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PLA blend /RHA permeable composite films for fruit packaging

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Abstract

Permeable films and their composites were produced from a biodegradable polylactic acid blend (PLA blend) and rice husk ash (RHA) fillers. These permeable films were designed for fruit packaging applications. The composite films were prepared by melt-compounding a biodegradable PLA blend with 0, 5, 10, and 20 wt% RHA fillers before subjecting the compounds to a film blowing processing with simultaneous film stretching at various screw speeds of the nip roll (150, 250, 350 and 400 rpm). The effects of RHA content and screw speed on the mechanical properties, oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of the PLA blend /RHA composite films were investigated. The results indicated that increasing RHA content led to an increased maximum tensile strength and percentage elongation at break of PLA blend / RHA composite films regardless of the stretching speed. For PLA blend /RHA composite films containing the same amount of RHA, it was observed that increasing the stretching speed resulted in higher WVTR and OTR values. The packaging application test indicated that the PLA blend /RHA composite film containing 20 wt% RHA made with a low screw speed of 150 rpm could preserve bananas for up to 14 days whereas the conventional LLDPE film was able to keep the freshness of bananas for only up to 8 days.

Keywords: Polylactic acid, Rice husk ash, Composite films, Permeable films, Fruit packaging

1. Introduction

Unlike most food products, fresh fruits and vegetables still stay alive after harvesting, continuing their metabolic processes, such as respiration, transpiration, and enzymatic activity [1]. These intrinsic activities significantly influence the quality (e.g., its taste, texture and appearance) and shelf life of fresh fruits and vegetables [2]. One of the keys to maintaining the freshness of produce for as long as possible is to reduce the respiration rate. During the past few decades, there has been development in packaging technologies to increase the shelf life of fruits and vegetables. One successful area of such development is called modified atmosphere packaging (MAP), in which the composition of the air in the package is altered in such a way that it would provide an optimal environment for maintaining good product quality as well as increasing its storage time. A MAP could be achieved either actively or passively. In an active MAP, the atmosphere in the packaged is initially modified by replacing the ambient air with a desired mixture of gases. In contrast, passive MAP is achieved by packaging the products within a carefully selected type of film, with certain permeability to gases and water vapor. Then a desirable atmosphere is allowed to develop naturally as a result of the product's respiration and the diffusion of gases through the packaging film [3-6]. Plastic films such as low density polyethylene (LDPE), polyvinyl chloride (PVC) or polypropylene (PP) are commonly used in MAP. However, these plastic films supply either low or a narrow range of gas permeability that rarely well matches with the respiration rate of fruits and vegetables. Thus, these types of films are only applicable to a few fresh products [5]. One possible solution to produce film with broader gas permeability range is to develop microporous film by blending polymer matrices with inorganic fillers such as calcium carbonate, silica, clay, montmorillonite and graphite [7-12]. The gas permeation property of microporous film is controlled by adjusting the filler content, particle size of filler and degree of film stretching [1]. Microporous film/sheets had been studied extensively with various types of polymer matrices and fillers. However, most of studies are associated with synthetic polymers like polypropylene (PP) [13-15], low density polyethylene (LDPE) [10, 12, 16-17], high density polyethylene (HDPE) [18-20] and polyvinylchloride (PVC) [21-25]. Additionally, most of films are formed by extrusion and post film stretching.

Rice husks (RH) are a by-product of rice milling. Their availability is tremendous as an agricultural waste. They are renewable, inexpensive and biodegradable [26-27]. About 20% ash is obtained when burning RH in air. The ash contains greater than 90 wt% silica [28-29].

