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Performance evaluation of a novel food packaging material based on clay/polyvinyl alcohol nanocomposite

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ABSTRACT

The effectiveness of a novel, laminated clay/polyvinyl alcohol nanocomposite food-packaging film was examined by barrier analysis and food shelf-life monitoring. The effect of storage conditions on the film's oxygen permeability was studied and compared to commercial LLDPE/PET film as control. Additionally, pouches of 14 cm × 10.5 cm prepared from both films were filled with tomato paste as the food model, and stored at different temperatures (20–50 °C) and humidities (20–85% RH) for 10 days. Incorporating a coating layer containing 30 wt% (d.b.) of clay into polymer was found to improve its barrier properties, with drastic reduction of oxygen transmission rates (OTR) up to 99%, especially at 20% RH. While surrounding humidity affected the OTR of composite film significantly more than that of control film, the OTR of composite film was lower and less susceptible to temperature changes. The changes of food physical-chemical properties with time showed that the pouches of composite film significantly decreased ascorbic acid and lycopene oxidation of tomato paste by up to 88 and 37%, respectively. Furthermore, no discolouration occurred to the samples packaged by the nanocomposite film as compared to the control.

Industrial relevance

A novel clay/polyvinyl alcohol nanocomposite film was developed with excellent barrier properties against oxygen. Evaluation of the performance of this food-packaging film indicated that incorporation of montmorillonite enhanced food preservation as suggested by decreased ascorbic acid and lycopene oxidation, and no discolouration of tomato paste. This new approach could be adopted by the food industry to assist commercial producers and retailers for preserving and extending the shelf-life of a variety of food products.

1. Introduction

Packaging protects foods and beverages from deterioration caused by oxygen, the presence or absence of moisture, spurious odours and gaseous emissions. By correct selection of materials and packaging technologies, it is possible to maintain food quality and freshness for the desired shelf-life of the product (Sorrentino, Gorrasi, & Vittoria, 2007). Over the past decades, polymers have become more popular and replaced conventional materials (metal, glass, paper) in many packaging applications due to their transparency, flexibility, low cost, ease of processing, heat seal ability and light weight. Polymers such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), and polyethylene (PE) are some of the most commonly used food packaging materials (Mangaraj, Goswami, & Mahajan, 2009). Unfortunately, in comparison with conventional materials such as metal and glass, polymers are characterized by relatively low-barrier properties which can result in reduced protection of the packaged food (Avella et al., 2007).

Developing and maintaining desirable atmospheric conditions largely depend on the gas permeability of the packaging materials used. The mechanism of gas permeation through a packaging material can be described in four stages (Fereydoon & Ebnesajjad, 2013; Mangaraj et al., 2009): (*i*) adsorption of the penetrating substance (*i.e.* the permeant) to the surface of the packaging, (*ii*) dissolution of the permeant in the packaging, (*iii*) diffusion through the packaging, and (*iv*) evaporation or desorption of the permeant on the other side of the

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packaging. Permeation occurs when polymer packaging is exposed to a permeant having different concentrations on its two sides, and the permeant will pass through the polymer packaging from the high to the low concentration side (Fereydoon and Ebnesajjad, 2013). Some factors that affect the gas and water vapour permeability of polymer packagings include the polymer's molecular structure, storage conditions such as temperature and humidity, and processing conditions (Limqueco, 2015). For example, the gas permeability of films is significantly affected by humidity when the film is hydrophilic in nature. After a certain humidity threshold, the gas permeability of hydrophilic films typically increases exponentially with humidity (Gontard, Thibault, Cuq, & Guilbert, 1996; Mujica-Paz & Gontard, 1997). Moreover, the permeability of films generally increases as the temperature increases.

In order to enhance the gas barrier of polymeric materials, gas-impermeable plate-like inorganic filler is incorporated into polymer to produce polymer composites with formation of “tortuous path” against gas molecules (Nielsen, 1967), a longer diffusion pathway for the permeating gas as they navigate around the impenetrable platelets. As a result, the diffusion rates of gaseous molecules across the polymer material are reduced, and the gas permeability of the film is decreased. Among these plate-like fillers, natural sourced clay, particularly montmorillonite (MMT), has been extensively studied and applied for gas barrier enhancement. Its structure is a crystal lattice consisting of 1-nm layers, with an octahedral sheet of alumina fused between two external silica tetrahedral sheets (Manias, Touny, Wu, Strawhecker, Lu, & Chung, 2001). The layers are negatively charged and joined together by interlayer cations (Cyras et al., 2008), hydrogen bonds, or van der Waals forces (Uddin, 2008). MMT is thus hydrophilic and sensitive to high relative humidity (RH) in the surrounding environment (Katti & Katti, 2006). The most important feature of nano-MMT contributing to the improved gas barrier property of polymer nanocomposite is its high aspect ratio ranging from 100 to > 300 (Cyras et al., 2008; Gopakumar, Lee, Kontopoulou, & Parent, 2002). This structure allows the nano-MMT plates to act as physical barriers with higher “tortuous path” efficiency in comparison with other fillers. Studies have demonstrated the effectiveness of various nanoclays in decreasing the permeability of PE-based materials for O_2 (Hu, Fang, Yang, Ma, & Zhao, 2011; Jacquelot, Espuche, Gérard, Duchet, & Mazabraud, 2006; Lotti, Isaac, Branciforti, Alves, Liberman, & Bretas, 2008), CO_2 (Jacquelot et al., 2006; Lee, Jung, Hong, Rhee, & Advani, 2005), water vapour (Hu et al., 2011; Lotti et al., 2008), and nitrogen (Lee et al., 2005). In addition, low-density PE (LDPE) (Arunvisut, Phummanee, & Somwangthanaroj, 2007; Siročić, Rešček, Ščetar, Krehula, & Hrnjak-Murgić, 2014; Xie, Lv, Han, Ci, Fang, & Ren, 2012), PP (Manikantan & Varadharaju, 2011), PET (Li et al., 2012) and polyimide (Khayankarn, Magaraphan, & Schwank, 2003) films showed improved O_2 barrier properties when incorporated with nanoclay, though a linear LDPE (LLDPE) film intercalated with clay developed by Hong and Rhim (2012) exhibited improved O_2 barrier but not water vapour. Furthermore, some studies using high-density PE (HDPE) reported improved gas barrier properties (Horst, Quinzani, & Failla, 2014; Lotti et al., 2008; Osman & Atallah, 2004).

