Physical properties of plasticized PLA/HNTs bionanocomposites: effects of plasticizer type and content

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Abstract. Halloysite nanotubes (HNTs) reinforced polylactic acid (PLA) nanocomposite films were utilized for different applications, such as packaging, drug recover and other applications. The incorporation of plasticizer into polymer nanocomposites modifies some of their functional and physical properties, such as increasing flexibility, moisture sensitivity, in addition to other functional properties. However, the effects of Polyethylen glycol (PEG) and sesame oil (SO) on selected physical properties (moisture content (MC), contact angle (CA) and water vapor permeability (WVP)) of PLA/HNTs bionanocomposite films were examined. The plasticized PLA/HNTs (5 wt % HNTs loading) bionanocomposite films were prepared using the solution casting method at room temperature. The concentrations of each plasticizer that used indivisually were (0, 10, 20 and 30 wt %). Results show that the increasing of PEG content led to increase in moisture content and water vapor permeability and decrease in contact angle of the films. On the contrary, the increasing of SO levels led to decrease in moisture content and water vapor permeability and increase in contact angle of the films. Differences in measured physical properties of films with plasticizer type and concentration may be attributed to differences in the hydrophilic and hydrophobic properties of the plasticizers. SO was the plasticizer that showed the most interested effect (low moisture content and water vapor permeability) on PLA/HNTs films for food packaging applications compared to PEG.

1. Introduction
Considerable attention has been given to biodegradable polymers as potential candidates for packaging due to the aforementioned challenges posed by non-degradable polymers. Biodegradable polymers are either obtained from biological resources (renewable resources) or from petroleum feed-stocks (non-renewable resources) and offer means of keeping a sustainable development of a technology that is both ecologically and economically attractive. To date, biodegradable polymers are considered as potential materials that can reduce waste disposal of packaging materials and greenhouse effect, as less carbon dioxide will be released into the atmosphere [1].

The development of environmentally-friendly and biodegradable polymeric materials has attracted extensive interest in materials science. Within biodegradable polymeric materials, Polylactic acid (PLA) is one of the best candidates particularly suitable for different application including of biomedicine, pharmaceutical and food packaging. Since it has a biodegradable composition, it is primarily used in developing bioplastic products such as disposable tableware, compost bags and loose-fill packaging. PLA is used in food-packaging industry either for hot drinks and beverages where they shape the lining of the disposable (yet compostable) cups or for whole cups of cold drinks, both should be biodegradable. A shorter polymer of lactic acid known
as OLA or Oligolactic acid had been in use within the pharmaceutical industry to act as a surfactant for liquids [2].

Polymer nanocomposites (PNC) are a new class of materials which has promising potential future applications such as high-performance materials. The main feature of the polymer nanocomposite basically consists of a host polymer that is reinforced with nanosized inorganic fillers. The nanofiller will significantly impact the overall macroscopic properties of the host polymer. The interfacial interaction between organoclay and matrix as opposed to conventional composites as well as the nanometre scale pertaining to dispersed fillers both offer the reason for the enhanced properties of nanocomposites [1-3].

Halloysite nanotubes (HNTs) reinforced polymer nanocomposites are gaining extensive popularity both from academic and industrial sectors due to their improved mechanical, thermal, electrical and fire-retardant properties. The unique features of HNTs such as high length to diameter ratio (L/D), nanoscale lumens, and high-temperature resistance are some of the reasons behind its widespread usage in various application sectors. Moreover, HNTs are abundantly available from nature, environmentally friendly material and biocompatible and hence find applications in the biomedical field, alone as well as with various polymer matrices [4].

However, the brittleness problem is still one of the inherent limitations which inhibits the extensive applications of PLA/HNTs nanocomposites, this problem can be solved by addition the plasticizers [5]. The aim of this work was to investigate the effect of polyethylene glycol and Sesem oil on some physical properties of PLA/HNTs bionanocomposites films, such as moisture content (MC), contact angle (CA) and water vapor permeability (WVP).

2. Experimental

2.1. Materials

PLA (grade 4032D) was kindly supplied by NatureWorks Ingeo™, USA. Halloysites Nanotubes (HNTs) used to reinforce PLA was purchased from Sigma-Aldrich chemicals company. Sigma Aldrich provided (PEG) having an average molecular weight of 400g/mole in liquid state. The SO, was purchased from a local grocery store KL, Malaysia.