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Table 1 Film composition and screw speed for blown film production

Sample designation	Sample composition (%)		Stretching degree	Screw speed (rpm)
	PLA blend	RHA		
PLAb no.1	100	0	100%	150
PLAb no.2	100	0	150%	250
PLAb no.3	100	0	200%	350
PLAb no.4	100	0	250%	400
PLAb/5RHA no.1	95	5	100%	150
PLAb/5RHA no.2	95	5	150%	250
PLAb/5RHA no.3	95	5	200%	350
PLAb/5RHA no.4	95	5	250%	400
PLAb/10RHA no.1	90	10	100%	150
PLAb/10RHA no.2	90	10	150%	250
PLAb/10RHA no.3	90	10	200%	350
PLAb/10RHA no.4	90	10	250%	400
PLAb/20RHA no.1	80	20	100%	150
PLAb/20RHA no.2	80	20	150%	250
PLAb/20RHA no.3	80	20	200%	350
PLAb/20RHA no.4	80	20	250%	400

This makes RH a renewable and economical source of silica [26]. Silica is usually added into polymer to reinforce its mechanical properties [30], improve antiblockage between polymer film layers [31] and enhance flame retardant properties [32-33]. However, adding silica from rice husk ash into a bioplastic and its effect on gas barrier characteristic have received much less attention. Additionally, there are very few studies that focus on producing permeable film from bioplastic/RHA blends by blown film processes with simultaneously film stretching for fresh fruit and vegetable packaging.

In order to produce a green packaging film with a broader gas permeability range, a biodegradable polylactic acid blend (PLA blend) and silica from rice husk ash are chosen to study. In this study, we want to explore the possibility of broadening the gas permeability range of permeable PLA blend based film by varying the rice husk ash (RHA) content and film stretching configuration. Properties such as tensile strength, oxygen and water vapor permeability range of PLA blend /RHA microporous composite films are evaluated and compared with a PLA blend film. In view of packaging applications, the effectiveness of a PLA blend /RHA microporous film on prolonging shelf life of fresh fruits are validated and compared with a conventional linear low density polyethylene (LLDPE) plastic film.

2. Materials and methods

2.1 Polymer sample

The polymer matrix used is Ecovio® F Blend C2224 (BASF, Germany). This is a blend of PLA with biodegradable copolyester Ecoflex® F. The PLA blend polymer possesses a melt flow rate (MFR) < 2.5 g/10 min (2.16 kg, 190°C) and a density of 1.24-1.26 g/cm^3. Linear low density polyethylene (LLDPE) film (Plastic Bag, B.C. Trading Ltd., Bangkok, Thailand) was used as a common film packaging in the packaging application test for comparison purposes.

2.2 Preparation of rice husk ash (RHA)

Rice husks (RH) were collected from local rice mills (Khon Kaen Province, Thailand). For each preparation, 250 g of rice husks were soaked in 1 L of 1 M HCl for 24 h and then washed with distilled water until the pH was 7. It was then dried at 100 °C for 6 h in a hot air oven. The treated rice husks were then incinerated in an electric muffle furnace at 575 °C for 5-6 h and finally the resulting white ash was obtained. The white ash then was ground using a ball mill to reduce its particle size and sieved through a 200 mesh screen. The particle size distribution and average particle size of RHA particles were measured using a particle size analyzer (Zetasizer Nano S90, Malvern Instruments, England).

2.3 PLA blend /RHA compounding

PLA blend pellets and RHA with three different contents (5, 10, and 20 wt%) were compounded using a twin-screw extruder (26 mm twin, Lab Tech Engineering, Michigan, USA) equipped with a strand die, cooling bath, and pelletizer. The twin-screw extruder has a 26 mm bore size and an *L/D* ratio of 40:1. PLA blend /RHA composite strands were pulled through a water bath at 20 °C and cut into pellets using a pelletizer. The barrel temperature of the extruder ranged from 160 °C in feed zone to 170 °C in the die zone.

