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# Biodegradable nanocomposite blown films based on poly(lactic acid) containing silver-loaded kaolinite: A route to controlling moisture barrier property and silver ion release with a prediction of extended shelf life of dried longan

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Novel biodegradable nanocomposite blown films based on compatibilized poly(lactic acid)-poly(-butylene adipate-*co*-terephthalate) blend are fabricated for use as a model package for dried longan. Silver-loaded kaolinite (AgKT) dispersing in the polymer matrix in intercalated-exfoliated fashion functions as an excellent property improver of the blend. The emphasis of this paper is enhancement of film moisture barrier property by inducing polymer crystallization coupled with formation of AgKT tortuous path. Additionally, controlled silver release which provides long-term antibacterial activity is attributed to AgKT's layered structure. The amount of released silver ions herein also complies with migration levels specified by the standard for food-contact plastic packages. Dried longan shelf lives as eventually predicted by experimental moisture sorption isotherm and by Peleg model are almost identical (~308 days) for the nanocomposite films being over two folds of that obtained from the compatibilized blend package at ambient condition.



## 1. Introduction

Golden dried longan is one of the important economic fruits of warm-climate countries. During longan harvest season, there is a great amount of longan produced exceeding the local demand. To add value to the harvest and especially to extend shelf life of the longan flesh, it is typically dried and packaged for distant markets. Effective drying of the longan flesh should yield water activity ($a_w$) of <0.6 which is able to inhibit growth of micro-organisms [1]. Since this dried product has a high moisture adsorption rate, its shelf life is usually shortened by bacterial and microbial contaminations. Temperature, oxygen and especially UV light radiation levels are typical storing conditions that cause product browning [2]. Not only does this colour change reduce product shelf life, but also ruins its physical appearance. Consequently, the dried longan loaded in the package with suitable properties; essentially, water, oxygen and UV barriers, as well as antibacterial activity, is required as an alternative way to prolong its shelf life.

Nowadays, one of the common packaging polymers for dried fruits is oriented poly propylene (OPP) which exhibits high tensile strength, good abrasion, and high chemical resistance. However, it is a solid residue in the environment and made from limited petroleum resources. The concern to move to renewable resources and reduced environmental impact has focused the study of biodegradable and bio-based materials as alternatives to replace petroleum-based packaging. One of most studied biodegradable polymers is poly(lactic acid) (PLA). Nevertheless, its intrinsic hardness and brittleness have been major bottlenecks for practical uses. Blending of PLA with high-toughness and more flexible biodegradable polymers, such as poly(butylene adipate-*co*-terephthalate) (PBAT), was proved as a route to solve such a problem. At the molecular level, PLA/PBAT blend showed immiscibility between the two polymers, attributing to significantly poor properties. The two polymer phases were linked together via transesterification using tetrabutyl titanate (TBT) as a compatibilizer [3–5].

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Packaging polymers for dried fruits should be able to prevent the permeability of water vapour and gas molecules. Polymer nanocomposites, rather than polymer blends, have been produced for this particular purpose by the incorporation of rigid layered nano-fillers, including montmorillonite (MMT), kaolinite (KT), vermiculite and talc [6]. The clay layers dispersing in a polymer matrix can create a tortuous path [7] that helps to reduce the water vapour and gas permeation though the packaging films. KT is the commercially-available clay used in this work. Although KT price is lower than MMT, there have been a very few literature reports on KT nanocomposites in comparison with MMT [8]. Generally, the KT was simply modified to improve the dispersion in the polymer by an organic solvent, i.e. dimethyl sulfoxide (DMSO) [9]. Moreover, the addition of metal nanoparticles such as silver (Ag) into the interlamellar space of KT, during reduction reactions by DMSO, can help to increase interlamellar space of KT [5,10,11], leading to higher clay dispersion in polymer matrix. The presence of Ag nanoparticle-deposited KT not only enhances gas barrier properties by action of the clay layers, but also inhibits bacterial growth on polymer film by function of Ag nanoparticles. In addition, the clay layer is likely to control Ag release for long-lasting antibacterial effect to save the product quality.

