The Study of Mechanical, Thermal, and Antibacterial Properties of PLA/Graphene Oxide/TiO_2 Hybrid Nanocomposites

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ABSTRACT: *This study attempts to improve the anti-bacterial, thermal and mechanical properties of Poly-Lactic Acid (PLA)/Graphene Oxide (GO) by incorporating the titanium oxide (TiO_2) nanoparticles. For this purpose, the TiO_2 nanoparticles were introduced into PLA/GO films in the content of 1, 3, and 5 wt%. The film samples were prepared by the solution casting method. The mechanical properties were evaluated by a tensile test to report the tensile strength, elongation, and elastic modulus. The thermal properties were investigated by Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) tests, and the agar disk diffusion method was carried out to investigate the antibacterial properties of the film samples. The Field Emission Scanning Electron Microscopy (FE-SEM) images showed the homogenous dispersion of the nanoparticles in the PLA matrix. TGA results showed that incorporating GO and TiO_2 nanoparticles improves the thermal stability of the PLA matrix considerably.*

KEYWORDS: *PLA/GO; TiO_2 nanoparticles; Antibacterial properties; Thermal properties.*

INTRODUCTION

Biological problems have increased the tendency of using biodegradable polymers [1,2]. Poly(lactic acid) (PLA) is a favorite biodegradable and biocompatible polyester formally obtained by condensation of lactic acid extracted from renewable sources such as corn, sugarcane, sugar beet pulp, and cassava [3,4]. PLA is used in various industries for different applications such as food packing, fabrics, and biomedicine (drug delivery, implant, and tissue engineering) [5-7]. However, PLA has some advantages such as suitable thermal stability, high processability, and good mechanical properties, the improvement in hydrophilicity, gas permeability, antibacterial properties, and mechanical properties for long-term applications is necessary. There are various methods containing blending with other polymers, adding plasticizers, and corporation of nanofillers to overcome the limitations of polymers, especially PLA. The addition of nanofillers at low content enhances the mechanical, thermal, electrical, and antibacterial properties of the polymer matrix. The most widely used plastics reinforced nanofillers are nano-clay [8-11], graphene [12], silica [13], carbon nanotube [14], aluminum oxide [15], titanium oxide [16,17].

Recently, Graphene Oxide (GO) has been an attractive nano-filler for researchers to use in polymer matrix nanocomposites due to its unique mechanical properties [18,19] (Young's modulus= 380 to 470 GPa [20]).

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The polar structure of GO, because of oxygen-containing groups such as epoxides, hydroxyls, and carbonyls, promotes the compatibility and interaction with the polymer matrix [21]. *Pinto et al.* [22] incorporated GO, in the content of 0.2 to 1 wt.%, into PLA, and founded PLA containing 0.4 wt% GO has the highest tensile modulus and strength. *Huang et al.* [23] increased the tensile strength of PLA from 60 MPa to 73.2 MPa by the addition of 1.0 wt% of GO- zinc oxide (ZnO). *Cao et al.* [24] improved the temperature for 5% weight loss of PLA by 10 °C, and the tensile strength of PLA from 47.7 MPa to 60 MPa with the introduction 0.2 wt% GO. *Klonos et al.* [25] investigated the thermal behavior of PLA/GO nanocomposites and observed GO decreases the heat capacity step of nanocomposites in the DSC test.

Titanium dioxide (TiO_2) is an important compound that is used in many industries such as the textile industry, food industry, cosmetics, and pharmacy [26]. TiO_2 nanoparticles possess attractive properties such as UV protection, good magnetic nature, good photocatalytic activity, and antibacterial properties [27,28]. *Buzarovska* [29] added TiO_2 nanoparticles to PLA and observed that TiO_2 nanoparticles increased the crystallinity and glass transition temperature (T_g) of PLA films. *Li et al.* [30] investigated the antibacterial properties of PLA/TiO_2 nanocomposite films and found the nanocomposite films showed good antibacterial properties. *Zhuang et al.* [31] found that the addition of TiO_2 nanoparticles in the content of 3 wt% into PLA, improves the mechanical, thermal, and antibacterial properties of PLA significantly. *Mohr et al.* [32] improved the UltraViolet (UV) resistance and biodegradability of the PLA film by incorporating 5 wt% of TiO_2 nanoparticles.