2.4 Blown film processing

The PLA blend pellets and the compounded PLA blend /RHA resin were dried for 6 h at 65 °C to remove moisture before blown film processing. They were then loaded into the extruder hopper of the 50 mm single-screw extruder (SE/HD 45MI, Southeast Machinery, Taiwan). A spiral flow blown-film die with a 60 mm diameter was used to produce the film. The blow-up ratio (BUR) of the bubble was 5:1. This setting produced a bubble with film thickness of 0.01-0.06 mm. To study the effects of stretching on the film's properties, the films were stretched during the blown film process by adjusting the screw speed of nip roll to 150, 250, 350, and 400 rpm. The temperature zones 1, 2, 3, and 4 were 145, 150, 155, and 160 °C, respectively. Film compositions and screw speed used to produce PLA blend and PLA blend /RHA composite films are listed in Table 1.

2.5 Mechanical testing

Tensile testing of the PLA blend /RHA film samples was carried out according to ASTM D882 with an Instron 5567A machine (Instron, USA). The sample was cut into rectangular shaped pieces with dimension of 25x180 mm^2. The gauge length of the tested samples was 50 mm and the grip separation was 150 mm. The tensile strength was tested at a grip separation rate of 500 mm/min. Five samples were used for each film formulation and the average tensile strength and elongation at breakage were calculated.

2.6 Surface morphology investigation

Surface morphology of rice husk ash particles and PLA blend /RHA composite films were examined using a Leo 1450VP (Carl Zeiss, Germany) scanning electron microscope (SEM) with an accelerating voltage of 30 kV. The surfaces of the samples were coated with a thin layer of gold by a sputtering coater prior to observation.

2.7 Gas transmission rate measurement

Gas transmission rate measurements were performed by measuring water vapor and oxygen transmission rates. Measurement of water vapor transmission rate (WVTR) was carried out in accordance with ASTM E96 using water vapor transmission analyzer (KBF 720, Binder, Germany). Four samples of each film formulation were used for WVTR measurement while the oxygen transmission rate (OTR) measurements were carried out in accordance with D3985 using an 8500 Systech Illinois Oxygen Permeation Analyzer (Illinois Instruments, USA). Five samples of each film formulation were used for OTR measurements. Both water vapor and oxygen transmission rate testing were carried out at atmospheric conditions.

2.8 Packaging application testing

The efficacy of PLA blend /RHA film for prolonging shelf life of fruit was investigated by packing Pisang Awak bananas in three types of film, namely a PLA blend, PLA blend /RHA, and conventional LLDPE film. The Pisang Awak bananas were washed with tap water and soaked in water containing 80 ppm chlorine for 15 min then wiped to remove water on the banana skins using paper towels. Two bananas, 10 – 12 cm in length, at stage 3 ripeness (light green with light yellow; more green than yellow), were packaged with a 20 cm x 25 cm film, then hot-sealed and stored at 25 ± 1 °C. The packed bananas were observed daily until changes in appearance and spoilage were observed. All experiments were performed in triplicate.

3. Results and discussion

3.1 Surface morphology of RHA particles and PLA blend /RHA films

SEM images of RHA particles at various magnifications are shown in Figure 1A and 1B. The surface morphology revealed that RHA particles are polyhedral in shape. They were agglomerated with a wide particle size distribution. This result was confirmed by Zetasizer measurements that indicated a RHA particle size distribution of 129–450 nm and an average particle size of 253 nm. The aggregation of RHA might be due to hydrogen bond formation among the abundant O-H groups and adsorbed water on RHA surfaces [30, 34]. The exterior surface of the PLA blend /RHA composite films with 5wt % RHA (the lowest RHA loading) and 20wt % RHA (the highest RHA loading) are shown in Figure 1C and 1D, respectively. Both the PLA blend /RHA composite films exhibited a smooth and homogeneous structure with no pores or cracks. This illustrated good compatibility of RHA with the PLA blend matrix. There was no phase separation of filler particles and PLA blend matrix. This implied good adhesion at the interface of RHA particle and PLA blend matrix. No significant difference was observed for PLA blend film containing low (5 wt% RHA) and high RHA content (20 wt%). White dots on the surface of PLA blend /RHA composite film represent RHA particles. The SEM image of PLA blend /RHA film at the highest screw speed (400 rpm) and with the highest RHA loading (20 wt%) is shown in Figure 1 E. It presents a rougher surface and conspicuous inclusions on the surface which indicate RHA aggregation and less dense film. This observation was pronounced only in the PLA blend /RHA nanocomposite film with the highest screw speed and the highest RHA loading.

