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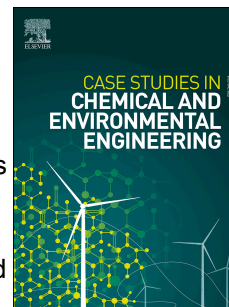
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# Effect and investigating of graphene nanoparticles on mechanical, physical properties of polylactic acid polymer

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## Abstract

Polylactic acid (PLA) is a linear aliphatic polyester thermoplastic made from renewable sources such as sugar beet and cornstarch. Methods of preparation of polylactic acid are

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biological and chemical. The advantages of polylactic acid are biocompatibility, easily processing, low energy loss, transparency, high strength, resistance to water and fat penetration and low consumption of carbon dioxide during production. However, polylactic acid has disadvantages such as hydrophobicity, fragility at room temperature, low thermal resistance, slow degradation rate, permeability to gases, lack of active groups and chemical neutrality. To overcome the limitations of polylactic acid, such as low thermal stability and inability to absorb gases, nanoparticles such as graphene are added to improve its properties. Samples were prepared by solution casting method using chloroform as solvent and in thin films. The mechanical, thermal, and structural properties of Polylactic acid pure and Polylactic acid / graphene nanocomposites were studied using tensile Test X-ray diffraction (XRD), Root mean square (RMS) and Differential Scanning Calorimetry (DSC). Also, by exposing the samples to Ultraviolet (UV) rays and then performing the tensile test, the resistance of the produced nanocomposites against Ultraviolet (UV) rays was investigated. With performing the above tests, it was found that by adding graphene nanoparticles to Polylactic acid, the crystallinity decreases and the strength and elongation of graphene particles (0.4% graphene) increase to a certain extent and then decrease. The loss modulus and storage modulus are also increased by the addition of graphene nanoparticles. By comparing the samples exposed to Ultraviolet (UV) rays with other samples, a significant decrease in elongation and a significant increase in modulus of elasticity were observed. In other words, Ultraviolet (UV) rays make Polylactic acid / graphene nanocomposites brittle.

**Keywords:** Polylactic acid, Graphene, Nanocomposite, solution casting method.

## 1. Introduction

Poly(lactic acid) (PLA) is a linear aliphatic polyester thermoplastic made from renewable sources such as sugar beet and cornstarch. Methods of preparing poly(lactic acid) are biological and chemical [1-4]. The advantages of poly(lactic acid) are biocompatibility, low energy loss, transparency, high strength, resistance to water and fat penetration and low consumption of carbon dioxide during production [5-9]. However, poly(lactic acid) has disadvantages, including hydrophobicity, brittleness at room temperature, low thermal resistance, slow degradation rate, permeability to gases, lack of active groups, and chemical neutrality [10-12]. Applications of poly(lactic acid) include medical use for sutures and surgical implants. Joints of surgical implants, such as pins and tubes, are also made of poly(lactic acid), which breaks down in the human body within six months to two years [13-17]. It is also used in food packaging and in the manufacture of disposable appliances, home appliances and sanitary ware. For this reason, poly(lactic acid) is known as a safe and secure plastic [18-20]. The challenges of using poly(lactic acid) in competition with industrial polymers are brittleness, high permeability to gases and water vapor, low glass transition temperatures, and poor thermal stability [21-24]. To overcome these limitations, nanoparticles are added to poly(lactic acid) to improve its properties one of these nanoparticles is graphene, which was discovered in 2004 and has unique properties. Improves mechanical properties such as tensile strength and acts as an impermeable agent for oxygen transfer even at high temperatures [25-29]. Thus, the addition of graphene as a reinforcement agent improves the thermal, physical and mechanical properties of the polymer matrix [30-31]. Graphene has a hexagonal ring structure made of hexagonal carbon layers called graphite. Graphene has outstanding properties such as high surface area, high Young's modulus, fracture toughness and good thermal conductivity [31-34]. Basically, polymer nanocomposites are polymer-based composites with at least one thermoplastic or thermosetting polymer backing phase and one nanometer-reinforcing phase [35-37]. Increasing nano-

reinforcements improves ground phase properties compared to large-scale reinforcements. These features include [39-42]:

1. Thermal properties: increase of thermal resistance, decrease of thermal expansion coefficient, decrease of shrinkage.
2. Mechanical properties: increase in elastic modulus, strength, elongation and toughness, increase in abrasion resistance.
3. Chemical properties: improve chemical resistance.
4. Electrical properties: reduce electrical resistance.
5. Optical properties: reduce oxygen permeability and moisture.

Today, plastic has an important role and application in human daily life, such as packaging industries, general industries, pharmaceutical industries and medical industries [43-46]. However, the massive consumption of these produced plastics leads to environmental pollution. Given this, the need to use materials that can be decomposed under environmental conditions is essential [47-51]. Today, bioplastics or biodegradable plastics have attracted a lot of attention. Bioplastics can be extracted from plant materials such as starch or synthetic biodegradable polymers such as polylactic acid, polyvinyl alcohol and poly(caprolactone) [52-54]. In addition, the degradation of bioplastics results in the production of carbon dioxide and water as the final product, which is not harmful to the environment. Therefore, bioplastics are one of the newest materials that are classified as environmentally friendly products [55-59]. However, bioplasts have disadvantages such as limited shelf life because they degrade faster and have less mechanical strength than conventional plastics [60].

Biodegradable plastics based on energy resources can be divided into three broad categories [61-65]:

1. Natural biopolymers such as carbohydrates, proteins and lipids derived from plants and animals.

2. Renewable-based environmental polymers such as aliphatic polyesters, polycaprolactone polymers, polyvinyl alcohol and polylactic acid.

3. Mixtures or composites of these biopolymers.

For many years, graphene was considered a scientific material, where the monolayer structure of carbon atoms was merely a theoretical model for describing the properties of graphene-based materials such as graphite, fullerenes, and carbon nanotubes [66-69]. Older theoretical predictions, in fact, the study of early two-dimensional crystals due to thermal fluctuations, assumed that graphene is unstable because it prevents the formation of long-distance crystal order at finite temperatures [70-72]. This idea was supported by various experimental studies on thin film layers. In those samples, the thickness of the sample was reduced by their instability [73-75]. Now, in the early 21st century, graphene has emerged as a real example. Some of the important properties of graphene that have been reported so far include large surface to weight ratio (for example, 1 gram of graphene can cover several football fields), approximate elasticity of 1100 GPa, fracture toughness of 125 GPa, high thermal conductivity and high surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ) [76-79]. Since the fabrication of graphene, which consists of one or more graphite layers with  $SP^2$  allotrope bonds of 2D carbon. Due to its excellent properties such as thermal conductivity and electrical conductivity, high charge density, mobility, optical conductivity and mechanical properties, it has become a unique material [80-84]. When a graphite monolayer forms a sphere, it is known as a fullerene, and when it orbits its axis, it forms a one-dimensional cylindrical structure called a carbon tube, and when two sides form a two-dimensional structure, it is composed of one or more layers [85-89]. A graphite layer is known as a monoatomic graphene with a single atom, and two or three layers of graphite are known as a two-layer or three-layer graphene. Graphenes larger than 5 to 10 layers are commonly referred to as low-layer graphene, and graphenes with approximately 20 to 30 layers are called multilayer graphene, thick graphene, or thin

nanocrystalline graphite [90-92]. Graphene, the new allotropic carbon, due to its remarkable electronic, thermal and mechanical properties, has been considered as an excellent mineral filler for the preparation of polymer-based nanocomposites with very low loading materials. Applications in nanocomposites, energy storage devices, various biomedical applications such as gene transfer, drug delivery, protein release, tissue engineering, imaging, anesthesia and packaging are some of the applications of graphene. Graphene has recently been recognized as a potential nano filler for the production of polymer nanocomposites [93-95]. This material has many properties such as mechanical strength and thermal conductivity ( $5000 \text{ W m}^{-3} \text{ K}^{-1}$ ) which is much higher than the certified standards for single wall CNTs. In addition to the very high level ( $2630 \text{ m}^2 \text{ g}^{-1}$ ), these properties together with gas permeability indicate the future applications of graphene to improve the mechanical, thermal and gas barrier properties of polymeric materials. Graphene oxide (GO) is similar to graphene, but has several oxygen-containing functional groups (such as hydroxyl epoxides and carbonyls) [96-99]. The presence of these polar groups reduces the thermal stability of nanomaterials, but may be to enhance interaction and compatibility with a particular polymer matrix [100-107]. Table 1 is constructed based on the type of graphene (GNP, GO, rGO) and then categorized based on the polymer matrix that has been used in each case. Mechanical properties of the nanocomposites have been investigated.

