Study the mechanical and thermal properties of biodegradable polylactic acid/polyethylene glycol nanocomposites

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Abstract
Polylactic acid (PLA) is biodegradable aliphatic polyester well suited for packaging applications. The thermal, mechanical properties of polylactic acid-based nanocomposite films that were prepared by casting method with polyethylene glycol (PEG), and nano (Titanium oxide and Silver) were studied. FTIR of PLA blend and nanocomposite were successfully to appear the miscibility and structure of blend and nanocomposites. The mechanical properties of PLA/PEG blend was show that the tensile strength and modulus of the blends decreased with addition of PEG for 6.3MPa and 1.2GPa respectively. The increase in elongation % that mean improved the ability of PLA to plastic deformation. The Young modulus of PLA/PEG/nano filler composites showed improvement while nano (TiO2 and Ag) concentration was at 5% wt (2.6 and 3.1) GPa respectively. The blend of PLA/PEG up to 80/20 incorporation reduced the (Tg) of neat PLA from (52 to 40) °C and were increased in (TiO2 and Ag) nano composites significantly (55, 60) °C respectively.

Key Words: Polylactic acid, polyethylene glycol, nano (TiO2, Ag), thermal, mechanical and water absorption.

Introduction
PLA is a biodegradable thermoplastic polyester and has attracted increasing attention due to their potential applications as biomedical and environment friendly materials. Polylactic acid (PLA) is the most attractive biodegradable polymer for food packaging applications by several advantages such as its high transparency, good mechanical properties, renewable origin and biodegradation [1]. PLA is rigid and brittle below the glass transition temperature (Tg) which is in the range of 50-60°C so plasticization is the good alternative in its various applications. Polyethylene glycol soluble in water shows hydrophilicity and biocompatibility and plasticizers is frequently used, not only to improve the process-ability of polymers, but also to increase the flexibility and ductility of glassy polymers and decrease the glass transition temperature of the polymer, meaning the plasticizer and polymer must be miscible[2]. Typically, amounts from 10 to 20wt% plasticizers(PEG) are required to provide a substantial reduction of the glass transition temperature (Tg) of the PLA matrix and adequate mechanical properties and can be any biodegradable product, sufficiently nonvolatile, with a relatively low molecular weight to produce a desired decrease in Young’s modulus value and increase in impact strength [3]. PLA plasticization is required to improve PLA ductility. Polyethylene glycol (PEG) has been used as PLA plasticizers increase the PLA thermal stability, which is detrimental for food packaging use. Nanomaterials for food packaging include metal, ceramic, paper and inorganic nanoparticles such as silica, titanium oxide or metal such as silver was usually considered to be an effective method to improve the properties of materials by interaction with components. Since the properties of films were settled by factors such as crystalline structures of ingredients, morphologies of films and molecular interactions, the investigation about the influences of inorganic nanoparticles on these properties will be highly necessary[4]. The objective of this investigation was to explore the effects of titanium oxide, silver on the PLA/PEG blend films, including structure, thermal, and mechanical properties.

Materials
Polylactic Acid PLA with density 1.25 g/cm³ was supplied by (Shenzhen Esun Industrial Co., Ltd. Chain) and polyethylene glycol with density of 1.25 g/cm³ was supplied from Aldrich (USA). TiO2 nanoparticles with average diameter of the particles was about 20 nm, nano silver Ag with average diameter of the particles was about 15 nm.
Perpetration method
Pure polylactide films were prepared by solution casting method by using chloroform. Films were cast on the glass plates and then kept at 60°C in room temperature for 24 hour to ensure complete solvent removal. PLA/PEG blend prepare with concentration of 80wt% PLA blended with 20 wt% PEG. Nanocomposite films were prepared by add titanium oxide and silver swollen in chloroform by mixing for 24 hours while polylactide dissolved in chloroform then solution was sonicated with ultrasonic probe sonicator (MISONIX 20±0.05 kHz) for an hour to increase distribution. The amount of TiO2 and Ag in PLA /PEG was 5wt%. Determination of Thickness of PLA and PLA/PEG blend PLA/PEG/5wt%(TiO2,Ag) composites calculated by electronic digital is 110µm.