3.2 Tensile strength

Figure 2 depicts the effects of RHA loadings and stretching on the tensile strengths of PLA blend and PLA blend /RHA composite films. As expected, an increase of tensile strength of PLA blend films as a function of RHA filler loading was observed. This is due to a contribution of silica in RHA that reinforced the polymer matrix as well as the presence of good interfacial adhesion of the PLA blend matrix and RHA particles. All of these contributed to tensile strength improvement of PLA blend film containing RHA filler. Consideration of PLA blend /RHA composite films containing the same RHA content, it was found that increasing the degree of stretching caused a reduction in tensile strength of the films. This is because the film thickness decreased with greater stretching (increasing screw speed), as shown in Table 2, resulting in tensile strength reduction. It was also observed that the best tensile strength (25 MPa) was obtained from a combination of the lowest screw speed (150 rpm) and the highest RHA content (20 wt%). The result was a tensile strength that was 26% greater than that of the PLA blend alone. This 26% improvement of tensile strength may be explained by good interfacial adhesion of RHA particles and the PLA blend matrix, which restricted the mobility of polymer chains under loading [35].

3.3 Elongation at break

Figure 3 shows a flexibility characteristic of PLA blend film and PLA blend /RHA composite films. Consideration at the same RHA content, higher stretching reduced elongation at breakage of films. Since film had been elongated to some point of its maximum elongation during the film forming, thus the increasing stretching would lead not only to a decreasing of film thickness but also the percent elongation at breakage of film. When considering films with the same stretching, the effect from RHA loading caused a slight increase in the elongation at breakage of PLA blend /RHA composite films. Only at the lowest screw speed of 150 rpm, the effect of RHA loading on increased elongation at break was more obvious. The behavior of increasing flexibility of PLA blend /RHA composite film is unusual. Generally, adding rigid inclusions into a polymer matrix reduces its elongation at breakage due to restraints on the mobility of the polymer chains caused by the intercalated filler [36]. Such an unusual trend could be ascribed to the very fine size and dispersion of RHA particles in the PLA blend matrix. This reduced the discontinuity of the structure and enhanced polymer chain mobility resulting in higher elongation at breakage.