2.2. Preparation of plasticized PLA/HNTs bionanocomposites

Plasticized polyactic acid/HNTs bionanocomposites with two different plasticizers (hydrophilic plasticizer polyethylene glycol (PEG) and hydrophobic sesam oil (SO) have been prepared via solution casting method at room temperature (23 ± 2 ºC). The method used in this study has been utilized by Al-Mulla et al with some modifications [6]. Table 1 lists the amounts of UHP HNTs and PLA/plasticizer that had been used in this research.

| Plasticizer loading (wt.%) | Sample Identity | Weight of PLA (g) | Weight of plasticizer (g) | Weight of HNTs (g) |
|---------------------------|-----------------|-------------------|--------------------------|-------------------|
| 0                         | PLA/HNTs        | 4.75              | 0                        | 0.25              |
| 10                        | PLA/HNTs-PEG10  | 4.25              | 0.5                      | 0.25              |
|                           | PLA/HNTs-SO10   |                   |                          |                   |
| 20                        | PLA/HNTs-PEG20  | 3.75              | 1                        | 0.25              |
|                           | PLA/HNTs-SO20   |                   |                          |                   |
| 30                        | PLA/HNTs-PEG30  | 3.25              | 1.5                      | 0.25              |
|                           | PLA/HNTs-SO30   |                   |                          |                   |

2.3. Film moisture content

A digital scale was used to weigh the film samples and the weights were recorded as Wi. The samples were weighed again after drying for a whole day below 50 °C, and the second weight was recorded as Wf. Eq. 1 was applied to assess the moisture content for the whole set of film samples. This process was repeated in triplicate in order to measure an average moisture content for each film.

\[ \text{Moisture content} = \frac{\left( \text{Wi-Wf} \right)}{\text{Wi}} \times 100 \]  \hspace{1cm} (1)

Where Wi and Wf symbolize initial and final weights of film sample, respectively. This method was used by Sanyang et al., (2015) with some modifications [7].

2.4. Contact angle
Contact angle (θ) measurements of the PLA/HNTs and plasticized PLA/HNTs films were carried out using a goniometer (Rame-Hart model 250 - Standard Goniometer-Tensiometer equipment) under room temperature. The medium was water and the droplet size was 4 μL. A total of 10 measurements at different places on the films were taken for each concentration.

2.5. Water vapour permeability

According to ASTM E96-95 and including a few modifications, WVP or water vapor permeability test was applied within this research. The test included using 20 g of silica gel within cylindrical cups. The open ends of the cylinders were sealed using circular films. The test included measuring the cups’ weights prior to keeping them in a relative humidity chamber having a relative humidity of 75 ± 2% and a temperature of 25 °C. To get this level of humidity, the test used a saturated solution of NaCl kept at 25 °C. A periodic set of measurements was implemented for the cups until the state of equilibrium was begotten. All increments in weight were observed and noted down, the WVP was obtained through the following calculations:

\[
WVP = \frac{(m \times d)}{(A \times t \times P)}
\]

Where m(g) represents the increment in weight pertaining to the test cup, d(m) represents the thickness of the film, A (m²) represents the area pertaining to the exposed film, t(s) represents time duration needed for permeation and P(Pa) represents the partial pressure across the films (of the water vapor). All results had been expressed in terms of g/s.m.Pa.

3. Results and Discussions

3.1. Film moisture content (MC)

Packaging films should maintain moisture levels within the packaged product. Therefore, the knowledge moisture content of the film is very important for food packaging applications. The results for moisture content (MC) for the PLA/HNTs bionanocomposite films plasticized by PEG and SO are shown in Figure 2.

Two opposite ways were detected for moisture content in PLA/HNTs bionanocomposites films plasticized by EPG and SO. In the case of plasticization by EPG, PLA/HNTs behaves like a hydrophilic polymer. Because of two factors. Firstly, the addition of HNTs to the PLA increases the moisture absorption of resulting nanocomposite films, probably due to the hydrophilic character of the HNTs. Furthermore, MC values have been increased by the addition of PEG due to its hydrophilic nature, these results were similar to the results of Ozkoc and Kemaloglu, which they studied the morphology, biodegradability, mechanical, and thermal Properties of bionanocomposite films based on PLA and Plasticized PLA by PEG [8].