Table 1. Mechanical properties of graphene polymer nanocomposites.

| Graphene | Matrix | Process           | Filler Loading (wt.%) | Matrix Modulus (GPa) | Tensile Modulus Increase (%) | Graphene Modulus E (GPa) | ref  |
|----------|--------|-------------------|-----------------------|----------------------|------------------------------|--------------------------|------|
| GNP      | PLA    | Solution blending | 0.4 wt.%              | 0.038                | 156                          | 250                      | [41] |
| GNP      | pp     | Melt mixing       | 10 wt.%               | 1.3                  | 41                           | 13                       | [42] |
| GNP      | pp     | Melt mixing       | 1.7vol%               | 1.3                  | 54                           | 14                       | [43] |
| GNP      | Epoxy  | Solution blending | 5 wt.%                | 2.5                  | 28                           | 30.5                     | [44] |

|     |       |                   |          |      |      |      |      |
|-----|-------|-------------------|----------|------|------|------|------|
| GNP | Epoxy | Solution blending | 1 wt.%   | 2.9  | 24   | 143  | [45] |
| GNP | Epoxy | Solution blending | 5 wt.%   | 2.7  | 49   | 55   | [46] |
| GNP | Epoxy | Shear mixing      | 6 wt.%   | 2.72 | 23.5 | 20   | [47] |
| GNP | Epoxy | Shear mixing      | 4 wt.%   | 2.7  | 8    | 11   | [48] |
| GNP | PE    | Melt mixing       | 4 wt.%   | 1.3  | 35   | 25   | [49] |
| rGO | PE    | polymerization    | 5.2 wt.% | 0.23 | 170  | 15   | [50] |
| rGO | PVA   | Wet spinning      | 2 wt.%   | 5.4  | 294  | 1036 | [51] |
| rGO | Epoxy | polymerization    | 2 wt.%   | 0.48 | 70   | 34   | [52] |
| rGO | Epoxy | Three roll mill   | 8 wt.%   | 2.8  | 22   | 14   | [53] |
| rGO | Epoxy | Solution blending | 0.2 wt.% | 2.9  | 8    | 243  | [54] |
| fGr | Epoxy | Solution blending | 0.3 wt.% | 1.5  | 32   | 321  | [55] |
| GO  | PVA   | Solution blending | 0.3 wt.% | 2.3  | 150  | 2335 | [56] |
| GO  | PVA   | Solution blending | 5 wt.%   | 2    | 190  | 162  | [57] |

## 2. Novelty of This Research Work

1. When using GO, brittle fracture has been observed in tensile test samples, but soft fracture has been observed when using stearic acid because the presence of stearic acid makes GO better compatible with the substrate.
2. Dsc analysis showed that in PLA-GO nanocomposites due to the presence of graphene, the mobility of polymer chains has decreased, as a result, T<sub>m</sub> and T<sub>g</sub> have changed compared to pure PLA. Also, stearic acid increased the compatibility of GO with the background and increased the crystallization temperature.
3. The use of graphene has a significant effect on the morphology of spherulite and the size of spherulite decreases with increasing amount of graphene and graphene acts as a nucleating agent.



4. with adding graphene, the Young's modulus and tensile strength increase but the elongation decreases. In high percentages of graphene, the accumulation of nanoparticles causes lumps and decreases the strength.
5. The addition of nanographenes increases the thermal conductivity of PLA. Also, with the increase in temperature, the thermal conductivity increases due to the increase in molecular vibrations.
6. Graphene improves the thermal stability of PLA, and the main degradation process starts above 300 °C, which is mainly attributed to trans-esterification.

### **3. materials and methods**

#### **3.1. Preparation of nanocomposites**

All samples were Preparation using the solution casting method. The solution casting method is used to Preparation of nanocomposites of solvent-soluble polymers. This method mainly consists of two steps. In the first step, by mixing the polymer solution and the distributed nanoparticles in a solvent, the polymer chains are distributed between the nanoparticles. In the second step, the solvent is obtained by evaporation or deposition of the nanocomposite. First 25 g PLA and 0.65 g graphene nanoparticles for complete removal of moisture for 2 hours at 60 ° C, then for one hour at 70 ° C and finally for half an hour at 80 ° C in a heated oven put. In order to Preparation pure PLA and PLA-GR nanocomposite samples, 5 g PLA was poured into 50 cc of chloroform solvent and dissolved for 3 hours by magnetic stirring to completely dissolve the PLA in the solvent. Pour 0.05 g of graphene nanoparticles into 30 cc of chloroform solvent and homogenize with ultrasonic for 60 minutes at 60 watts. The solution containing polylactic acid and chloroform was then added to the solution containing graphene nanoparticles and homogenized in ultrasonic for 60 minutes at 60 watts. Carefully and gently pour the resulting solution on the made glass plates so that no bubbles are created in it and also

the thickness of the Preparation film is the same. We placed the glass plates at room temperature for 24 hours and after 24 hours, transferred them to a heated oven at 60 ° C for 9 hours to remove the solvent, and again the glass plates containing the samples for 7 days. We set it at room temperature to ensure the complete removal of chloroform in the Preparation films. The Preparation films are easily separated from the glass plates.

### **3.2. Methods of preparation of PLA-Gr nanocomposite**

A composite is made up of two or more components. Usually, if the polymer base phase and the other phase use nanomaterials, that material is called nanocomposite. In the case of nanocomposites, mechanical and thermal properties are increased by adding a small percentage of nanometer amplifiers. The uniform distribution of the amplifier phase creates a large interface between the nanometer amplifier phase and the matrix ground phase. There are two major challenges to producing a nanocomposite. In the first step, select the nanoparticles in such a way that it creates the necessary compatibility with the ground phase and also can create the expected properties. In the second step, a suitable method for the production of nanocomposites must be selected so that a suitable distribution of the amplifier takes place in the ground phase. Preparation of nanocomposites by three methods of in situ polymerization, melt mixing and solution, for polymer nanocomposites has long been industrially developed and used. In the process of preparing a sample of PLA/GO composites, GO was dispersed in THF by ultrasonic for 90 minutes at room temperature. A certain amount of PLA was also dissolved in THF at a concentration of 100 mg ml<sup>-1</sup>. The PLA solution with a volume of 20 ml and the GO solution with 10 ml of THF are mixed and mixed with a magnetic stirrer to form a homogeneous mixture. In Table 2 showed Different PLA-Gr nanocomposite samples preparation method.

Table 2. Different PLA-Gr nanocomposite samples preparation method.

| preparation method   | Ref   |
|--|-------|
| Dissolve graphene in chloroform by ultrasonic for 2 h, keep for 1 month in the same state, add polylactic acid polymer and chloroform mixture to graphene-chloroform mixture, dry samples for 12 h in a vacuum oven at 75 °C.  | [58]  |
| Dissolve 8.91 g of polylactic acid polymer resin in 45 ml THF at 50 °C, dry in an oven vacuum at 70 °C for 12 hours, dissolve 0.09 g of graphene oxide by sonication in 30 ml, THF for 30 min, mix GO solution with polylactic acid polymer solution, prepare polylactic acid polymer -GO composite films by a hot pressure process by pressing and heat the powder for 60 min at 180 °C | [59]  |
| Dissolve 0.95 g of polylactic acid polymer in 30 ml, chloroform by continuous shaking for 2 h, disperse graphene by weight ratios (0.1, 0.1 and 0.5) wt% in 20 ml, chloroform in sonication bath for 30 min, adding the two solutions together and placing the sonication bath for 15 and 30 min, drying the solution on Teflon plates for 24 h.   | [64]  |
| Dry polylactic acid polymer at 105 °C for at least 4 h before use, dissolve GO in acetone solvent and then chloroform for 20 min and sonicate and homogenize, dissolve polylactic acid polymer at 40 °C in chloroform, add suspension GO in chloroform to solution to achieve weight ratios (0.1, 0.2, 0.3, 0.4 and 0.5), drying in an oven at 35 °C                                     | [108] |

### 3.2.1. In situ polymerization method

In situ polymerization method, the distribution of nanoparticles is considered. This method creates a very good interface between the reinforcing particles and the ground. Graphene-containing polymer nanocomposites with high electrical conductivity and low permeability are prepared by this method. With surface modification, the proper distribution of nanoparticles can be done uniformly to prevent clumping of the nanometer components of the nanoparticles and to provide a proper distribution of the amplifier phase [60].

### 3.2.2. Melt mixing method

This method involves mixing polymers and nanoparticles at a high glass transition temperature or polymer melting point. After mixing, the mixture is cooled to the transition temperature of glass and a nanocomposite structure is formed. In this method, due to the ground melt state, mixers such as single-screw, double-screw extruders and internal mixers are used. In the melt mixing method, the establishment of polymer chains will depend on the proper interaction between the nanoparticles and the polymer substrate. Melt mixing has limitations for the nanocomposite production process, the most important of which are the formation of defects and cavities in the field as well as the inability to distribute uniformly for particles with different morphologies [61].

### 3.2.3. Solution method

The solution method is based on the fact that the polymer, solubility and nanoparticles can be properly distributed in the solvent. In this way, polymer nanocomposites can be produced in two ways. If the polymer substrate and the nano fibers are miscible, the resulting solution can be cast into a mold and the nanocomposite produced, otherwise the nanocomposite mixture is dissolved in a solvent and finally the nanocomposites are obtained by evaporation of the solvent. The solution method mainly consists of two steps. In the first step, by mixing the polymer solution and nano particles distributed in a solvent, the polymer chains are distributed between the nanoparticles. In the second step, the solvent is obtained by evaporation or precipitation of the nanocomposite. The solution method is suitable for non-polar polymers, or polymers with low polarity with nanoparticles. So far, several graphene polymer nanocomposites prepared by solution method, melt method or *in situ* polymerization have been reported. Among these methods, the solution method is widely used and can be used to facilitate mixing and dispersion of graphene due to the low viscosity of the mixing system in

solution. One of the key points in solution formulation is to use a suitable solvent to create a uniform composition of polymers and nanofillers [62].

### **3.3. Graphene synthesis**

There are many reports on graphene synthesis, many of which are based on mechanical peeling of graphite, reduction of graphene oxide and, more recently, chemical vapor deposition [16-17].

### **3.4. Chemical synthesis of graphene from reduced graphene oxide**

Chemical synthesis is a top-down indirect graphene synthesis method, and the first chemical method is graphene synthesis. This method involves the synthesis of graphite oxide by graphite oxidation, the dispersion of graphite flakes by ultrasonic agent and its reduction to graphene. Three common methods are available for GO synthesis [18-20]. Brody method, Meyer method and Hummers' method. These three methods include graphite oxidation using strong acids and oxidants. The degree of oxidation can vary depending on the reaction conditions (e.g., temperature, pressure, and stoichiometric type). Hummer proposed a method for making graphene by mixing graphite with sodium nitrate, sulfuric acid, and potassium permanganate, known as the Hummers' method [21-22].