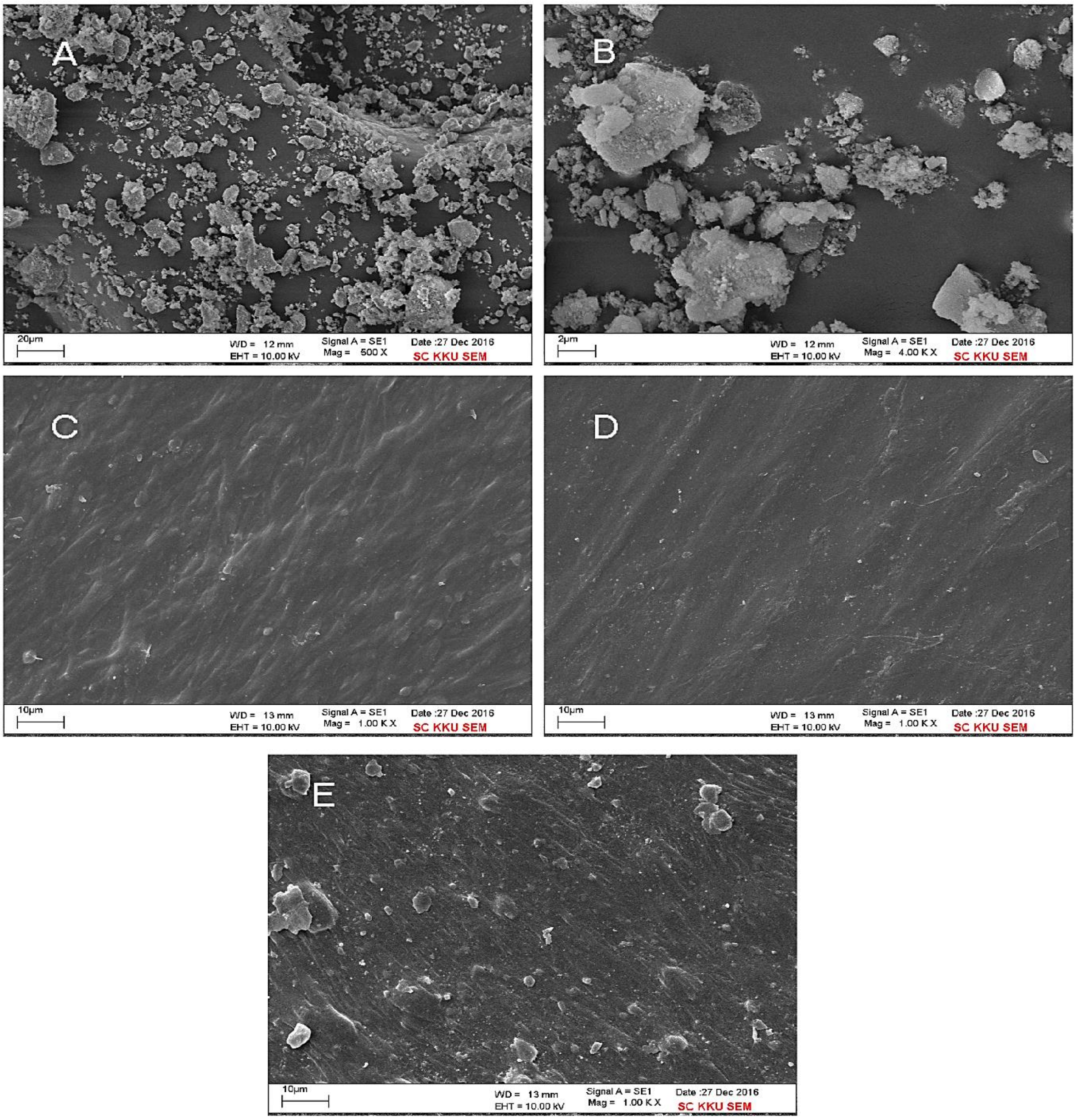

Figure 1 SEM images of RHA particles at 500x magnification (A), 4000x magnification (B), SEM images of PLA blend /RHA composite films containing 5 wt% RHA (C) and 20 wt% RHA (D). (C) and (D) are at the same screw speed, 150 rpm, and the PLA blend /20 wt% RHA had a screw speed of 400 rpm (E)

Table 2 Film thickness of PLA blend films with various RHA contents and degree of stretching

RHA contents	Film thickness (mm)			
	Screw speed 150 rpm	Screw speed 250 rpm	Screw speed 350 rpm	Screw speed 400 rpm
0%	0.04-0.06	0.03-0.04	0.02-0.03	0.01-0.02
5%	0.04-0.06	0.03-0.04	0.02-0.03	0.01-0.02
10%	0.04-0.06	0.03-0.04	0.02-0.03	0.01-0.02
20%	0.04-0.06	0.03-0.04	0.02-0.03	0.01-0.02

The maximum elongation at breakage was 139% for a PLA blend film containing 20 wt% RHA with the lowest stretching (screw speed 150 rpm). This was about 106% higher than that of the PLA blend film at the same stretching. A similar result has been observed in nanocomposites of polymers with the incorporation of montmorillonite nanoclay [37] and montmorillonite layered silicate [11]. However, at higher screw speeds (250, 350, and 400 rpm), the increased RHA content had very little effect on increasing elongation at breakage. It may have been that the increased screw speed reduced film thickness.

