical properties [18]. Because of the weak interactions between materials and the host matrix, low-stress transfer between immiscible components has become much more pronounced, resulting in low mechanical properties. The lack of functionalities on the surface of these carbon-based materials limits the chemical reactions that can be used to modify them [19]. The proposed mechanism was referring to previous studies. Ren *et al.*, [20] tailored the thermal transport properties of graphene paper and Jayakumar *et al.*, [21] polyamidoamine/graphene nanoparticles for electrochemical DNA hybridization detection.



**Fig. 7.** The proposed mechanism of interaction between a) PLA/Gt and (b) PLA/PEG/Gt

Graphene oxide can be distributed into individual sheets in a solvent, and is best acknowledged for its oxygen-rich functional group found on the basal plane and edges. As a result, molecular level dispersion can be achieved if the GO and PLA matrix are dispersed in the same solvent. As shown in Figure 8, during blending, the surface-grafted PLA matrix acts as a nucleating site for the development of PLA crystals on the nanofiller surface. Muralikrishna *et al.*, reported a similar mechanism for synthesizing GO from graphite to produce GO-Cu<sup>2+</sup> hybrid electrodes [22]. The electrode showed low overpotential in acid solution and good electrocatalytic activity for hydrogen evolution reaction (HER).



**Fig. 8.** The proposed mechanism of interaction between (a) PLA/GO and (b) PLA/PEG/GO

#### 4. Conclusions

The modified GO was confirmed by FT-IR and UV-Vis analysis, and also by the appearance of a single sheet in FESEM analysis. Poor morphology fracture could be seen for PLA/Gt composites and the loading of PEG was not effective. The PEG loading helped in better dispersion of GO in the PLA matrix without agglomeration, as proved by smoother surface analysis. The FESEM results were supported by the proposed mechanisms. The –OH and –CO functional groups in GO assisted in the dispersion of the nanomaterial in the PLA matrix with high chances of hydrogen bonding.

#### Acknowledgement

I am grateful to the Faculty of Engineering, University College TATI, for providing me with facilities to carry out my laboratory works. This research was not funded by any grants.

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