### **3.5. Advantages Graphene / Graphene oxide**

Graphene, the new allotropic carbon, due to its remarkable electronic, thermal and mechanical properties, has been considered as an excellent mineral filler for the preparation of polymer-based nanocomposites with very low loading materials [23]. Applications in nanocomposites, energy storage devices, various biomedical applications such as gene transfer, drug delivery, protein release, tissue engineering, imaging, anesthesia and packaging are some of the applications of graphene [24-25]. Graphene has recently been recognized as a potential nano filler for the production of polymer nanocomposites. This

material has many properties such as mechanical strength and thermal conductivity ( $5000 \text{ W m}^{-3} \text{ K}^{-1}$ )<sup>156</sup> which is much higher than the certified standards for single wall CNTs. In addition to the very high level ( $2630 \text{ m}^2 \text{ g}^{-1}$ ), these properties together with gas permeability indicate the future applications of graphene to improve the mechanical, thermal and gas barrier properties of polymeric materials. Graphene oxide (GO) is similar to graphene, but has several oxygen-containing functional groups (such as hydroxyl epoxides and carbonyls). The presence of these polar groups reduces the thermal stability of nanomaterials, but may be to enhance interaction and compatibility with a particular polymer matrix [26-27].

#### **4. Discussion & conclusions**

##### **4.1.XRD analysis**

One of the most reliable methods to prove the opening of graphene plates and their distribution in the polylactic acid matrix is to perform an X-ray diffraction analysis. As is clear from Figure 1, in the pure graphene sample there is a peak at an angle of  $2\Theta = 25.4$  which is not observed in PLA / Gr nanocomposites, indicating that graphene is well dispersed in polylactic acid. Also, according to the diagram of pure polylactic acid, two peaks are observed at angles of  $2\Theta = 16.9$  and  $19.38$ , which is evidence of the existence of two types of crystal structures in pure polylactic acid [24]. for pure polylactic acid, peaks of  $2\Theta = 16.7$  and  $19.0$  are reported [24], which is very close to the peaks observed in this study. The main peak observed in polylactic acid is also visible in the rest of the nanocomposites and is in the range of about 1%, which can be due to the very small amount of nanoparticles added to pure polylactic acid, which failed the crystal structure of polylactic acid polymer. The second peak in pure PLA is similar to the main peak in all nanocomposites at a short distance from it [24] that examined the crystal structure of PLA/ODAG .

In the samples of 0.3% PLA / Gr, 0.4% PLA / Gr, 0.5% PLA / Gr 0.5%, a third peak is also observed, which occurs at an angle of  $2\theta = 22.4$ . This peak is not present in pure PLA and may indicate some accumulation of graphene particles. Given the distance of this peak from the peak of pure graphene, it can be assumed that there is little accumulation in the samples.

also shows XRD patterns of PLA and PLA/GO nanocomposites in fig 1 . He observed that the peaks in nanocomposites are in the range of about 0.3% compared to pure PLA, which may be due to the very small amounts of fillers.

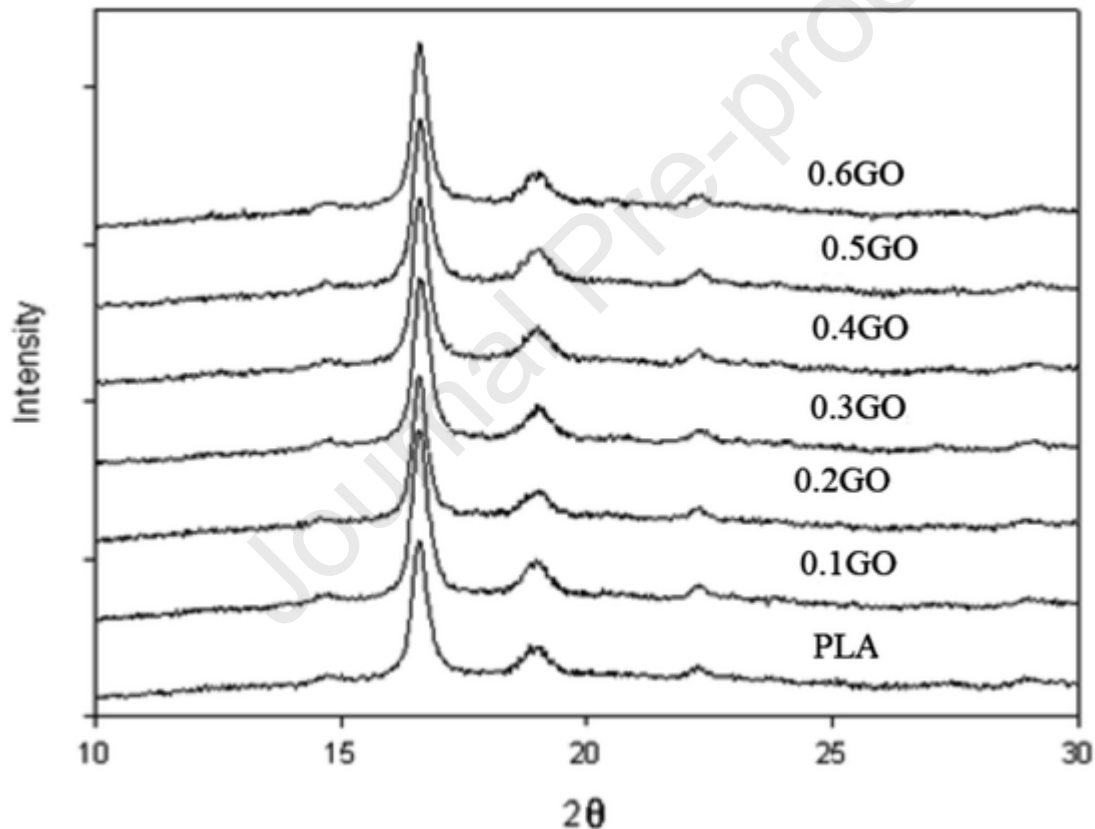


Figure 1. XRD diagrams of pure graphene, pure polylactic acid, graphene, and polylactic acid nanocomposites.

#### 4.2. FE-SEM and TEM analysis

Using TEM and FE-SEM images in Fig. 2, found that graphene with a corrugated structure was homogeneously dispersed in the PLA matrix and no aggregation was observed in the nanocomposite.

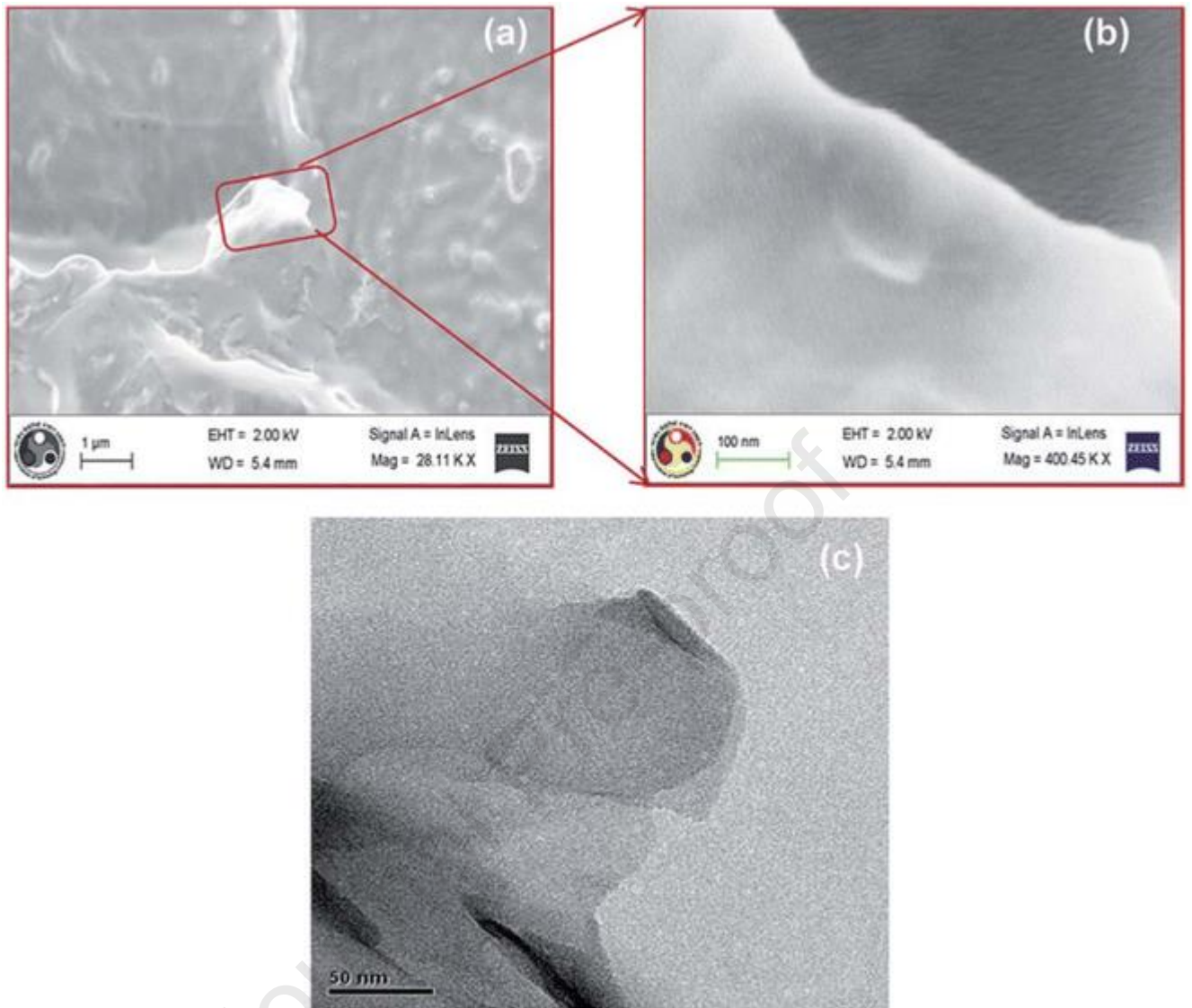


Fig. 2. FE-SEM images of (a) PLA-GR composite (low magnification) (b) PLA-GR composites (high magnification) and (c) TEM image of PLA-GR-0.1. ( $T = 25\text{ }^{\circ}\text{C}$ ).

#### 4.3.RMS analysis

RMS test was used to evaluate the effect of graphene content on the rheological properties of PLA. For this purpose, the storage modulus, loss modulus, and viscosity of pure PLA complex and PLA/Gr nanocomposites were calculated. The storage modulus ( $G'$ ) is shown in Figure 3(a), the dissipation modulus ( $G''$ ) in Figure 3(b), and the viscosity of the  $\eta^*$  complex in Figure 3(c).