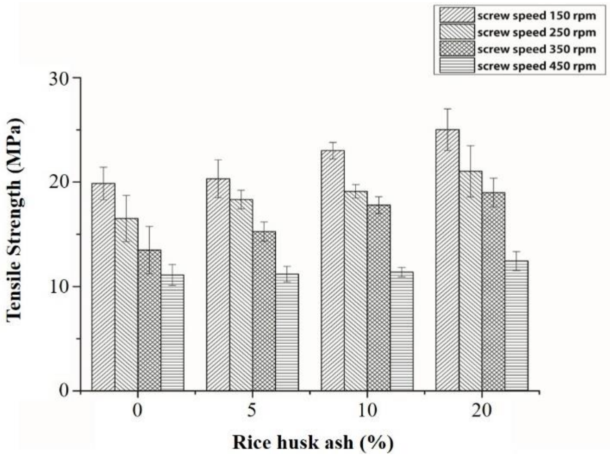

Figure 2 Tensile strength of PLA blend and PLA blend /RHA composite films at various RHA contents and screw speeds

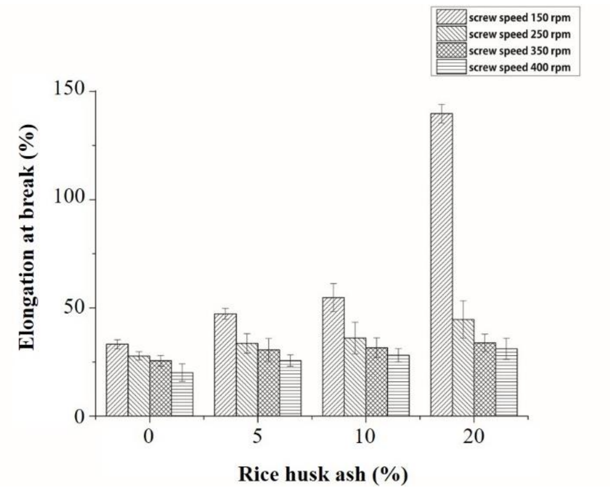

Figure 3 Elongation at break of PLA blend and PLA blend /RHA composite films at various RHA contents and screw speeds

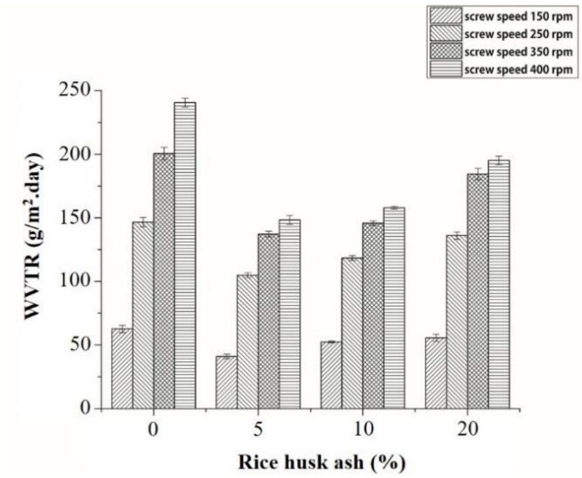

Figure 4 Water vapor transmission rates of PLA blend and PLA blend /RHA composite films at various RHA contents and screw speeds

3.4 Water vapor transmission rate (WVTR)

WVTR results of the PLA blend and PLA blend /RHA composite films are shown in Figure 4. In all cases, the WVTR values of PLA blend /RHA composite films were lower than those of the PLA blend film made at the same speed screw of the nip roll, i.e., all composite films were better water vapor barriers comparing to the PLA blend film. This may have been because the presence of RHA particles in the PLA blend matrix creates more tortuous pathways through composite films, resulting in longer distance for water vapor diffusion and therefore decreased water vapor permeation [11, 38].