Previously, there have been several studies regarding KT as a filler for polymer matrices, particularly ethylene-vinyl alcohol (EVOH) copolymers [12], poly(*m*-xylene adipamide) (MXD6) resin [8], polylactide [13], cassava starch [14,15], polyolefin/iron [16], polyimide [17] and poly(lactic acid)/poly(butylene adipate-*co*-terephthalate) (PLA/PBAT) [5]. The authors consistently reported that KT-polymer nanocomposites exhibited a significant improvement in tensile strength, elongation at break, thermal resistance, UV blocking, and dramatically better waterproofing, including water vapour and gas barrier properties [5,8,12–17]. These papers presented preparation and characterizations of the polymer nanocomposites with proposed applications. However, how such polymer materials actually work as packaging material in blown-film form has been shown in very few literature reports. Packaging film performance can be recognized via experimental or simulational investigation of products' shelf life. To predict shelf life of the dried longan, water vapour permeability (WVP) of the packaging materials is one of the important criteria used to predict a rate of moisture uptake [18]. Moreover, water activity ($a_w$) is also generally applied for shelf life prediction of dried fruit as the main parameter since water is required for cell metabolism and, hence, micro-organism growth [19]. The $a_w$ values are obtained by measurements of water sorption isotherm of the product [20] which is mathematically simplified to many equations. For example, Brunauer–Emmett–Teller (B.E.T.) and Guggenheim–Anderson–de Boer (G.A.B.) models are classified as theoretical, while Halsey and Peleg models are considered as semi-empirical and Oswin model is categorized as empirical [19,21].

Herein, PLA/PBAT blends and their nanocomposites with silver-loaded kaolinite (AgKT) are developed as polymeric materials for biodegradable packaging of dried longan. Blown film properties studied include morphological, mechanical and thermal properties, as well as WVP and antimicrobial activity. Finally, shelf life prediction of the dried longan is made by mathematical models based on the moisture sorption isotherm of the dried longan and WVP of the developed film. Film properties and the shelf life are related and discussed in details. To the best of our knowledge, this work is the first report on blown films of such polymer nanocomposites prepared by extrusion blowing inclusively with model demonstration of their effective function in extending shelf life of the dried longan.

## 2. Experimental section

### 2.1. Materials

PLA pellets (4043D grade) with the number–average molecular weight ($\overline{M}_n$) of 1.50 × $10^5$ gmol$^{-1}$ and the weight–average molecular weight ($\overline{M}_n$) of 1.30 × $10^5$ gmol$^{-1}$ were supplied by NatureWorks LLC (Minnetonka, USA). PBAT pellets (Ecoflex® F blend C1200) with the $\overline{M}_n$ of 2.44 × $10^4$ gmol$^{-1}$ was provided by BASF Chemical Company (Ludwigshafen, Germany). The TBT compatibilizer, a product of Fluka Analytical (Sigma–Aldrich. Co, USA), was obtained as viscous clear liquid. Ag-loaded KT (AgKT) powder, as an antimicrobial agent (Fig. 1), was synthesized using the previously reported reduction method [5]. The yellow-brownish powder comprised 3.4 wt.% of Ag particles whose average diameters ranged from 20 to 50 nm. All polymer pellets and the antimicrobial agent were vacuum dried at 60 °C for 24 h prior to use.

### 2.2. Preparation of blend and nanocomposite films

Neat PLA, neat PBAT, PLA/PBAT blend, and PLA/PBAT/TBT compatibilized blend were compounded using melt blending technique in a rotating twin screw extruder (pilot scale, JSW TEX 30 α) at the temperature of feed to die zone ranging between 165 °C and 180 °C, coupled with a screw speed of 60–70 rpm. The absolute composition of PLA/PBAT blend, PLA/PBAT/TBT compatibilized blend and PLA/PBAT/TBT/AgKT nanocomposite were chosen from our previous work [5] being 70/30, 70/30/0.5 and 70/30/0.5/4, respectively, where 70, 30, 0.5 and 4 represent 70 wt.% PLA, 30 wt.% PBAT, 0.5 phr TBT and 4 phr AgKT.

Prior to the fabrication of PLA/PBAT/TBT/AgKT nanocomposite films, a masterbatch was prepared by mixing and dispersing the filler phase (AgKT) into the polymer matrix (PBAT) using an internal mixer (HAAKE Polylab internal mixer, Rheomex 252p) at 185 °C and 60 rpm for 15 min. The masterbatch was then melt blended with PLA pellets and TBT.

For the screw speed setting, the melt flow index (MFI) of the sample is an important consideration in helping to set an appropriate screw speed for safeguarding the machine and for indicating the melt-rheological properties of the polymer. The MFI of PLA/PBAT with TBT and AgKT was determined using a Davenport MFI-10 Melt Flow Indexer (Lloyd Instruments). The samples were melted at 190 °C and extruded through a capillary die using a 2.16 kg piston according to ASTM D1238. The weights of extrudate were measured at 10 min intervals. The MFI value was taken as the average of at least 15 measurements.

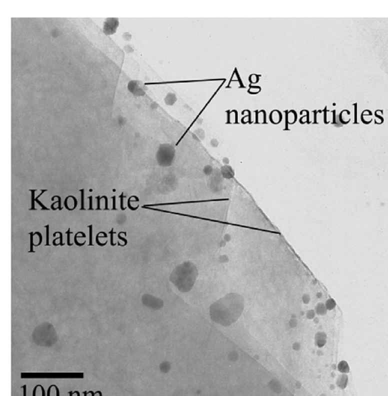


**Fig. 1.** TEM micrograph of AgKT powder.

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