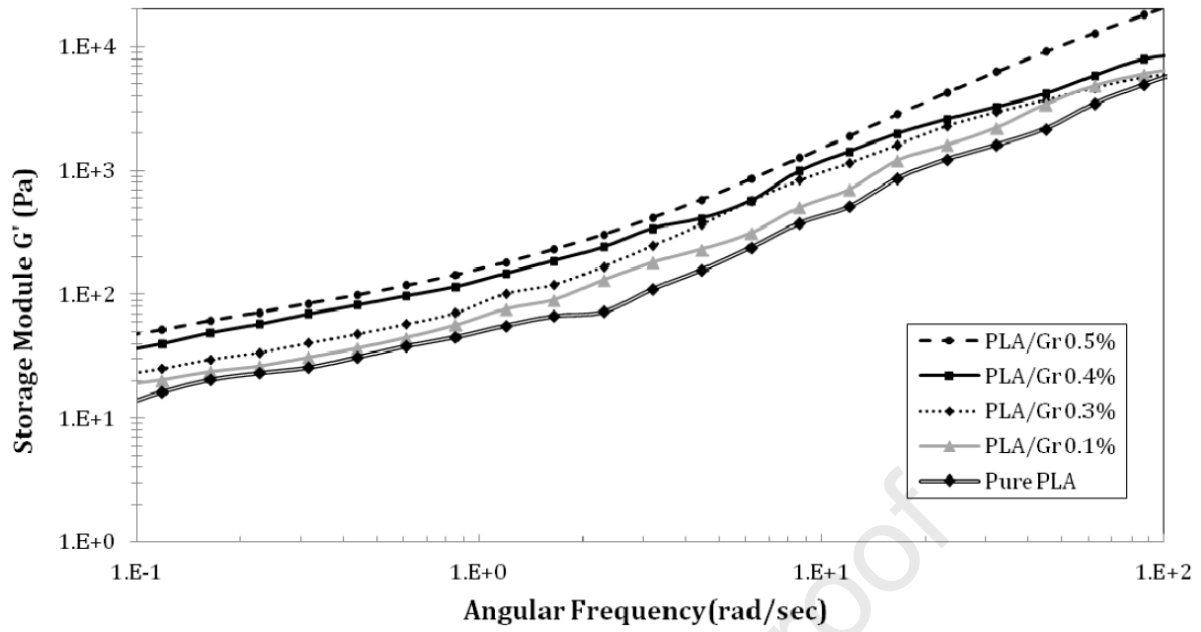


Figure 3(a). PLA Pure storage module and PLA / Gr nanocomposites.

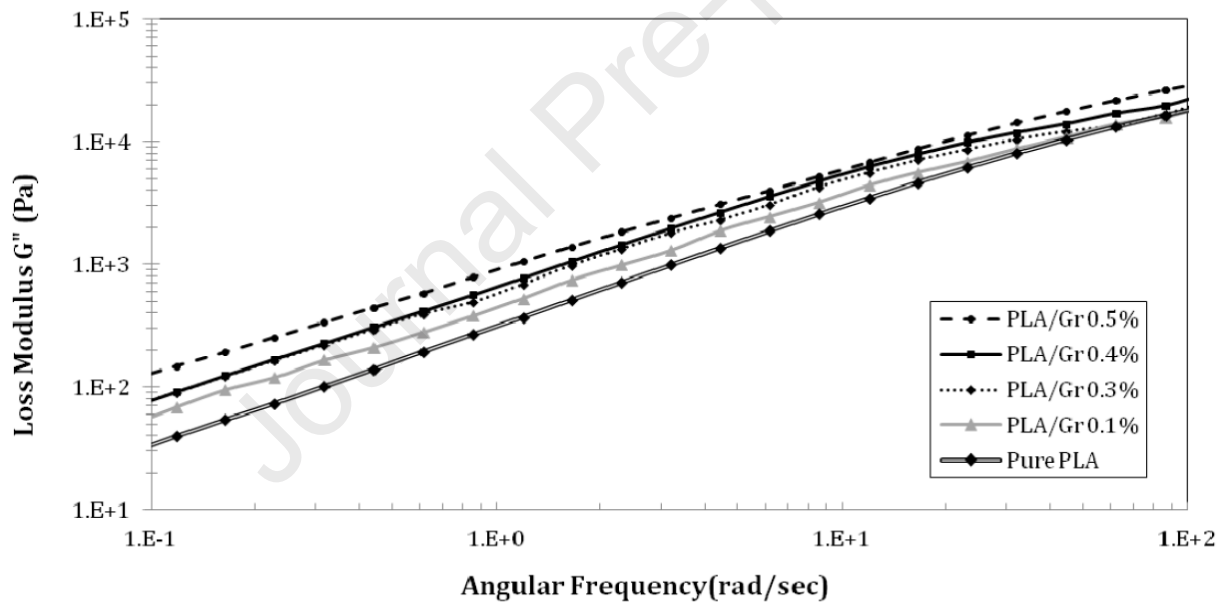


Figure 3(b). Loss modulus of pure PLA and PLA/Gr nanocomposites.

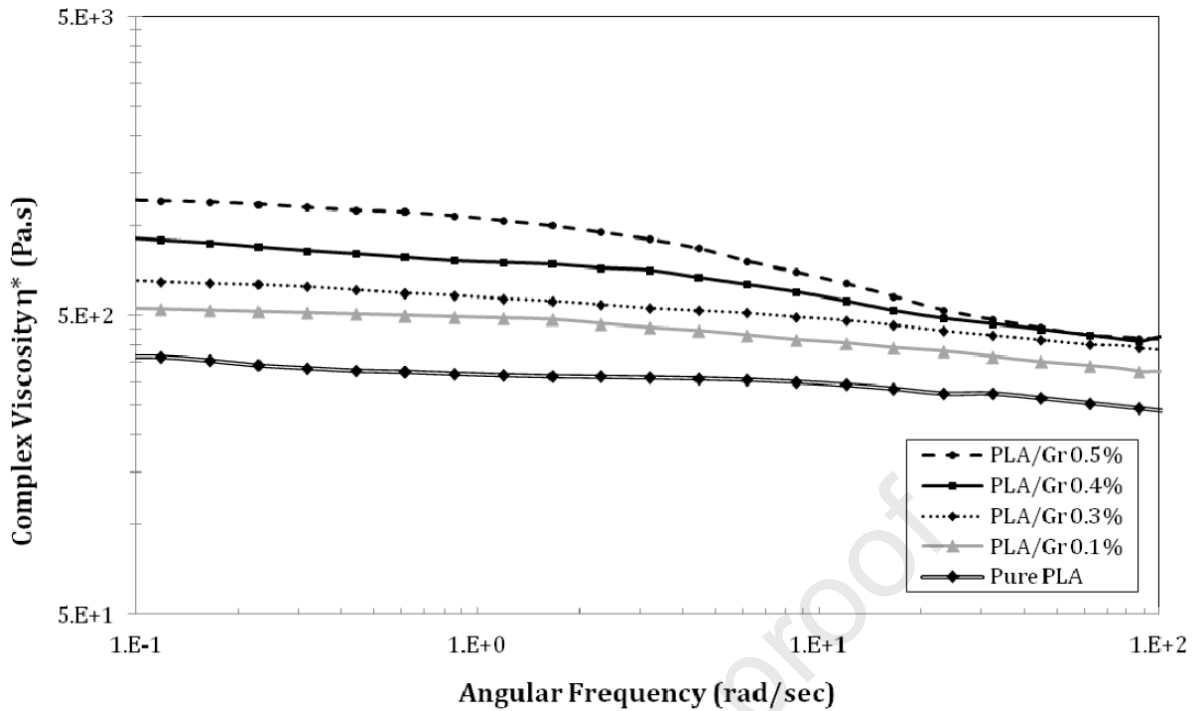


Figure 3(c). The viscosity of pure PLA complex and PLA/Gr nanocomposites.

According to Figure 3(a-b), it can be seen that  $G'$  and  $G''$  PLA/Gr nanocomposites are higher than pure PLA and increase with the increasing amount of graphene. The reinforcing effect of graphene nanoparticles that form a network of internal bonds with the PLA matrix, leads to an increase in elasticity in PLA/Gr nanocomposite[25]. As the frequency increases, the difference between pure PLA and PLA/Gr nanocomposites decreases. Figure 3(c) shows the viscosity changes of pure PLA complex and PLA/Gr nanocomposites. In a Newtonian fluid, the viscosity of the complex must be a line with a constant slope. In pure PLA, 0.1% PLA/Gr, 0.3% PLA/Gr, the viscosity remains constant with a good approximation over the whole range, but with further increase in graphene content, the complex viscosity no longer remains constant and with increasing frequency, the complex viscosity decreases. According to the obtained results, it can be concluded that with the increase of graphene, the behavior of PLA/Gr nanocomposites has changed from a Newtonian state to a Newtonian-like state. In addition, according to Figure 3(c), it can be seen that with the increasing amount of graphene,  $\eta^*$  increases, which is more evident at low frequencies.

The results obtained from the RMS test are very similar to the results of Kuang et al. [25]. pure PLA and increases with increasing amount of GO. Differences in low-angle frequencies increase the elasticity of PLA/GO nanocomposites relative to pure PLA due to the amplifying effect of GO nanofiller, which forms networks bonded to a polymer matrix. The log [thin space (1/6-em)]  $G'$  versus' log [thin space (1/6-em)]  $G''$  is also shown in Fig. 4.