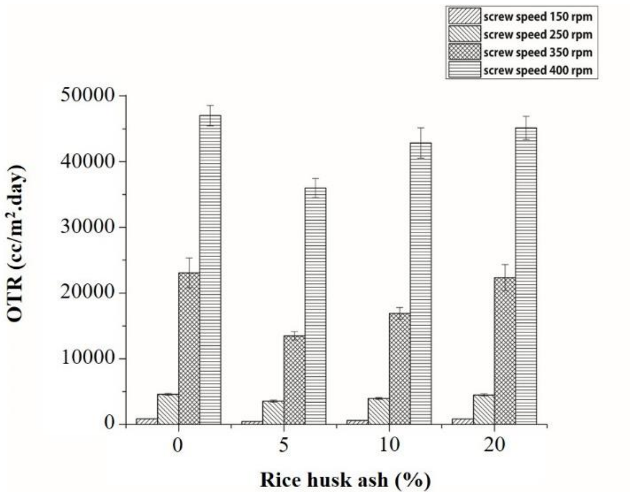

Figure 5 Oxygen transmission rates of PLA blend and PLA blend /RHA composite films at different RHA contents and screw speeds

Table 3 Shelf life of Pisang Awak bananas packaged in various types of films

Packaging film	Screw speed (rpm)	Shelf life (days)
LLDPE	-	8
PLAb no. 1	150	8
PLAb no. 2	250	8
PLAb no. 3	350	8
PLAb no. 4	400	8
PLAb/5RHA no. 1	150	12
PLAb/5RHA no. 2	250	8
PLAb/5RHA no. 3	350	8
PLAb/5RHA no. 4	400	8
PLAb/10RHA no. 1	150	12
PLAb/10RHA no. 2	250	8
PLAb/10RHA no. 3	350	8
PLAb/10RHA no. 4	400	8
PLAb/20RHA no. 1	150	14
PLAb/20RHA no. 2	250	8
PLAb/20RHA no. 3	350	8
PLAb/20RHA no. 4	400	8

Improved water vapor barrier properties due to addition of various types of fillers into polymers was studied [11, 39-40]. However, when comparing the PLA blend /RHA composite films with RHA contents (5, 10, and 20 wt%) under the same stretching, it appeared that higher RHA contents in the composite films resulted in higher WVTRs. It is believed that the more RHA particles present, the more likely they would form aggregates as well as become poorly distributed. These, in turn, led to a shorter tortuous pathways in the PLA blend matrix, resulting in higher permeability to water vapor. When we considered the effect of screw speeds on WVTR value, it was evident that higher screw speeds led to higher WVTR values across both PLA blend and PLA blend /RHA composite films. This effect was expected because higher screw speeds led to higher degree of stretching and, as a result, thinner films (Table 2) which could be easily permeated. Moreover, the stretching creates micropores at the interface of RHA particles and the polymer matrix which makes the film more porous. Accordingly, water vapor permeability increases with increased stretching [7, 41].

3.5. Oxygen transmission rate (OTR)

One important aspect for a material suitable for fresh fruit and vegetable packaging is a suitable OTR to maintain the optimum oxygen concentration for the respiration of packed fruits. The oxygen transmission rates of the prepared PLA blend /RHA composite films were measured and are shown in Figure 5. The OTR value of PLA blend and PLA blend /RHA composite films are affected by both the presence of RHA filler and degree of stretching. With changes of the RHA loading and stretching, PLA blend /RHA composite film with various OTR values (416-47008 cc/m^2 day) could be produced. The PLA blend /RHA composites exhibited much improved barrier properties to oxygen permeation compared to that of the PLA blend film. Again, this could be explained by the tortuous pathway theory discussed in Section 3.4. Similar trends were reported when various types of fillers were added into a polymer matrix [11, 39-40]. However, when we compared the PLA blend /RHA composite films containing different RHA contents, there was an increasing trend of OTR values with increasing RHA contents. This was very similar to the increasing trend of WVTRs observed with higher RHA contents, and the explanation might very well be the same. Also, the effect of screw speeds on OTR value was similar to that of the WVTR. Higher screw speeds led to greater stretching and, as a result, thinner films with micropores at the interface between RHA particles and the polymer matrix. These altogether contributed to higher OTR values. The results showed similar trends to Garofalo et al. [42]. They found that the oxygen permeability of an organoclay /polyamide nanocomposite film increased with increasing draw ratio.