The main purpose of this study is the preparation of polymer films with high mechanical, thermal, and antibacterial properties. For this purpose, GO in the content of 0.4 wt% was used to improve mechanical properties, especially elastic modulus, and TiO_2 nanoparticles in the content of 1, 3, and 5 wt% were used to improve the thermal and mechanical properties of PLA films. Tensile, Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA), and antibacterial tests were carried out on the samples to evaluate the mechanical, thermal, and antibacterial properties.

EXPERIMENTAL SECTION

Materials

PLA grade of Bio-flex®F 6510 with a density of 1.3 g/cm^3, a molecular weight of 197000 g/mol, and a melting point of 160 °C was prepared from Fkur GmbH Co. (Germany). GO with an average thickness of 3.4-7 nm, and TiO_2 (rutile) nanopowder with an average diameter of 30 nm, were supplied from NANOSANY corporation (Iran).

Preparation of PLA/GO/TiO_2 films

Before processing, the materials were dried in a vacuum oven (model of VO49, Memmert Co., Germany) at 80 °C for 24 h. The solvent casting method was used to produce pure PLA and nanocomposite films [22,24,36]. In this method, 5 g of PLA was dissolved in 100 mL of $ChCl_3$(Merck Co., Germany) and stirred with a mechanical mixer (FALC Co., Italy), for 4 h. To prepare PLA/GO nanocomposite films, 0.04 g of GO were dispersed in 10 mL acetone (Iranian Industrial Stone, Pilar Trading Co., Iran) by ultrasonic homogenizer (Hielscher Co., Germany) at the power of 70 W for 30 min, and then added to a solution of PLA/$ChCl_3$ and stirred for 1 h. then the solution was poured into the glass molds. The PLA/GO/TiO_2 hybrid composite solutions containing 1, 3, and 5 wt% of TiO_2 were prepared in the same method. Table 1 shows the composition of the prepared samples. Drying the films was done in two steps; first, the films were dried at room temperature for 10 days. In this step, there is still a significant amount of solvent in the films (about 4 wt.%). In step 2, the films were placed in a vacuum oven at 40 °C for 7 days to remove the remaining solvent. By weighing the films before and after putting them in a vacuum oven, it was found that the films are solvent-free approximately.

Characterization

The morphology of the nanoparticles (GO and TiO_2) and the hybrid nanocomposite films was revealed using Field Emission-Scanning Electron Microscopy (FE-SEM), a model of MIRA3 TESCAN. The films were broken in liquid nitrogen, and after coating the cross-section of the films with a thin layer of gold (about 100 °A), FE-SEM images were taken. The tensile tests were done on the films (with dimensions of 160 mm×20mm×0.3 mm) by H25KS tensile test machine (HOUNSFIELD Co.,

Table 1: The composition of the samples.

sample	GO (wt.%)	TiO_2 (wt.%)	PLA (wt.%)
PLA	-	-	100
PGO	0.4	-	99.6
PGOT1	0.4	1	98.6
PGOT3	0.4	3	96.6
PGOT5	0.4	5	94.6

Salfords, United Kingdom) at room temperature at the speed of 30 mm/min to determine tensile strength, elastic modulus, and elongation. For each sample, 5 tests were done, and their average was reported. DSC test was done in the temperature range of 25 to 200 °C at a heat rate of 10 °C/min using a SANAF DSC analyzer (Iran) to determine thermal properties of the films such as melting point temperature (T_m), glass transition temperature (T_g), crystalline temperature (T_c), melting and cooling enthalpy (to calculate the crystallinity). TGA test was carried out to investigate the thermal stability of the nanocomposite films using a SANAF TGA analyzer (Iran). The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min. The agar disk diffusion method was used to evaluate the antibacterial properties of the samples. The standard strains of staphylocomLus aureus (S. aureus) (ATML: 25923) and E. coli (ATML: 25922) [32], in the form of powder, were cultivated in the culture media of the blood agar (BA) and Tryptic Soy Broth (TSB). Based on Kirby-Bauer method, the microbial suspension of 0.5 MacFarland (1.5×10^8 CFU/mL) was prepared to use for the agar disk-diffusion test. The samples were located on the bacterial agar plate, and the dishes were incubated at 37 °C for 24 h.