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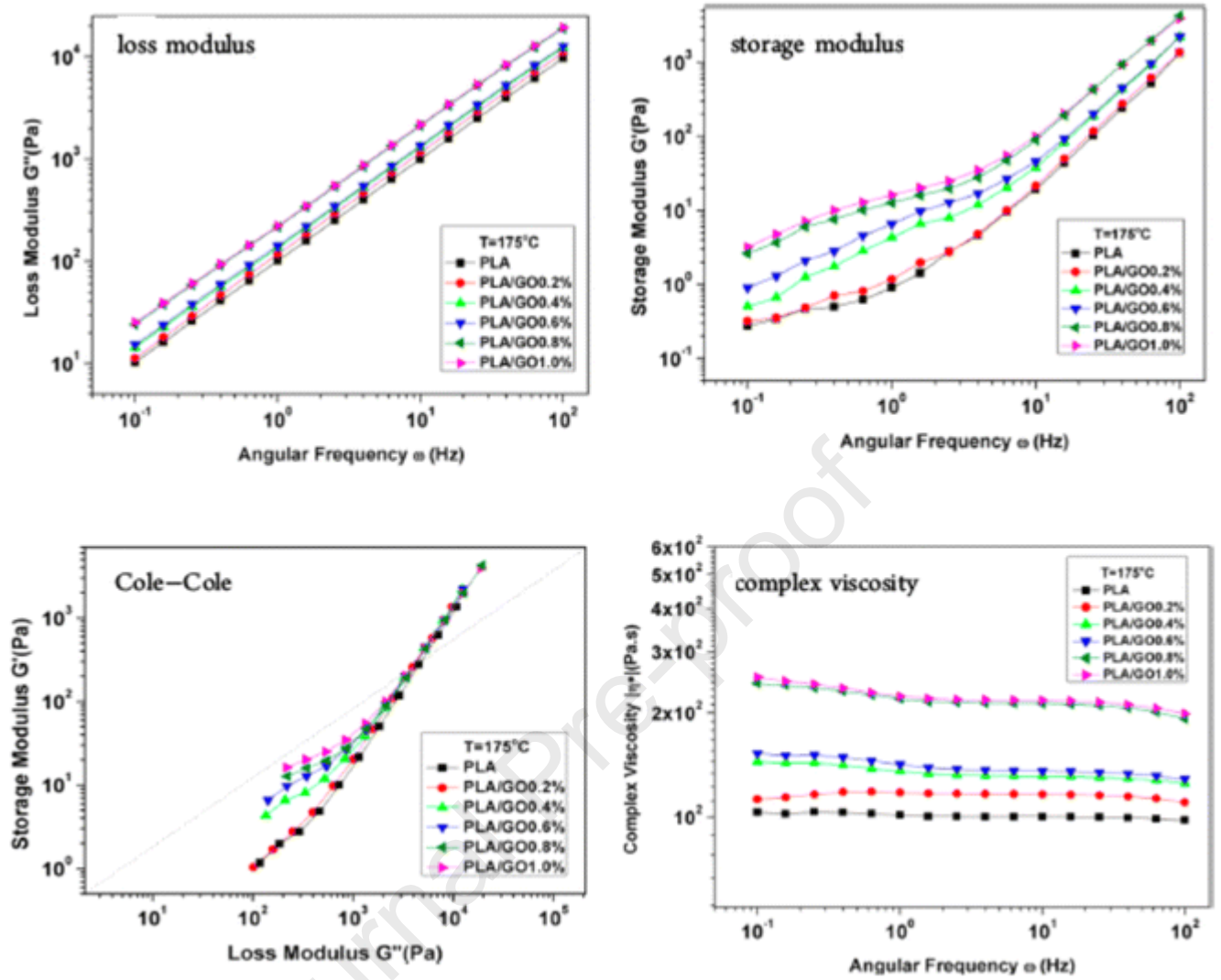


Figure 4. Rheological properties of PLA and PLA/GO composites.

### 4.3.DSC analysis

It is useful to study the effect of graphene nanoparticles on the non-temperature crystallization behavior of polylactic acid. With the help of DSC test results, heater peak temperature, and peak heights, information about the size of crystals and their distribution can be obtained. The results of DSC include the exothermic peak temperature of crystallization,  $T_c$ , melting point  $T_m$ , the glassing temperature  $T_g$ , the peak melting point  $\Delta H_m$  and the percentage of crystallization,  $X_c$ . DSC profiles of pure PLA samples and PLA / Gr nanocomposites are shown in Figure 5.

Using DSC analysis, Chen *et al.* [58] the addition of graphene to the PLA matrix had a slight change in melt temperature  $T_m$  and was slightly higher than pure PLA, indicating that graphene could reduce the mobility of polymer chains. Also, the cold crystallization temperature of the nanocomposite shifts to higher values compared to pure PLA. studying the PLA/Gr microstructure under non-isothermal crystallization. In this study, the cooling rate in the DSC test was not the same and varied from 0.5 to 4 °C min<sup>-1</sup>. It is clear that as the cooling rate increases, the TP and TC temperatures decrease. He also attempted to model the asynchronous crystallization of PLA/Gr nanocomposites using Qzawa Avrami models.

Chartarrayawadee et al.,[59] from observations of DSC analysis, found that the addition of GO did not affect  $T_g$  and  $T_m$ ; Addition of stearic acid reduces  $T_m$  and  $T_g$  because it has a emollient effect and increases the compatibility of GO particles with the PLA matrix, which leads to a nucleation effect in the matrix. Nanoparticles in the matrix act as nucleating centers for crystallization, but only if the nanoparticles are well dispersed and have minimal interphase adhesion to the PLA matrix.  $\Delta H_m$  results here show that there is a link between compatibility and crystallizable and that the coating of stearic acid on the GO particles can enhance both.

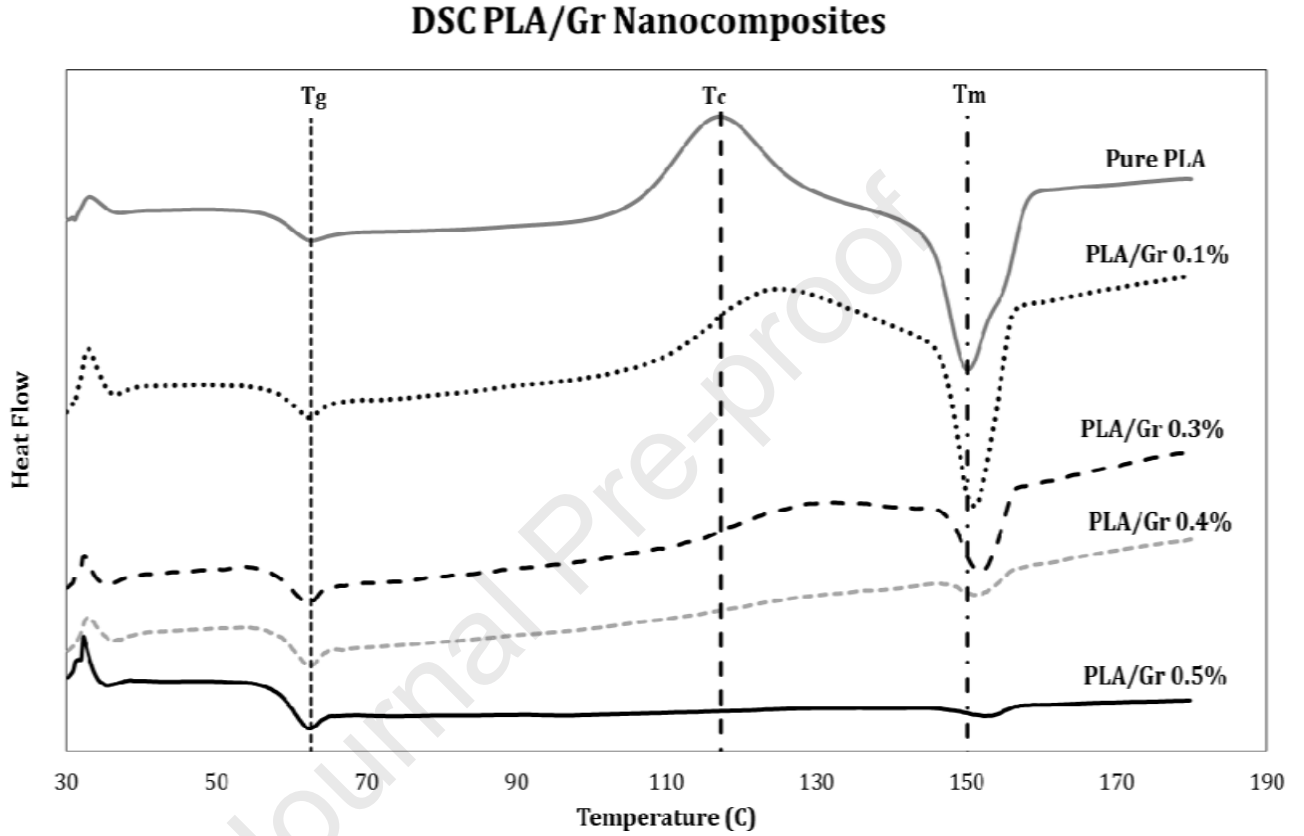


Figure 5. DSC analysis for PLA/Gr nanocomposites.

The values of glassing temperature, melting temperature, and melting enthalpy are directly among the test outputs. To obtain the crystallization percentage, Equation 1 is used [24], in which  $\Delta H_{mPLA}$  enthalpy of melting polylactic acid with a crystallinity of %100, the value of which is equal to 93.6 j/g. The following is a Table 3 of glass, melting temperature, melting enthalpy, and crystallization percentage for pure PLA and PLA/Gr nanocomposites.

$$X_c = \frac{\Delta H_m}{\Delta H_{mPLA}} * 100 \quad (1)$$

Table 3. Parameters obtained from DSC analysis.

| Sample      | T <sub>g</sub> (°C) | T <sub>m</sub> (°C) | ΔH <sub>m</sub> (j/g) | X <sub>c</sub> (%) |
|-------------|---------------------|---------------------|-----------------------|--------------------|
| Pure PLA    | 60.3                | 150.2               | 24.08                 | 25.89              |
| PLA-GR-0.1% | 60.7                | 151.1               | 17.29                 | 18.59              |
| PLA-GR-0.3% | 61                  | 151.8               | 6.006                 | 6.45               |
| PLA-GR-0.4% | 62                  | 152.3               | 1.3                   | 1.47               |
| PLA-GR-0.5% | 62                  | 152.5               | 0.73                  | 0.78               |

According to Table 2, it can be seen that the T<sub>g</sub> and T<sub>m</sub> variations for pure PLA and PLA/Gr nanocomposites are relatively small. However, the T<sub>g</sub> values of PLA/Gr nanocomposites are slightly higher than pure PLA, indicating that graphene can reduce the mobility of polymer chains. The addition of graphene reduces the crystallization percentage, which is probably due to the poor accumulation and dispersion of graphene in the PLA matrix [24, 25, 26]. with increasing the amount of graphene, the amount of crystallinity has decreased, which is in accordance with the results of this study [27]. the melting temperature of pure PLA was 148°C, which reached 152°C by 0.5% PLA/Gr with increasing graphene nanoparticles. It is also clear from Table 1 that the melting temperature of pure PLA increased from 150°C to 152°C at 0.5% PLA/Gr, and the good agreement between the results is quite evident.