3.6 Evaluation of packaging application of PLA blend /RHA composite films

To evaluate the efficacy of PLA blend /RHA composite films, shelf life of Pisang Awak bananas packed with PLA blend /RHA films from various formulations and conventional LLDPE film were evaluated and compared. The shelf lives of bananas packed in various films are summarized in Table 3. Most of films could extend the shelf life of bananas to 8 days. PLAb /5RHA No. 1 and PLAb /10RHA No. 1 composite films could extend the shelf life of

Figure 6 Physical appearance of bananas as received (A) and after storing for 8 days without packaging (B) with a conventional LLDPE bag (C); PLA blend film, stretched at 150 rpm screw speed (D); PLA blend /20 wt% RHA, stretched at 150 rpm screw speed (E)

Figure 7 Physical appearance of bananas packaged for 12 days in a bag made of PLA blend /5 wt % RHA (A); PLA blend /10 wt% RHA (B); PLA blend /20 wt% RHA (C) and PLA blend /20 wt% RHA for 14 days (D), all films were stretched at a 150 rpm screw speed

bananas to 12 days, while PLAb /20RHA No. 1 composite film gave the longest shelf life, 14 days. Digital images of some representative bananas packaged in LLDPE, PLA blend and PLA blend /RHA composite films for 8 days are shown in Figure 6. It can be seen that most bananas became spoiled, with black peels, mold growth, soft or bruised flesh. Those which had been packaged in bags made of PLA blend /20 wt% RHA composite films with low stretching (150 rpm screw speed, Figure 6E) were not spoiled. These results suggest that films that were stretched to a higher degree (higher screw speed), and therefore exhibited high WVTRs and OTRs, were not suitable for Pisang Awak banana packaging. The explanation could be that when the bag allowed oxygen and water vapor to cross quite freely, the bananas could undergo their normal physiological changes (e.g., respiration, sugar metabolism) which speed up the ripen and spoiling processes. Furthermore, among those films which were stretched at a 150 rpm screw speed, only the composite film containing 20 wt % RHA exhibited the longest shelf life (14 days). This indicated that PLA blend /20 wt% RHA composite film with low stretching (low screw speed of 150 rpm) is a suitable film to prolong the shelf life of Pisang Awak bananas. Figure 7A-C depict the physical appearance of bananas packed in PLA blend /RHA composite films containing various RHA contents for 12 days. Black peels, mold growth and bruised flesh were clearly observed for bananas packed with PLA blend /RHA composite films containing 5 and 10 wt% RHA (Figure 7A-

B), while bananas packed with PLA blend /20 wt% RHA presented yellow and brown peels and firm flesh with a decent color (Figure 7C). When the storage time of this banana was extended to 14 days, the peels were black but the internal flesh was not bruised (Figure 7D). This result indicates that the composite film with 20 wt% RHA loading under low stretching (screw speed 150 rpm) was suitable for packaging Pisang Awak bananas, almost doubling the shelf life compared to using LLDPE as a packaging material.

4. Conclusions

PLA blend and PLA blend /RHA composite films with various RHA loadings were prepared by simultaneous blow-film and film stretching processes. The prepared PLA blend /RHA composite films had improved tensile strengths compared to the PLA blend film. PLA blend /RHA composite films with broader gas permeability range can be produced by this process. Packaging application test results indicated that PLA blend /20 wt% RHA composite films with stretching at a 150 rpm screw speed are suitable for use as a packaging films to prolong the shelf life of Pisang Awak bananas. Their shelf life could be extended by as much as 75% longer than when packaging in a conventional LLDPE film. Moreover, a variety of water vapor and oxygen permeability results indicated that PLA blend /RHA composite films could be used for various kinds of fruit as a green packaging material for extending the shelf-life of fresh fruits.

5. Acknowledgements

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