In our previous work, a transparent, MMT-based polymer nanocomposite film with remarkably improved oxygen barrier properties has been developed and patented (Li, He, Low, & Wong, 2010), with adequate safety guarantees to be applied for food packaging (Huang, Chieng, Li, & Zhou, 2015; Huang, Li, & Zhou, 2015). The composite film was prepared by applying gelatinous clay/polymer suspension onto plastic film followed by drying and laminating with second layer of plastic film. The clay-sheets were oriented along the plastic substrate under the shearing force produced by application because of the thixotropic behaviour of the clay/polymer gelatinous suspension. The clay content could be as high as 70 wt% against the polymer matrix. Therefore, such prepared MMT-based composites showed excellent oxygen barrier. At the same time, the laminated plastic film is transparent because of the high degree of clay sheet orientation. However, since MMT is hydrophilic, it is hypothesised that a high relative humidity would compromise the O_2 barrier property of the composite film, especially in the context of high humidity and temperature conditions in Southeast Asia. In order to evaluate the packaging performance of the clay/polyvinyl alcohol nanocomposite film, this study investigates the effects of storage humidity and temperature on the oxygen permeability of the developed composite film, and the quality changes of food product packaged under established storage conditions. Such information will be crucial for understanding the appropriate storage conditions applicable to the composite film.

2. Materials and methods

2.1. Packaging material

The nanocomposite film developed by Li et al. (2010) was investigated in this study. In brief, a 2.5-μm thick nanocomposite layer was prepared by applying modified MMT/poly(vinyl alcohol) (PVA) gelatinous suspension with a solid concentration of 4 wt% onto a 13-μm PET film (outer layer). Another 47.5-μm LLDPE film (inner layer, contacting with food) coated with adhesive was then laminated against the coated PET film to sandwich the nanocomposite layer between PET and LLDPE films to form a three-layer barrier film. While PET was used for the outer layer because of its good mechanical stability and glass-like transparency, LLDPE was chosen as the inner layer based on its heat-sealing characteristics due to the low melting point (105–115 °C). Commercial LLDPE (50 μm)/PET (12 μm) film with a 1.5-μm thick adhesive layer purchased from Promens (Kristiansand, Norway) was used as the control in this work. The composition of the composite and control films are summarised in Table 1. Pouches with dimension of 14 cm × 10.5 cm and total volume of 175 cm^3 fabricated from nanocomposite and control films were used to package food samples.

2.2. Oxygen permeability

The oxygen transmission rate (OTR) of film samples was measured according to the ASTM standard method D3985 using OTR analyzers (Mocon OX-TRAN 2/21, Minneapolis, USA; Systech Illinois M8001, Thame, UK). A film was placed on a stainless steel mask with an open testing area of 5 cm^2 and tested at different temperatures (10–50 °C). The LLDPE side of the film was exposed to nitrogen gas flow, and the PET side was exposed to oxygen gas flow with relative humidity (RH) ranging from 0 to 85%.

2.3. Packaging experiments

Commercial tomato paste of 20 g (Leggo's, Mentone, Australia) and propionic acid of 60 μl (Sigma Chemicals, St Louis, USA) as preservative were packaged into pouches under a laminar flow cabinet, to minimize microbial contamination. Each pouch was flushed with nitrogen, sealed using a vacuum-packing machine, and double-sealed to ensure no gas leakage. The pouches were stored at different temperature (20–50 °C) and RH (20–85%) conditions for 10 days in a climate chamber (MMM, Climacell, Munich, Germany). The headspace gas and quality parameters of the tomato paste of triplicate samples were analyzed every

Table 1
Composition of composite and control films.

Film (thickness)	Component		
	Inner layer	Core layer	Outer layer
Composite (63 μm)	LLDPE (47.5 μm)	MMT (4 wt%)/PVA/ adhesive (2.5 μm)	PET (13 μm)
Control (63.5 μm)	LLDPE (50 μm)	Adhesive (1.5 μm)	PET (12 μm)