#### 4.4. Tensile Test

A tensile test has been used to investigate the effect of graphene addition on the mechanical properties of PLA. For this purpose, stress and strain curves for pure PLA and PLA/Gr nanocomposites were extracted using a tensile tester. Also, the values of yield stress, elongation in the elastic part, and Young's modulus were calculated by the machine. It should be noted that the output of the tensile test is in the form of force in terms of elongation, which should be converted to stress in terms of strain using the cross-section and length of the specimens. Figure 6(a) shows the stress-strain diagram. Figure 6(b) shows the elongation changes (in the

percentage of initial length) and yield stress at the end of the elastic section, and Figure 6(c) shows the young modulus changes.

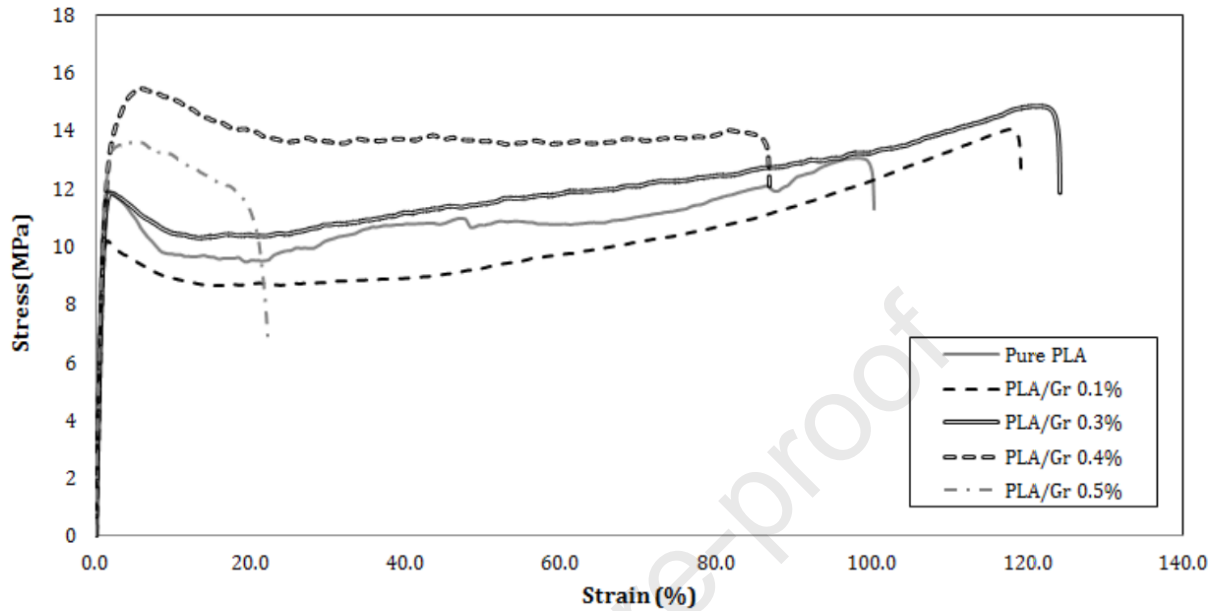


Figure 6(a). Stress-strain diagram of pure PLA and PLA / Gr nanocomposites.

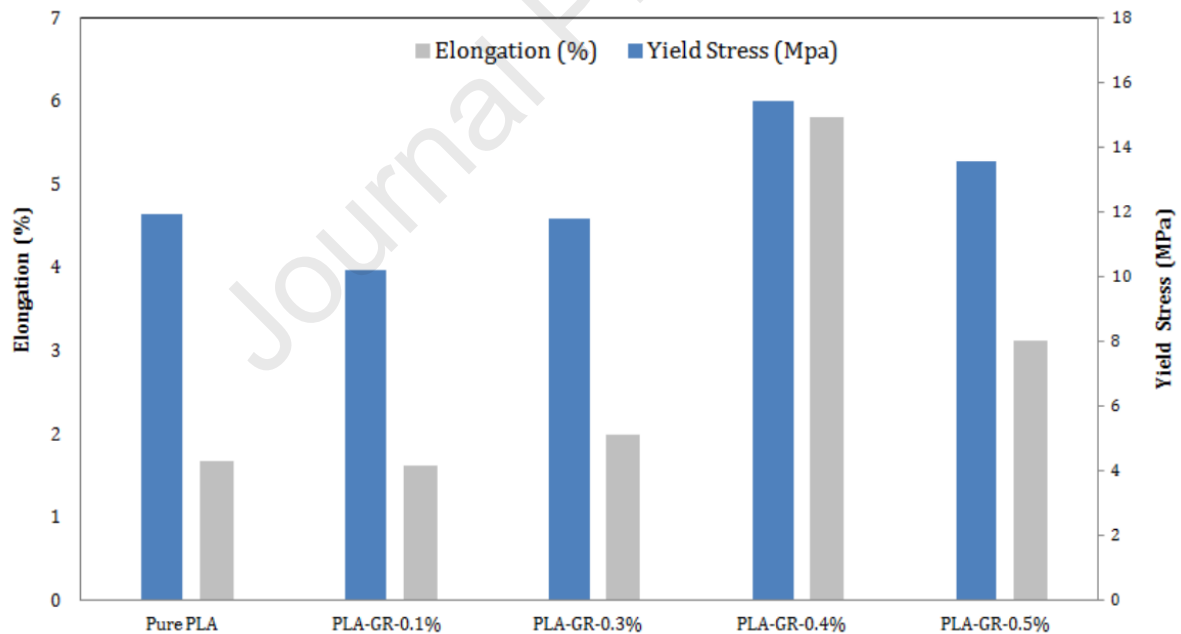


Figure 6(b) Elongation changes at the end of the elastic section and yields stress of pure PLA and PLA/Gr nanocomposites.



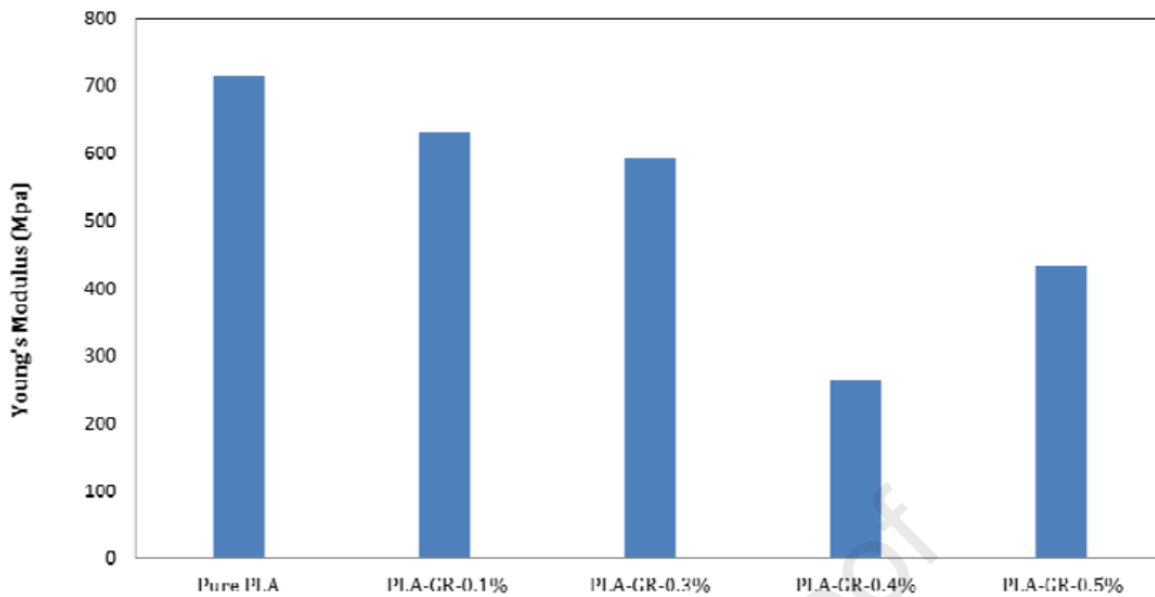


Figure 6(c). Yang modulus changes of pure PLA and PLA / Gr nanocomposites.

According to the obtained results, it is quite visible that with increasing the amount of graphene, the elongation and yield stress has an increasing trend and reaches their maximum in 0.4% PLA / Gr, and then with increasing the amount of graphene, the yield stress and elongation decrease. The reason for this can be the accumulation of particles in the form of lumps in 0.5% PLA / Gr, which these lumps have a destructive effect on the PLA matrix and cause its attenuation. Young's modulus also decreased with increasing graphene content until it reached its minimum at 0.4% PLA / Gr, then Young's modulus increased with increasing graphene content. The results obtained in this test are in accordance with the results of the XRD analysis that the presence of the third peak indicates the presence of limited lumps of graphene particles in nanocomposites of 0.4% PLA / Gr and especially 0.5% PLA / Gr. In almost all research on the mechanical properties of PLA / Gr nanocomposites, the trend of changes has been such that first with increasing the percentage of graphene, there is an improvement in the properties and then the trend is reversed due to the possibility of clumps.