Fourier Transform Infrared (FTIR) of PLA, PLA/PEG and PLA/PEG/5wt%(TiO2, Ag) FTIR analysis gave information on the chemical structures of the nanocomposites, presence of polylactide and titanium oxide. IR spectra were taken in the range of 400 to 4000 cm⁻¹ with a FTIR Schimadzu 8201 Model. 48

Mechanical Properties of PLA and PLA/TiO2 Films
According to ASTM D-882 standard modulus of elasticity, tensile strength, and percent elongation equipped with a 5 kg load cell in tensile mode. Tested films were cut in 10 mm width and 80 mm in length. Tensile strength (σs), Young’s modulus (E) were determined according to the following equation:

\[ \sigma_s = \frac{F}{A} \]  \[ E = \frac{F L_0}{A \Delta L} \]

Where \( F \): force exerted on an object under tension, \( L_0 \): original length, \( A \): cross section area, \( \Delta L \): length of the object changes

Thermal Analysis of PLA, PLA/PEG and PLA/PEG/5wt%(TiO2, Ag)
Differential Scanning Calorimeter (DSC) using (Shimadzu DSC-60) was performed to determine glass transition temperature \( T_g \), \( T_m \), \( X_c \), where \( T_g \) regarded as the most important parameter for evaluating the thermal properties of polymer and polymer matrix composites. Initially films were heated up to 250°C with the heating rate 5°C/minute, the analyses were performed in a dry nitrogen atmosphere. Melting and cold crystallization temperatures and enthalpies \( (T_m, T_c, \Delta H_m \text{ and } \Delta H_c) \) were determined from the first heating scans while glass transition temperature \( (T_g) \) were measured from the heating and cooling scans. Crystallinity was calculated by equation (3)[5]

\[ X_c = \frac{\Delta H_m - \Delta H_c}{93.1} \]

Where: \( X_c \): degree of crystalline, \( \Delta H_m \): enthalpies of fusion and \( \Delta H_c \): enthalpies of crystallization, 93.1 J·g⁻¹ is the enthalpy of fusion of 100% crystalline polylactic acid.

Result and Dissections
Fourier Transform Infrared (FTIR) Analysis of PLA and PLA/TiO2 Films:
The PLA spectrum (Fig. 1) shows the bands CH3 stretching at (3000-2850)cm⁻¹, 3421 cm⁻¹ O–H, and C=O stretching vibration (2343-2035 cm⁻¹), 2921 cm⁻¹ corresponding to the –CH2– asymmetric and symmetric stretching vibrations, 1414 for the –CH3 bending vibration, (934 - 851) cm⁻¹ for C–C single bond, the strong C=O absorption band at 1736 cm⁻¹, C-O-C asymmetrical and symmetrical valence vibrations were found at 1150 cm⁻¹. These statements are similar those described by Nikolic et al., 2010 [6]. Bending PLA/PEG appear the absorption bands at 3246 cm⁻¹ was due to the O–H stretching band, 2901 cm⁻¹ was due to the aliphatic C–H stretching, 1442, 1374 and 1339 cm⁻¹ were due to C–H bending vibrations, and also the combination band of O–C–H and C–O–H deformation is calculated from 1442 to 1339 cm⁻¹. Then the in plane C–H and O–H deformation from 1220 to 998 cm⁻¹ can be observed. In the region from 1145 to 554 cm⁻¹, the C–O and C–C groups vibration modes are present and the carbohydrates generally show their characteristic bands. PLA/PEG and PLA/PEG nanocomposite shows almost same absorption peaks as pristine PLA with agree with Buong Woei Chieng et.al [7].
Mechanical properties:

PLA materials are stiff, brittle and exhibit limited extendibility. PLA /PEG blend is able to increase the free volume between polymeric chains. In doing so, the ease of movement of polymeric chains with respect to each other is dramatically enhanced. The addition of plasticizers to edible film is required to overcome film brittleness caused by extensive intermolecular force. The prepared new ductile materials had very high elongation at break (increased by 10–25 times when compared to neat PLA), but with lower tensile strength [8].

Fig(1) FTIR spectra of PLA, PLA/PEG blend and PLA/PEG/5wt%(TiO2, Ag) nanocomposite.
The tensile strength and Young Modulus of PLA, PLA/PEG blend and PLA/PEG/5wt % (TiO₂, Ag) nanocomposite are shown in Table (1). Usually the addition of PEG increased the elongation at break while the tensile strength and Young’s modulus were decreased. In packaging, a plasticizer is a substance added to materials to impart flexibility, workability, and elongation. Showing more flexibility in the blends that appear in low contact 20 wt % PEG and agree with Kullawadee Sungsanit [9] were investigated the plasticized PLA, with 20 wt% of PEG (MW = 1.5 x 10³) by melt blending. They found that the addition of PEG to PLA led to a decrease of both tensile strength and elasticity modulus but an increase of percentage elongation at break. In addition nano (TiO₂ and Ag) that appear increase in tensile strength , and Young Modulus because a good distribution of nano TiO₂ and Ag particles in the PLA/PEG blend solution.