![Figure 1. Moisture content of PLA/HNTs bionanocomposites plasticized by PEG and SO plasticizers.](image)

On the other case, which PLA/HNTs plasticized by SO, The MC values of films were significantly lower than the corresponding to the non-plasticized PLA/HNTs film, that was due to the inclusion of sesame oil. Moreover, the decrement of MC values was in parallel of the increase of SO loading. More than one factor could affect the MC values in presence of SO as plasticizer. First, the hydrophobicity nature of sesame oil is a main reason to prevent water to penetrate inside PLA/HNTs films. The small ratio that was found could be attributed to the hydrophilicity nature of HNTs, which it is able to form hydrogen bonding with water by the side groups of O-H. In addition, the diminished availability of OH groups of HNTs and carboxylic groups of PLA to make hydrogen bonding with the carboxylate groups of fatty acids of sesame oil cause limited access
of water molecules to PLA/HNTs films plasticized by SO, thus resulting in a decrease of moisture content of composite films. Similar results were observed for pistachio globulin protein and fatty acid emulsified films [9]. Partial protein–water interactions replaced with protein–olive oil interactions may account for the MC reduction occurred in the emulsified films.

3.2. Contact Angle (CA)

Water contact angle values are good indicators of the hydrophilic or hydrophobic character of films, being higher when hydrophilicity is lower, so thus the final state of the water drop on the film surface can be taken as an indication of surface wettability [10]. To understand the effect of the hydrophilic and hydrophobic plasticizers on the film wettability, contact angles were investigated for films with different contents of the PEG and SO and were related to the control film PLA/HNTs, as it is shown in Figure 3.

Figure 2. Contact angles of PLA/HNTs bionanocomposites plasticized by PEG and SO as plasticizers.

It can be seen that as the loading of PEG increases, the water contact angle gradually decreases. This could be attributed to hydrophilic nature of PEG which enhanced the surface hydrophilicity of the films. PEG enrichment at the surface observed in the morphology section earlier is in consistent with this theory. Hence, excellent hydrophilic nature led to increase in hydrophilicity of the films and reduced their water contact angle. These results were confirmed by FE-SEM results, which exhibited an increasing of the surface smoothing with the increase of PEG loading. Enhancement in hydrophilicity of bionanocomposite films due to addition of PEG has been reported in literature previously [11].

According to Figure 3, increasing sesame oil concentration caused a slight increase of contact angle values, from approximately 52 for 0% SO to 60º for 30% SO, which is due to the hydrophobic nature of the added lipid. Other authors found also similar behaviors, for example Ojagh et al. (2010) reported that the incorporation of cinnamon essential oils into chitosan films resulted in decreasing hydrophilicity of the composite films, which was attributed to the loss of free functional groups (amino and hydroxyl groups) [12].

3.3. Water vapor permeability (WVP)

As shown in Figure 4, the WVP value of unplasticized PLA/HNTs film was $1.43 \times 10^{-10}$ g.s$^{-1}$. m$^{-1}$. Pa$^{-1}$. At the same HNTs contents, the WVP values of PLA/HNTs films plasticized by PEG increased with plasticizer content (10 – 30 wt.%). Which increased from $2.720 \times 10^{-10}$ to $5.37 \times 10^{-10}$ g. s$^{-1}$. m$^{-1}$. Pa$^{-1}$. Meanwhile, the plasticization by SO resulted in decreasing the WVP, which the increasing of SO concentration from 10% - 30% decreased the WVP from $1.03 \times 10^{-10}$ to $0.62 \times 10^{-10}$ g. s$^{-1}$. m$^{-1}$. Pa$^{-1}$. Similar findings have been reported by Yu et al., (2008) [13].

The PLA/HNTs plasticized by PEG behaves like a hydrophilic material. It has a high WVP due to the presence of hydrophilic groups in the PEG component of the blend. In addition, there was significant difference in WVP between the PLA/HNTs plasticized by PEG and PLA/HNTs plasticized by SO films. Incorporation of SO decreased WVP of the PLA/HNTs films due to the hydrophobic nature of the SO. Furthermore, the more SO contents were, the less the values of WVP, due to the moisture barrier of hydrophobic plasticizer. On other hand, with the increasing of PEG contents, the values of WVP got increase, due to the increase of free volume around the polymer [14-15].
Figure 3. Water vapor permeability of PLA/HNTs films plasticized by PEG and SO with different plasticizer loadings.

4. Summary

Without plasticizers, PLA/HNTs films are brittle with many visible cracks and not easily peeled from the casting surface. Hence, the introduction of plasticizers helped to overcome brittleness and enhance flexibility and peelability of PLA/HNTs films. Two plasticizer types with different concentrations were exploited to investigate their effect on physical properties of PLA/HNTs films. The results demonstrated that plasticizer type and concentration influence film moisture content, wettability and water vapor permeability. Gradually, increasing the SO plasticizer concentration from 10 to 30 % decreases the moisture content and water vapor permeability, but increases the film contact angle. PEG plasticized films exhibited higher moisture content, water vapor permeability but lower contact angle than SO plasticized films. Overall, SO plasticized PLA/HNTs films showed the best performance with respect to physical properties.

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