Moisture Sorption Characteristic and their Relative Properties of Thermoplastic Starch/Linear Low Density Polyethylene Films for Food Packaging

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Abstract

With an attempt to develop permeable packaging film for fresh produce, a series of linear low density polyethylene (LLDPE) / cassava starch blend films with starch content ranging from 10 to 40% were prepared by extrusion. Their moisture sorption characteristic, mechanical properties, barrier properties (gas transmission rate, water vapour transmission rate) and surface morphology were studied. The results indicated that at studied relative humidity (99%RH) initial moisture absorption rate and moisture capacity of the blend films were affected by starch content and temperature. Tensile strength slightly decreased with the increase in starch content in the LLDPE films. Before conditioning at 99%RH, 25°C for 72 h there was no significant difference in mechanical properties among the blend films, unlike after conditioning. The blend films showed high oxygen and carbon dioxide transmission rates (O2TR and CO2TR) and moderate water vapour transmission rate (WVTR). SEM micrographs verified micro-void structure possibly influencing barrier properties of the films.

Key words: Moisture sorption, Starch/LLDPE film, Gas permeability, Water permeability

Introduction

The production of minimally processed, fresh produce is an emerging industry offering nutritious, convenient products with fresh-like qualities. Thereafter the shelf life of the products becomes one of the foremost challenging problems in commercialisation. A new packaging technology consisting of Equilibrium Modified Atmosphere Packaging (EMAP) combined with chilling is used for prolonging the shelf-life of respiring products. However, the packaging films used until now are often not adapted to the needs of the packaged fresh produce. In addition, the materials most used for food packaging are the petrochemical-based polymers due to their availability in large quantities at low cost and favourable functionality characteristics. With limitation of fossil resource and their degradation when discarded, a number of bio-based materials and their innovative applications in food packaging have gained much attention over the past several years. Because of its annual availability, low cost and being environmentally friendly, starch is one of the most promising bio-based raw materials. The first studies about use of starch in food packaging were based on substituting part of the synthetic matrix like polyethylene by starch (below 10%), however, the main difficulties found were attributed to chemical incompatibility of starch with synthetic polymers. To overcome some problems caused by high intermolecular hydrogen bonds, many workers dealt with the addition of plasticizers such as water, glycerol, sorbitol, to pure starch and accompany with high temperatures and under shear. The obtained products are called as thermoplastic starch (TPS). Although, starch-based plastics have been reported by many researchers, their development was not as expected, mainly because of their deficiencies with regard to mechanical properties and water transmission. Due to its inherent hydrophilic nature, starch tends to absorb large quantities of water at elevated relative humidity conditions. The moisture content can affect significantly the physical and barrier properties of starch-based...
films. Hence, there is a need to address the sorption influence of starch present in the films in order to make it suitable for food packaging.

In the present study, LLDPE/cassava starch films were prepared and targeted as a packaging material for fresh fruits and vegetables, which require controlled CO2, O2 and water vapour transports to extend shelf life of products. Since moisture loss or transpiration is an important physiological process that affects the main qualities of the fresh fruits and vegetables such as saleable weight, appearance, texture and flavour. The scope of this contribution is focused on the effect of starch content on moisture sorption characteristics at studied conditions. Meanwhile, morphology, mechanical properties, gas transmission rate and water vapour transmission rate of the blend films were also investigated.

Materials and Experimental Procedures

Materials

Linear low density polyethylene (LLDPE) was purchased from Dow Chemical Co. Ltd. Cassava starch (ca. 10% moisture) containing approximately 20% amylose and 80% amyllopectin was obtained from a local market. Glycerol and maleic anhydride were used as a plasticizer and a compatibilizer, respectively. All other chemicals were of the highest quality obtainable commercially.

Film Preparation

After having been thoroughly blended in a high-speed mixer at room temperature, LLDPE, compatibilizer, glycerol, and cassava starch (10-40%) were extruded using a twin-screw extruder (LTS20-32, Lab Tech Engineering). The temperature profile along the barrel ranged from 150 to 190°C. The screw speed was approximately 100 rpm. After extrusion, thermoplastic starch/polyethylene films were prepared by a conventional blown film process. The films with a thickness of 30 - 40 μm were collected and kept in a desiccator at room temperature until use.

