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Effect of silver-loaded kaolinite on real ageing, hydrolytic degradation, and biodegradation of composite blown films based on poly(lactic acid) and poly(butylene adipate-*co*-terephthalate)

Sutinee Girdthep [a,b], Patnarin Worajittiphon [b,*], Thanawadee Leejarkpai [c], Robert Molloy [d], Winita Punyodom [b]

[a] Department of Chemistry, Faculty of Science, Silpakorn University, Nakhon Pathom 73000, Thailand
[b] Polymer Research Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c] National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani 12120, Thailand
[d] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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ABSTRACT

Effect of silver-loaded kaolinite (AgKT) on real ageing, hydrolytic degradation inclusive of biodegradation of blown films of partially compatibilized poly(lactic acid) (PLA)/poly(butylene adipate-*co*-terephthalate) blend was investigated. Neat PLA showed the highest degradation extent, followed by the blend and the composite, respectively. The AgKT in the composite films induced crystallization, during film fabrication and hydrolysis, and acted as barrier to water adsorption, thus retarding polymer degradations. The composite film maintained its mechanical properties over a six-month ageing period with tensile strength and elongation at break as high as about 32 MPa and 140%, respectively, in transverse direction. The composite showed its biodegradation extent of 69.94% (after 90 days), conforming to the Chinese National Standard (GB/T 20197-2006) and thus offering good biodegradability for use as a material for the production of degradable plastic bags. This article demonstrated that the ageing, hydrolytic degradation, and biodegradation of PLA-based films could be tailored by AgKT incorporation. Our hypothesis on degradation phenomena at the molecular level was also suggested. Moreover, this composite formulation could be used for high-performance packaging with good biodegradability conformity.

1. Introduction

Non-biodegradable plastic residues and scarcity of petroleum resources have drawn much interest in biodegradable polymers. Using biodegradable polymers as a replacement to petroleum-based ones in packaging applications is considered as an alternative way to overcome increasing environmental problems. One of the biodegradable polymers gaining interest nowadays is poly(lactic acid) (PLA) due to its promisingly versatile properties. PLA is recognized as appropriate for green packaging uses since its ester bonds can undergo degradation in humid environments. However, PLA is usually blended with other flexible polymers such as poly(butylene adipate-*co*-terephthalate) (PBAT) to reduce the brittleness of PLA-based

* Corresponding author.
E-mail address: pworajittiphon@gmail.com (P. Worajittiphon).

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products [1,2]. Since PBAT is a biocompostable copolymer, the PLA/PBAT blend is still environmentally friendly. Enhancement of the gas barrier properties of PLA and its blends for packaging applications can be achieved by incorporation of layered silicates such as montmorillonite (MMT) and kaolinite (KT) into the polymer matrices [3–8]. In fact, investigations regarding degradation are able to determine the usefulness of polymer composite films based on biodegradable polymers in view of their long-term uses and their degradability in the environment. To date, there have been several reports of degradation studies on MMT composites based on PLA [4–7]. However, those related to KT are fewer in number [6,8].

A number of studies in literature reviews have reported regarding degradation of PLA, and its blends and composites with focus on ageing [9], hydrolytic degradation [4,5,7,10], and biodegradation [6,11–13]. Ageing has become a crucial matter to be studied for any product since relevant characteristics are prone to change over time. It was found that the mechanical properties of PLA film depended on its composition and storage temperature [9]. Hydrolytic degradation study of films based on polyester polymers is also crucial in understanding the polymer molecular phenomena during service time and after its use under moisture. With regard to the film composition of our interest, it was reported earlier that PBAT did not have a pronounced influence on PLA hydrolysis [10]. Hydrolytic degradations of PLA composites containing MMT have been widely studied [4,5,7]. However, very little has been reported on the hydrolytic degradation of PLA/KT composites [8]. In remote areas where plastic waste management cannot be thoroughly controlled, understanding of how plastic films degrade on land is helpful in saving the environment. This can be performed by designing the film composition for the film to be degradable in a decent time after its use. Biodegradation test of the films in real soil and composting conditions has been a typical route for such investigations [6,11–13]. For the blend of our interest, a different degradation process of PLA and PBAT was proposed and, when combined to form the PLA/PBAT blend, each of them underwent biodegradation in a different manner as compared to the parent polymers alone [11]. Biodegradation under the controlled composting condition of the PLA/clay composite was also demonstrated as a comparative study between PLA/KT and PLA/MMT composite films [6].

According to literature reviews, there have been many reports on the degradations of PLA, PLA/PBAT, and PLA/KT, with different degradation results. However, there is a lack of comprehensive reports on real ageing and hydrolytic degradation which are inclusive of biodegradation in the same article for a particular PLA/PBAT/KT composite. Our earlier article demonstrated that novel blown films of the quaternary composite system containing partially compatibilized PLA/PBAT blend and silver-loaded kaolinite (AgKT) delivered potential performance for the packaging of dried products [14]. Due to enhanced moisture barrier property, the composite films could offer a predicted shelf life of ~308 days for dried longan. However, the polymers can be degraded by atmospheric moisture; hence, whether or not some of these characteristics can be maintained has not yet been investigated. In fact, a study of real ageing, hydrolytic degradation, and biodegradation in the same work will disclose important properties of the composite film during its service time and will develop a profound understanding of the degradation process in the environment after the use of the film.

Herein, our developed blown films were accordingly used as a model to demonstrate the degradation behavior of the PLA/PBAT blend in the presence of AgKT. The present work was aimed to investigate the effect of AgKT on the ageing performance and degradation response of composite films in comparison with PLA and compatibilized PLA/PBAT blend films for the whole lifetime of the prepared blown films. A study on real ageing, instead of typical accelerated ageing, was conducted under different conditions, such as ambient and controlled conditions, for the long duration of one year. The real ageing was evaluated from the change in the mechanical properties which are of utmost importance for packaging materials. In addition, this work suggests possible molecular phenomena in the films when disposing them both in moist environments and on land through hydrolytic degradation and biodegradation, respectively. The findings will be beneficial in predicting possible service time range as well as tailoring the degradation extent by formulation of the film components.

2. Experimental

2.1. Materials, preparation, and properties of produced films

The quaternary composite system used in this work comprised of PLA, PBAT, tetrabutyltitanate (TBT) compatibilizer, and AgKT in the ratio of 70 wt%, 30 wt%, 0.5 phr, and 4 phr, respectively. The designations of neat PLA, partially compatibilized blend (PLA/PBAT/TBT), and composite (PLA/PBAT/TBT/AgKT) in this article are PLA, the blend, and the composite, respectively [14]. All films with average thickness of 50–55 μm were prepared using a twin screw extruder and, subsequently, a film-blowing machine. Film fabrication details are described in a previous report [14]. The properties of the various formulations are summarized in Table 1.

2.2. Ageing conditions and characterization of aged packaging films

The films were placed in an ambient condition (27.0 ± 1.0 °C and 69 ± 5% relative humidity, RH) and a controlled or storage condition (30.0 ± 1.0 °C and 30 ± 5% RH). The samples underwent ageing for 1 year and were carefully tested every month to evaluate their mechanical properties in terms of tensile strength (TS), elongation at break (EB), and Young's modulus (Y) in both machine direction (MD) and transverse direction (TD) using a Universal Testing Machine (Lloyds LRX). By following ASTM Method D882, the initial grip separation was set at 50 mm and the cross-head speed used was 5 mm min^{-1}. The tests were performed at 25 °C and seven determinations were made for each sample.