Valapa et al. [27] observed the highest tensile strength and elongation in 0.1-PLA-Gr composite and decreased tensile strength and elongation with increasing graphene content.

Zhang et al. [24] also found the highest young modulus and yield stress at 0.2% PLA / ODAG and the highest breakdown elongation at 0.6% PLA / ODAG, followed by a downward trend. Kim SW et al. [28], the yield stress increased with increasing graphene oxide and increased to 0.5% by mass and then decreased.

#### 4.5. Mechanical resistance test of materials against UV rays

To evaluate the mechanical strength of pure PLA and PLA/Gr nanocomposites against UV rays, the samples were placed in a UV cabin for 20 days and then subjected to tensile tests. The following is shown in Figure 7 of the stress-strain diagram for samples exposed to UV radiation.

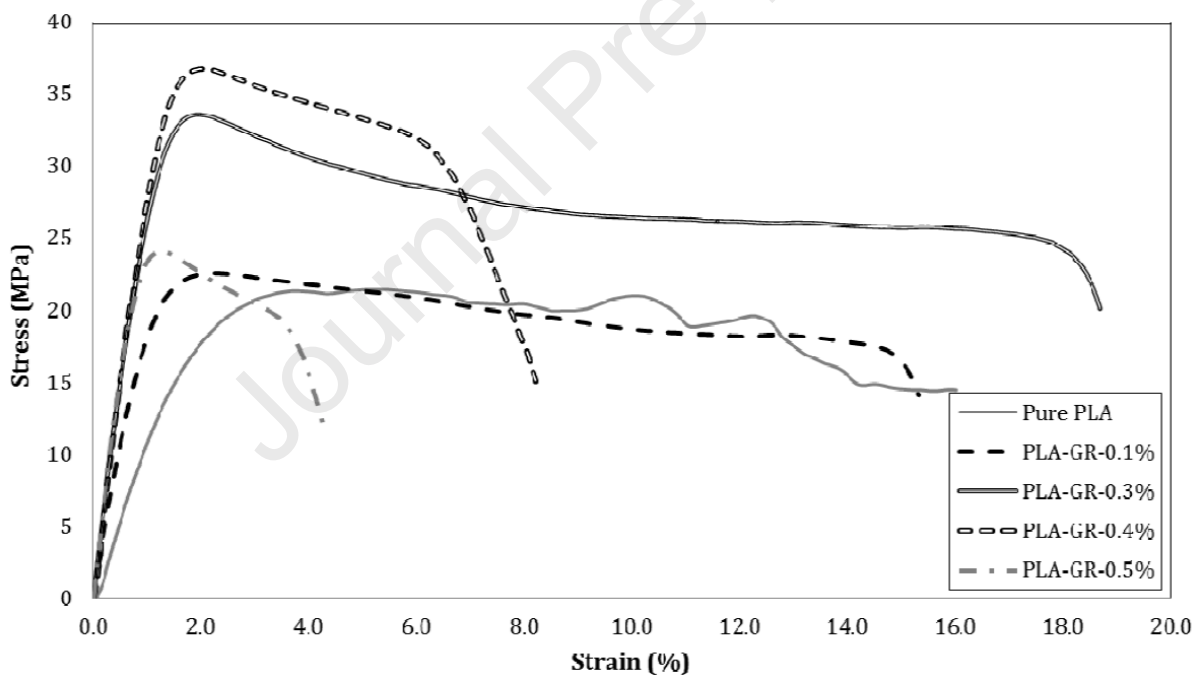


Figure 7. Stress-strain diagram of samples exposed to UV rays.

Figures 8(a-c) compare the mechanical properties of pure PLA and PLA/Gr nanocomposites under the influence of UV rays and without UV rays. With UV exposure, the elongation of PLA/Gr nanocomposites is significantly reduced. There is also a large increase in Young's modulus of PLA/Gr nanocomposites and an increase in yield stress, indicating that UV radiation causes PLA/Gr nanocomposites to become more brittle. In other words, PLA/Gr

nanocomposites are similar to ceramics in that they have low elongation and high yield modulus. UV-Crosslink can be considered as the main reason for the behavior of PLA/Gr nanocomposites under UV radiation, which has led to increased yield stress.

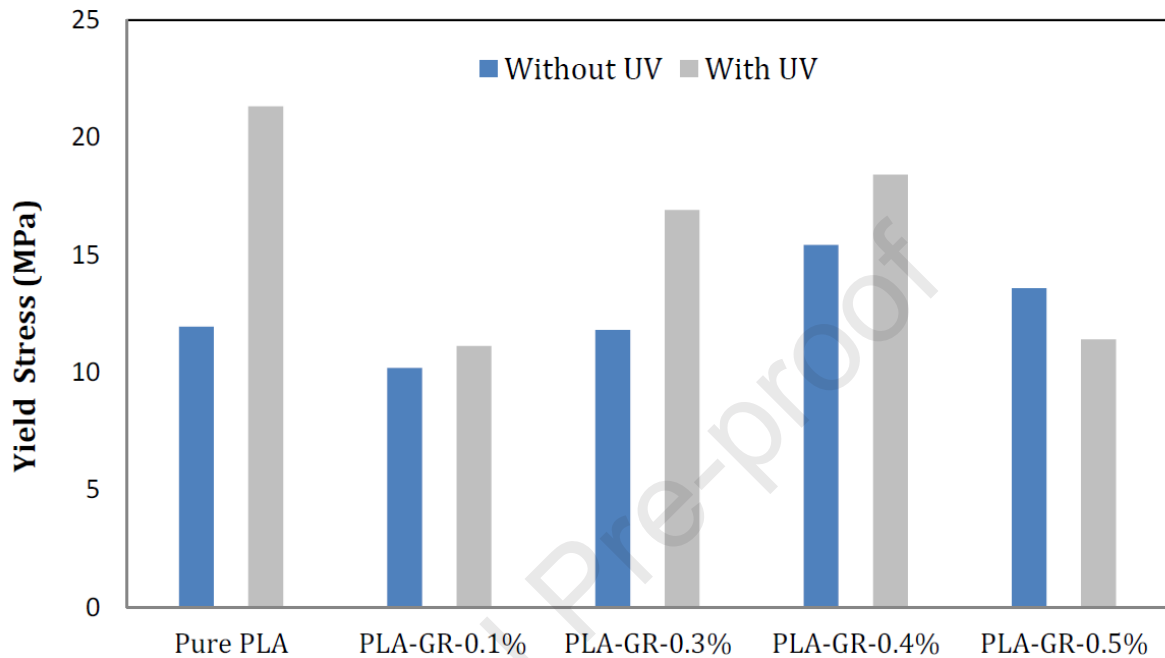


Figure 8(a). yield stress changes of pure PLA and PLA/Gr nanocomposites with and without UV radiation.

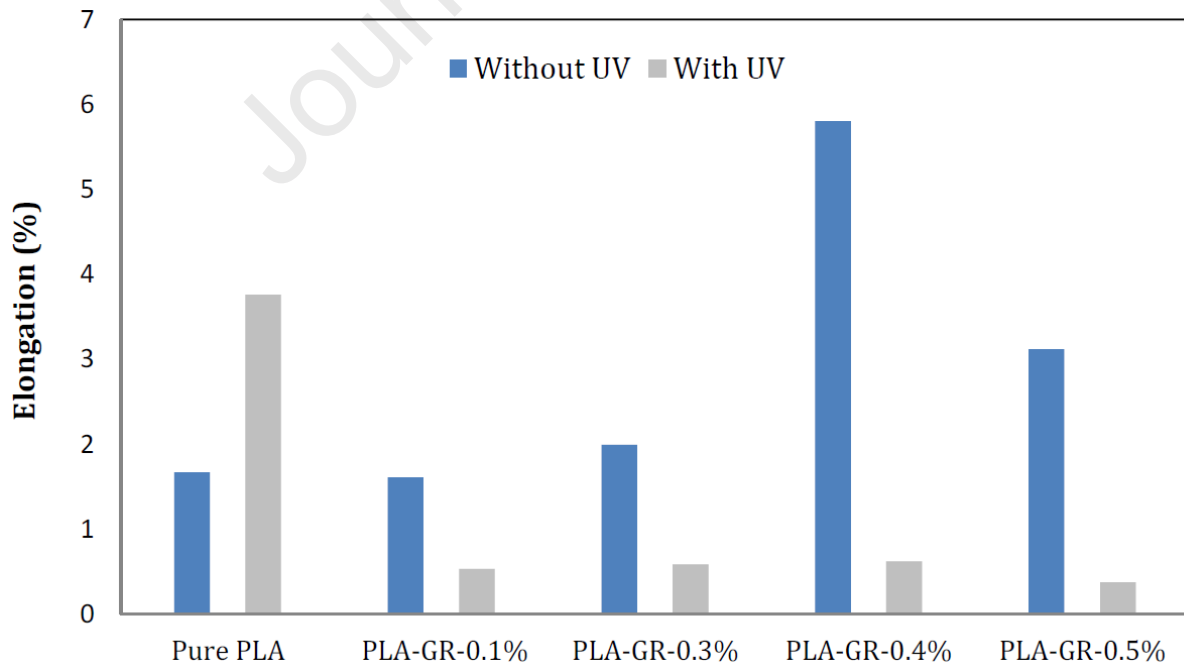


Figure 8(b). Elongation changes at the end of pure PLA elastic section and PLA/Gr nanocomposites with and without UV rays.