RESULTS AND DISCUSSION

Morphology

Fig. 1 shows the dispersion of GO and TiO_2 nanoparticles throughout the PLA film containing 0.4 wt% GO and 3 wt% TiO_2 (PGOT3 sample) in three different magnifications. As can be seen in Fig. 1(a), the nanoparticles are uniformly dispersed within the PLA matrix. Fig. 1.b and c show the dispersion of nanoparticles in higher magnifications and approve the good and uniform dispersion of nanoparticles. Due to the small size of TiO_2 nanoparticles, some small aggregates can be seen in Fig 1.b and c. The planar graphene oxide platelets with a length of about 2 μm embedded in the PLA can be seen in Fig 3.c.

Mechanical properties

The tensile test was performed to evaluate the mechanical properties of the neat PLA, PLA/GO, and PLA/GO/TiO_2 nanocomposite films. The stress-strain curves of the samples have been shown in Fig. 2. The results of the tensile test containing Young's modulus, tensile strength, and strain at the breakpoint (elongation) have been presented in Table 2. Based on the data in Table 2, tensile strength, Young's modulus, and elongation of the film containing 0.4 wt% of GO (PGO) increased by 18%, 32%, and 21%, respectively. The TiO_2 nanoparticles in the content of 1, 3, and 5 wt% were added to PLA/GO films to investigate the effect of TiO_2 nanoparticles on the tensile properties of PLA/GO films. The results show that the introduction TiO_2 nanoparticles decreased Young's modulus of PLA/Go films from 3760 to 3300 MPa, but increased the tensile strength from 39.1 MPa to 41.1 MPa. By increasing the nanoparticle content from 1 to 5 wt%, the tensile modulus and tensile strength increased by 6% and 10%, respectively, and the elongation at the breakpoint decreased by 50%. AmLording to the results, it can be concluded that the TiO_2 nanoparticles improved the tensile strength of the PLA/GO film. Adding GO and TiO_2 nanoparticles increases elongation at the breakpoint compared to pure PLA. This behavior was observed by *Wenhui Li et al.* [30].

Thermal properties

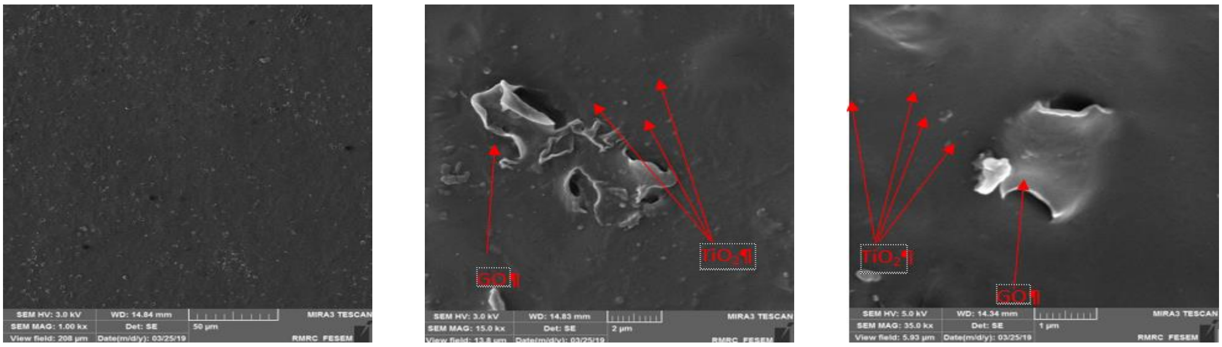
DSC test was performed to investigate the thermal behavior of the nanocomposite films. The melting and cooling diagrams have been shown in Figs. 3 and 4, respectively. The DSC test data such as glass transition temperature (T_g), crystallization peak temperature (T_c), melting peak temperature (T_m), heat of crystallization in the cooling cycle (ΔH_c), the heat of fusion in the melting cycle (ΔH_m), and the degree of crystallinity (χ) have been presented in Table 3. The following formula presents the degree of crystallinity of the samples [34]:

$$\chi_c(\%) = \frac{\Delta H_m + \Delta H_c}{\Delta H_m^c} \times 100 \tag{1}$$

Where ΔH_m^c with a value of 93 J/g is the heat of diffusion for 100% crystallite PLA.