### Table (1): Mechanical properties PLA, PLA/PEG blend and PLA/PEG/5wt % (TiO₂, Ag) nanocomposite

<table>
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<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Young modulus (GPa)</th>
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<tbody>
<tr>
<td>PLA</td>
<td>29</td>
<td>2.3</td>
</tr>
<tr>
<td>PLA/PEG</td>
<td>6.3</td>
<td>1.2</td>
</tr>
<tr>
<td>PLA/PEG/5wt% TiO₂</td>
<td>33</td>
<td>2.6</td>
</tr>
<tr>
<td>PLA/PEG/5wt% Ag</td>
<td>37</td>
<td>3.1</td>
</tr>
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Differential Scanning Calorimetry (DSC) Analysis

Thermal analysis of PLA and its blends has of great technological importance in flexible food packaging. DSC results given together in the Table 2, variations in glass transition, melting and crystallization temperatures as well as degree of crystallinity of PLA, PLA/PEG blend and PLA/PEG/5wt% (TiO₂, Ag) nanocomposite were observed. The Tg for all samples is seen Fig.(3) Such an observation Tg of neat PLA (52°C) and decreased in the case of PLA/PEG. The addition of PEG plasticizer lowered the glass transition temperature (Tg) and increased the crystallinity and crystallization rate of the blends as expected. This was attributed to the enhanced segmental motion of the PLA molecular chains. Plasticizer lowers Tg and makes material more flexible. Plasticizer interacts with the polymer chains on the molecular level as to speed up its visco-elastic response (or increase chain mobility) [10]. PLA is crystallisable at higher temperature than the PEG crystallization temperature. Thus, during the formation of PLA crystals, plasticizers might slow down the formation of PLA crystalline structures because they interfere in spherulites growth since they are present in fold surfaces of crystalline lamellae. In addition some amounts of PEG probably could be trapped in the intra-spherulitic region of PLA and led to hindering the crystallization of PLA. Nevertheless, the addition of more wt% of PEG would be able to enhance the crystallization rate of PLA. For that reason, the addition of a plasticizer would increase the polymer chain mobility and would enhance the crystallization rate by reducing the energy required during crystallization for the chain folding process [10,11].In PLA/PEG/5wt% (TiO₂, Ag) increase in Tg, Xc and Tc, this may be due to the favorable interaction between PLA, PEG and (TiO₂, Ag) particles and strong adsorption which appear the chemical interaction in FTIR (refer to Fig1) between the PLA, PEG and (TiO₂, Ag) nanoparticles.

### Table (2): DSC of PLA, PLA/PEG blend and PLA/PEG/5wt % (TiO₂, Ag) nanocomposite

![Stress-Strain](image-url)
2) Samples 3) Tg° 4) Tc° 5) Tm° 6) Xc% 

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<tr>
<td>7) PLA</td>
<td>8) 52</td>
<td>9) 90</td>
<td>10) 168</td>
</tr>
<tr>
<td>12) PLA/PEG</td>
<td>13) 40</td>
<td>14) 93</td>
<td>15) 168</td>
</tr>
<tr>
<td>16) PLA/PEG/5wt%TiO2</td>
<td>17) 55</td>
<td>18) 98</td>
<td>19) 168</td>
</tr>
<tr>
<td>21) PLA/PEG/5wt%Ag</td>
<td>22) 60</td>
<td>23) 98</td>
<td>24) 168</td>
</tr>
</tbody>
</table>

Fig(3) DSC of PLA, PLA/PEG blend and PLA/PEG/5wt%(TiO2, Ag ) nanocomposite

Conclusion

1- the addition of PEG increased the elongation at break while the tensile strength and Young’s modulus were decreased because increase the free volume between polymeric chains. In addition nano (TiO2 and Ag ) that appear increase in tensile strength and Young Modulus because a good distribution of nano TiO2 and Ag particles in the PLA/PEG blend solution.

2- The addition of PEG plasticizer to PLA is lowered the glass transition temperature (Tg) and increased the crystallinity and crystallization rate of the blends as expected this was attributed to the enhanced segmental motion of the PLA molecular chains.

3-In PLA/PEG/5wt%(TiO2, Ag) increase in Tg, Xc and Tc, this may be due to the favorable interaction between PLA, PEG and (TiO2, Ag) particles appear in FTIR bonds.

Reference