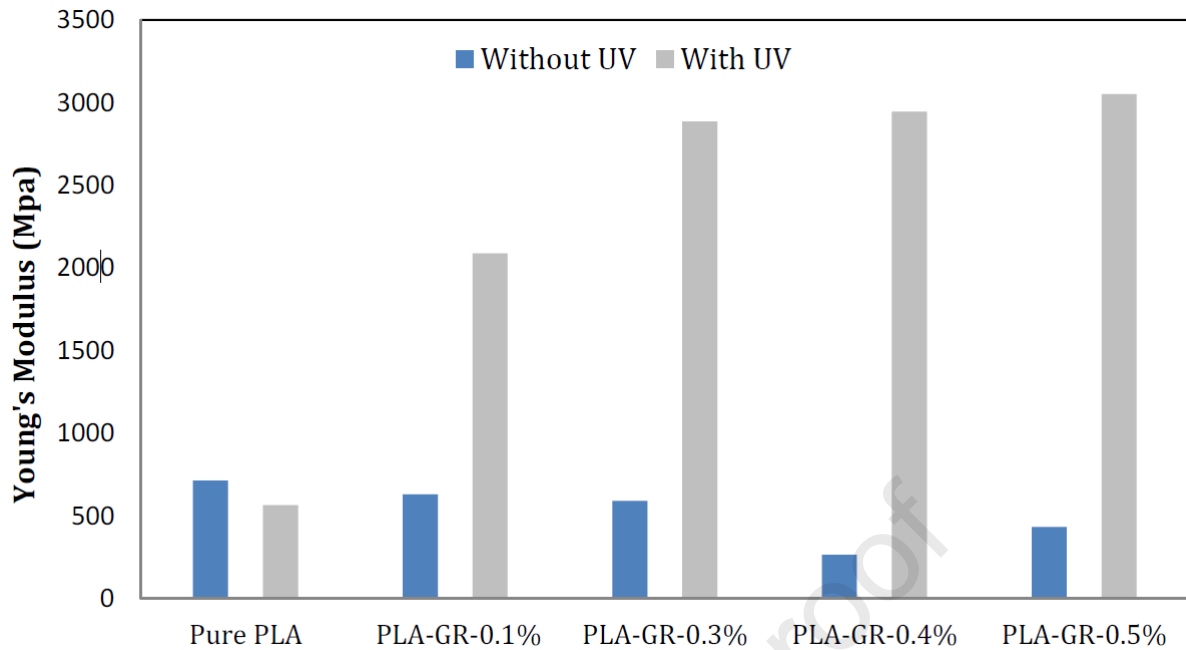


Figure 8(c). Yang modulus changes of pure PLA and PLA/Gr nanocomposites with and without UV.

Huang et al.,[65] the percentage of light passing through PLA and PLA/GONS nanocomposites was obtained in terms of UV wavelength (Fig. 9). As the wavelength increases, the light transmitted through pure PLA increases, while for PLA/GONS nanocomposites the light transmittance changes are very small in terms of wavelength.

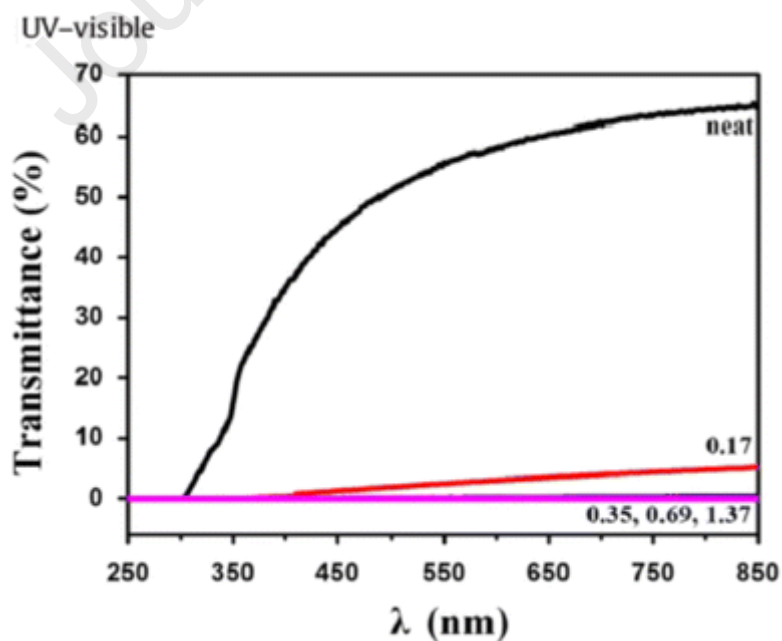


Fig. 9 Percentage of light passing through PLA and PLA/GONS nanocomposites in terms of UV light wavelength ( $T = 25\text{ }^{\circ}\text{C}$ )[65].

Kim et al. [66] investigated the possibility of using graphene oxide nanocomposite films in food packaging film and evaluated the degree of optical transparency. They observed that the addition of GO reduces the transparency of the nanocomposite film due to the increase in light scattering.

Manish Kumar Lila et al. [67] investigated accelerated thermal ageing behavior of bagasse fibers reinforced poly (lactic acid) based bio composites. Specimens of iocomposites were fabricated and exposed to temperature cycles of  $-20\text{ }^{\circ}\text{C}$  and  $65\text{ }^{\circ}\text{C}$  (12 hours each) for 12 weeks and characterized after every 4 weeks of exposure. Tensile and flexural properties exhibited steady improvement on exposure up to 8 weeks, followed by a reduction after ageing for 12 weeks.

Ming-Hung Tsai *et al.* [68] investigated effects of ultraviolet irradiation on the aging of the blends of poly (lactic acid) and poly (methyl methacrylate). They used differential scanning calorimetry to analyze the effect of ultraviolet (UV) irradiation on the physical aging of the blends of poly (lactic acid) (PLA) and poly (methyl methacrylate) (PMMA). The analyses shown the linear decrease of the maximum enthalpy loss of the aged specimen at the equilibrium state with the increase of the aging temperature, and the decreasing rate increases slightly with increasing the UV irradiation dose for the same PLA/PMMA blends. The activation energy associated with the kinetic contribution decreases with the UV irradiation dose for the PLA/PMMA blends of the same compositions.

##### **5. Advantages and Disadvantages polylactic acid polymer /graphene nanocomposites**

The combination of polylactic acid polymer /graphene can potentially create a material with improved properties as compared with those of the individual materials. Graphene acts as a reinforcement in these nanocomposites to enhance the electrical, mechanical, and thermal

properties of the polylactic acid polymer matrix. Moreover, combining a biodegradable and renewable polymer with a high-performance material such as graphene makes polylactic acid polymer /graphene nanocomposites environmentally friendly and attractive for various applications. Table 4 summarizes the characteristics of Advantages and Disadvantages polylactic acid polymer /graphene nanocomposites.

Table 4. Advantages and Disadvantages polylactic acid polymer /graphene nanocomposites.

| composites  | Preparation method                                 | Application   | Advantages and Disadvantages  | Ref   |
|---|--|---|---|-------|
| polylactic acid polymer/<br>graphene                        | Numerically<br>designed interface<br>treatment.    | Biomedical  | Small functional groups can<br>significantly improve the<br>interfacial interactions of these<br>nanocomposites.  | [109] |
| polylactic acid polymer/<br>graphene                        | Stereo complexation.                               | Regenerative<br>medicine, tissue<br>engineering, and<br>other biomedical<br>disciplines | Stereo complexation improved<br>the mechanical qualities and<br>resilience to heat and<br>hydrolysis of polylactic acid<br>polymers   | [110] |
| graphene nanoparticles /<br>polylactic acid polymer         | Melt blending<br>method                            | Medical   | The addition of GNP improved<br>the antibacterial activity of the<br>nanocomposites against <i>L.</i><br><i>monocytogenes</i> , <i>S. aureus</i> , <i>S.</i><br><i>typhimurium</i> , and <i>E. coli</i> . | [111] |
| polylactic acid polymer /<br>Polyvinyl alcohol<br>/graphene | Solution mixing and<br>freeze-drying<br>techniques | To improve the<br>mechanical and<br>thermal   | he addition of graphene<br>improved the mechanical and<br>thermal properties of polylactic  | [112] |

|  |                      |  |   |       |
|--|----------------------|--|---|-------|
|  |                      | characteristics of polylactic acid polymer | acid polymer composites due to the improved dispersion of graphene in the polylactic acid polymer matrix                |       |
| Polyethylene glycol /carboxylated GO-poly(lactic acid) /graphene | Melt blending method | -  | The thermal stability of poly(lactic acid) /graphene nanocomposites is considerably enhanced by adding graphene sheets. | [113] |

## 6. Conclusion

1. Increase in elongation and yield stress by adding graphene nanoparticles and its maximum in 0.4% PLA / Gr and then decrease in yield stress and elongation by increasing the amount of graphene due to aggregation of particles in 0.5% PLA / Gr.
2. Decrease Young's modulus by increasing the amount of graphene and minimize it by 0.4% PLA / Gr and then increase Young's modulus by increasing the amount of graphene.
3. No change in the main peak of polylactic acid in PLA / Gr nanocomposites according to the XRD analysis and as a result no change in the main crystal structure by adding graphene nanoparticles.
4. Observation of the third peak in XRD results in 0.3% PLA / Gr, 0.4%, PLA / Gr, 0.5% PLA / Gr samples due to limited accumulation of graphene particles.
5. Increase of storage modulus and dissipation modulus of PLA / Gr nanocomposites compared to pure PLA.
6. The viscosity of the complex remains constant in pure PLA, 0.1% PLA / Gr , 0.3% PLA / Gr and the viscosity of the complex decreases in 0.4% PLA / Gr , 0.5% PLA / Gr by

increasing the frequency and thus changing the behavior of these two samples Newton to pseudo-Newton.

7. Slight changes of T<sub>g</sub> and T<sub>m</sub> for pure PLA and T<sub>g</sub>. PLA / Gr nanocomposites. Higher PLA / Gr nanocomposites compared to pure PLA can be due to the reduced mobility of polymer chains under graphene.
8. Reduction of crystallization percentage by adding graphene is due to poor accumulation and dispersion of graphene in the PLA matrix.
9. Significant reduction in elongation, very high young modulus, and increased yield stress of PLA / Gr nanocomposites by UV exposure.
10. Creating a similar state of ceramics in PLA / Gr nanocomposites by exposure to UV rays.

Declarations

#### **Data availability**

All data generated or analyzed during this study are included in this published article.

#### **Ethics approval and consent to participate**

Not applicable

#### **Consent for publication**

Not applicable

#### **Competing interests**

The author declare that they have no competing interests.

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Ehsan kianfar: Investigation, writing, reviewing and editing .

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**Declaration of interests**

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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