Table 2: Tensile properties of various films.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PLA	2850±120	33.2±2.5	2.40±0.10
PGO	3760±210	39±3.4	2.92±0.12
PGOT1	3300±110	41.1±3.6	5.12±0.23
PGOT3	3450±150	40.2±2.8	3.840±0.11
PGOT5	3490±110	45.1±3.4	2.60±0.15



(a) (b) (c)

Fig. 1: FE-SEM images of TiO_2 and GO after dispersion in PLA matrix (PGOT3 sample) in magnification of a) 1000X, b) 15000X, and c) 35000X.

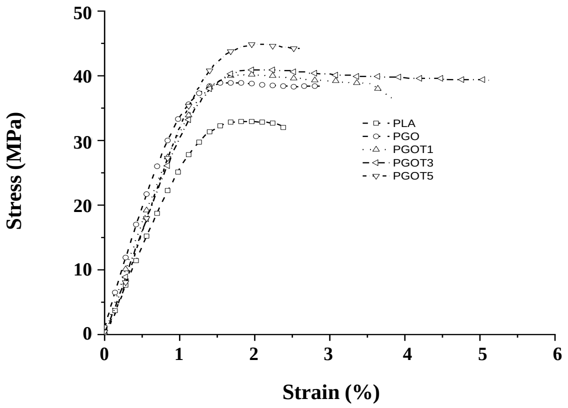


Fig. 2: Stress-strain curve for PLA, PLA/GO, PLA/GO/TiO_2 films.

The data in Table 3 show that GO has no considerable effect on the thermal properties of PLA film, because the values of T_g, T_m, T_c, ΔH_m, ΔH_c, and χ for neat PLA film and PLA/GO film are close together. Based on the data in Table 3, it can be found that by introducing the TiO_2 nanoparticles in the content of 1 wt% into PLA/GO, the T_g increased from 37.7 °C for the pure PLA to 41.8 °C for the PGOT1. This indicates that the nanoparticles could restrict the mobility of the molecular chains of the PLA matrix in PLA/GO/TiO_2 hybrid nanocomposites more compared to a neat PLA sample. The increase in T_g by using the nanoparticles in the PLA matrix was reported in the other literature. Adding the hydroxyapatite and GO nanoparticles increased the T_g of PLA [35,29]. For the PGOT5 samples, the T_g decreased to 38.2 °C. The TiO_2 nanoparticles were not effective on T_c, so the T_c has remained constant. The T_m of the nanocomposite films containing 1 and 3 wt% of TiO_2 is 151.5 °C, which is 3.7 °C higher than neat PLA. This increase in the melting point temperature of PLA has been observed in other research [35]. This increase in melting temperature is due to an increase in lamellae thickness. The degree of crystallinity of neat PLA film is 18.5%, while for the PGOT1 is 25.4 %. Thus, the TiO_2 nanoparticles were effective in providing more nucleation sites in the crystallization of the PLA matrix. *Frone et al.* [36] observed that 2.5 wt% of nano-cellulose increases the degree of crystallinity of PLA from 39% to 47%. *Mukherjee et al.* [37] improved the degree of crystallinity of PLA by 4% by adding 2.5 wt%

Table 3: The DSC data for the film samples

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (Jg^{-1})	ΔH_c (Jg^{-1})	χ (%)
PLA	37.7	147.8	111	8	9.26	18.5
PGO	37.5	146.9	111.1	9.4	9.5	20.4
PGOT1	41.8	151.5	110	13.21	10.49	25.4
PGOT3	41.3	151.5	110.5	11.95	10.92	24.7
PGOT5	38.2	148.5	110.1	10.25	10.63	22.4

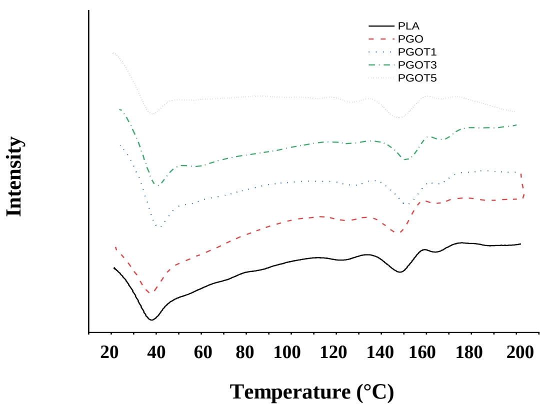


Fig. 3: DSC melting scans for the samples.

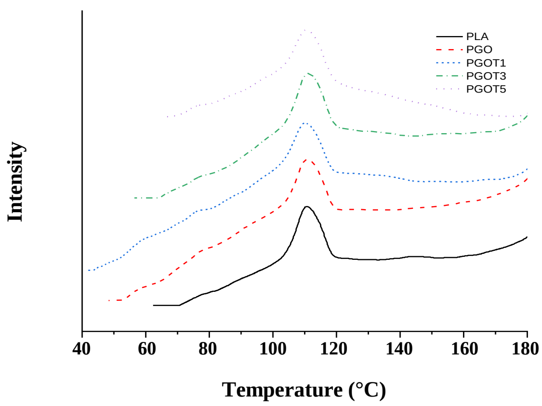


Fig. 4: DSC cooling scans for the samples.

of microcrystal cellulose. The decrease in T_g, T_m, and χ in the PGOT5 sample compared to the PGOT1 sample can be due to the agglomeration of the nanoparticles in the PGOT5 sample.

The thermal stability of the nanocomposite films was studied by TGA analysis. Fig. 5 shows the TGA curve of the PLA/GO/TiO_2 nanocomposite films. As shown in Fig.5, it could be concluded that the neat PLA film and nanocomposite films have suitable thermal properties because the maximum mass loss of the samples is around 350 °C. Two important criteria for expressing the thermal stability of polymer materials in the TGA test are the onset degradation temperature (T_{onset}) and the temperatures at which degraded polymer material is 50%, ($T_{50\%}$). The T_{onset} of neat PLA film is nearly 320 °C and the complete degradation temperature is approximately 455 °C. T_{onset} for PGO, PGOT1, PGOT3, and PGOT5 is 322 °C, 325 °C, 325 °C, and 330 °C, respectively, showing the T_{onset} for all the nanocomposite films are higher than neat PLA films. $T_{50\%}$ of the samples are 389 °C, 405 °C, 403 °C, 393 °C, and 398 °C for pure PLA, PGO, PGOT1, PGOT3, and PGOT5, respectively. From data obtained from TGA test for T_{onset} and $T_{50\%}$, it could be concluded that the nanoparticles (especially GO) improved considerably the thermal stability of the PLA matrix at high temperatures. This behavior can be due to suitable interaction between PLA matrix and GO nanoparticles by van der Waals force and hydrogen bond during the mixing process [38], or heat barrier characteristic of TiO_2 nanoparticles at the beginning of the thermal decomposition stage [39,40]. The interaction between the epoxide group of GO and hydroxyl group of PLA through hydrogen bonding can improve the thermal stability of PLA matrix. On the other hand, the high aspect ratio of GO prevents the small gaseous molecules' emission during thermal degradation. In TiO_2 structure, as shown in Fig. 6, there are dangling bonds (unpaired electrons) on the surface of O and Ti. The PLA molecules can interact with these dangling bonds to increase crosslinking, and as a result, the thermal stability could improve.

Antibacterial properties

The antibacterial test was done by the agar disk diffusion method. In this method, the circular samples in diameter of 20 mm are cut from the film samples, and next placed on the Mueller Hinton Agar (MHA) plate on which positive

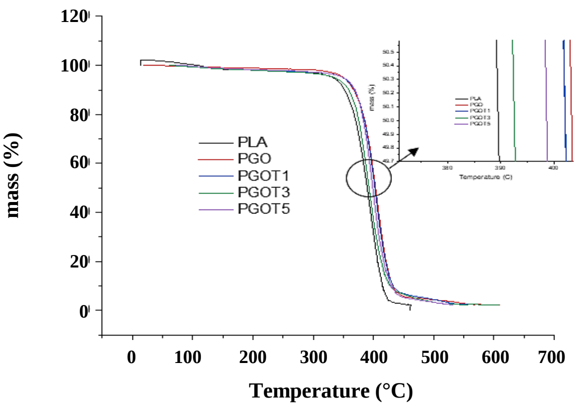


Fig. 5: TGA curves of the PLA/CNF/TiO2 nanocomposite films.

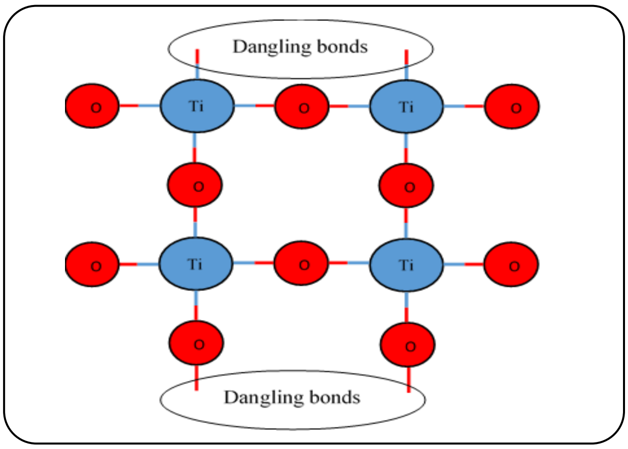


Fig. 6: Molecular structure and dangling bonds of nano-TiO2.

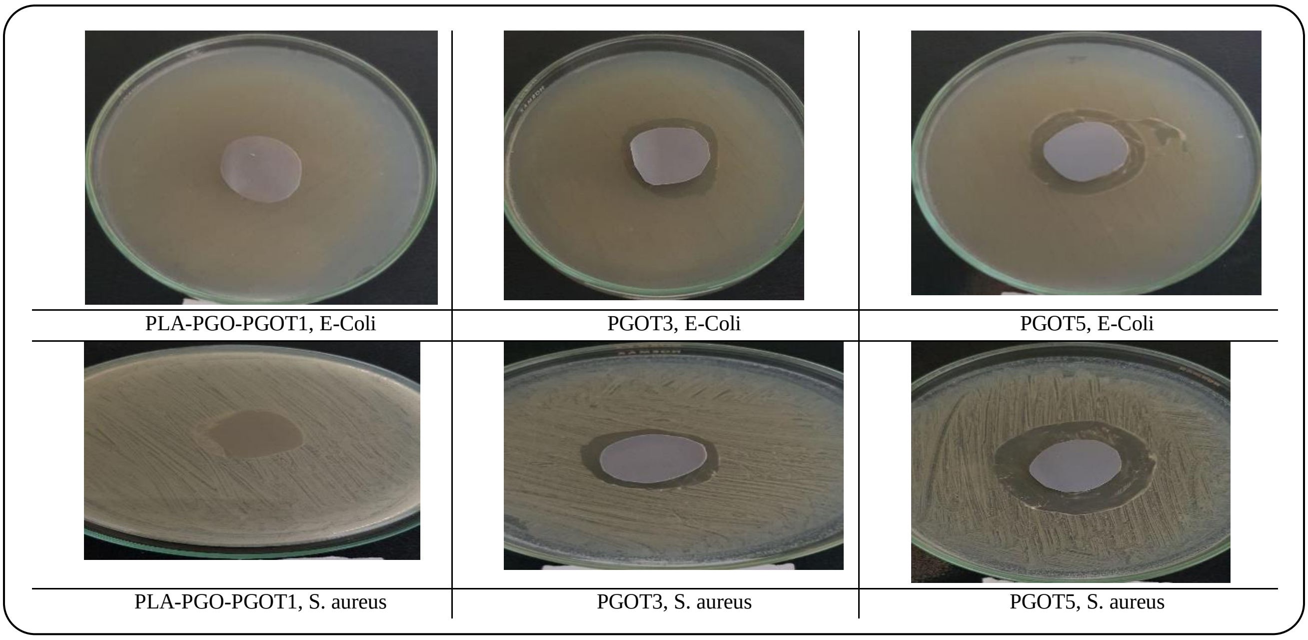


Fig. 7: Sample images in agar disk-diffusion test.

the strain of S. aureus and negative strain of E. coli have been cultivated. Then the circular samples are transferred to the incubator at a temperature of 37 °C and kept for 24 h, and finally, the diameter of the inhibition growth zone is measured. The diameter of the inhibition growth zone indicates how much the nanoparticles have been able to prevent the growth of the bacteria. The higher antibacterial property of the nanoparticles produces a larger diameter of the inhibition growth zone. Fig. 7 shows the images of the samples in the agar disk diffusion test. The diameter of the inhibition growth zone for the samples has been presented in Table 4. Based on Fig. 7 and Table 4, it can be seen that for the neat PLA, PGO, and PGOT1 films, no inhibition growth zone is observed for both bacteria (S. aureus and E. coli). This indicates that the GO nanoparticles have no effect on the antibacterial properties of the PLA film. In the PGOT1film sample, due to the low content of TiO_2 nanoparticles (1 wt.%), there no inhibition growth zone is observed too. By increasing the TiO_2 nanoparticles content from 1 wt% to 3 wt%, the inhibition growth zone is observed, as the diameter of inhibition growth is 26 mm for E-Coli and 29 mm for S. aureus. Higher loading of TiO_2 nanoparticles enhanced the inhibition diameter to 32 mm for E-Coli, and 41 mm for S. aureus. These results indicate the considerable effect of the TiO_2 nanoparticles on the inhibition of bacterial growth. The TiO_2 nanoparticles could effectively kill the bacteria due to the very small size of the TiO_2 particles which generate

Table 4: The diameter of the inhibition growth zone of the samples.

Sample / Bacteria	PLA-PGO-PGOT1	PGOT3	PGOT5
E-Coli	20 mm	26 mm	32 mm
S. aureus	20 mm	29 mm	41mm

many electron-hole pairs. The antimicrobial mechanism of TiO_2 nanoparticles is these electron-hole pairs, which induce a redox reaction on those microorganisms [41]. By comparing the results for two different strains of E-Coli and S. aureus, it can be found that E-Coli strain has shown greater resistance to growth. In other words, TiO_2 nanoparticles have better prevented the growth of staphylocomLus aureus strains compared to E-Coli strains. *Li et al.* [16] found that introducing the 5 wt% of TiO_2 nanoparticles can improve the antibacterial of PLA film by 50% for application in the food packaging industries.

CONCLUSIONS

In this research, the effect of GO and TiO_2 nanoparticles on the thermal properties, mechanical properties, and antibacterial properties of PLA matrix polymer was investigated. It was found that with the incorporation of nanoparticles into the PLA matrix, tensile strength, tensile modulus, and elongation at the breakpoint increased. The maximum improvement of tensile strength and tensile modulus was observed in PGOT1 (41.1 MPa) and PGO (3760 MPa), respectively. The DSC scans showed that TiO_2 nanoparticles enhanced the T_m, T_g, and χ% of PLA matrix, but GO had no effect on T_m, T_g, and χ%. By incorporating 1wt.% of TiO_2 into PLA, the χ, $T_{m,}$ and T_g of PLA increased from 18.5%, 147.8 °C, and 37.7 °C to 24.7%, 151.5 °C, and 41.8.7 °C respectively. Based on TGA results, the thermal stability of the nanocomposite films improved considerably by introducing GO and TiO_2 nanoparticles. T_{onset} of PLA improved from 320 °C to 330 °C for PGOT5, and $T_{50\%}$ of PLA improved from 389 °C to 405 °C for PGO. The PLA/GO nanocomposite film containing TiO_2 nanoparticles inhibited positive bacteria of staphylocomLus and negative bacteria of E-Coli due to the bacterial inhibition ability of TiO_2 nanoparticles. The results showed that TiO_2 nanoparticles have better prevented the growth of staphylocomLus aureus strains compared to E-Coli strains. The inhibition growth diameter increased from 20 mm to 32 mm in the PGOT5 sample for E-Coli, and from 20 mm to 41 mm for staphylocomLus aureus.

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