Moisture Sorption Characteristics of Films

LLDPE/cassava starch films (30 mm x 150 mm) were placed at 10 and 25 ± 2°C over saturated potassium sulfate (K2SO4) solution in separated chambers having 99% relative humidity (RH) condition. Weights of the film specimens were measured as a function of time. All tests were carried out in duplicate. Moisture absorption data were fitted according to a mathematical model suggested by Peleg (1988).

\[ M_t = M_0 + \frac{t}{k_1 + k_2 t}; \]

where \( M_t \) is the moisture content after time (%), \( M_0 \) is the initial moisture content (%), \( k_1 \) is the Peleg rate constant, \( k_2 \) is the Peleg capacity constant, and \( t \) is time (hr).

Mechanical Properties of Films

Five film specimens (15 mm x 70 mm) of each formulation were placed over saturated K2SO4 solution (99% RH, 25 ± 2°C) for 72 hr. Tensile properties of the samples before and after conditioning were determined using the Instron Universal Testing Machine at load cell 1 N, crosshead speed 500 mm/min and initial grip distance 50 mm in accordance with ASTM D-882. Q-test and ANOVA were performed for statistical analyses.

Gas transmission Rate of Films

Carbon dioxide transmission rate (CO2TR) and oxygen transmission rate (O2TR) were determined using PERMATRAN-C Model 4/41 and OX-TRAN® Model 2/21 (MOCON Inc., USA), respectively. Tests were performed at RH of 0% and at a temperature of 23±1°C.

Water Vapor Transmission Rate (WVTR)

WVTR was determined using ILLINOIS 7002 at 90%RH and 38°C, according to ASTM D-1249.

Scanning Electron Microscopy (SEM)

Surface morphology of the LLDPE/starch films before and after conditioning was observed with a scanning electron microscope (JSM-6301F). An accelerating voltage was set at 15 kV. The films were coated with gold powder to avoid charging under the electron beam and then micrographs of the films were taken at magnifications of x5000.
Results and Discussion

Moisture Sorption of Films

With starch being hydrophilic in nature, there is a need to address the sorption influence of starch present in the LLDPE/starch films, to make it suitable for fresh produce packaging. Effect of starch content on the moisture sorption characteristic of the LLDPE/starch films is shown in Figure 1. Plain LLDPE film did not exhibit any moisture sorption. In contrast to the LLDPE/starch films, moisture sorption rate and capacity of the films were proportional to starch content due to higher sorption of water molecules by starch. As time increased, the sorption was more rapid at the initial stages and lower amounts of water were absorbed. Then, the moisture content of the films reached a plateau indicating that they became equilibrated with surrounding RH. To improve the investigation about moisture sorption behavior of the films, the moisture content data obtained at different time were fitted using Peleg model. The Peleg constants, \( k_1 \) and \( k_2 \), are shown in Table 1. As \( k_1 \) is a constant related to mass transfer, the lower \( k_1 \), the higher the initial moisture absorption rate; \( k_2 \) is a constant related to maximum moisture absorption capacity and the lower \( k_2 \), the higher the absorption capacity.\(^{10}\) From the obtained results, it indicated that starch content and temperature influenced on moisture equilibrium time (or moisture absorption rate) and moisture absorption capacity of the films. The higher starch content, the higher absorption rate and capacity it tended to be. However, there are no obvious differences in absorption rate (\( k_1 \)) among the films comprising 20 - 40% starch. As would be expected for the temperature effect, it was shown that the higher temperature, the higher absorption rate and capacity. In addition, it is worth noting that temperature significantly affects absorption rate rather than absorption capacity.

Mechanical Properties of Films

Tensile strength is a capacity of the film to take the load and percent elongation is its ability to stretch. Figure 2. exhibits the tensile strength and percentage of elongation of the LLDPE/starch films with various starch contents. The results indicate that, although the incorporation of starch in the LLDPE leads to lower tensile strength (ca. 8 - 9 MPa), the blends are still operational. These results were consistent with numerous previous works.\(^{15, 14, 5, 11}\) On the other hand, the incorporation of starch had no statistically pronounced effect on elongation (ca. 497 - 565 %, \( p >0.05 \)). In comparison to the mechanical properties of the LLDPE/starch films before and after conditioning at 99%RH, 25°C for 72 h, it was found that decrease in mechanical properties attributed to moisture surrounding. This can be
explained that, as well known, PE and TPS could form immiscible blends because of the high interfacial tension between a non-polar polymer and highly polar one. Immiscibility was greatly enhanced in the presence of moisture; the higher starch content, the higher moisture absorbed. It was also corresponded well with the SEM results which displayed some swollen starch granules after the films were conditioned.

![Figure 2](image_url1)  
**Figure 2.** Tensile strength and elongation of the LLDPE/starch films before (♦) and after (■) kept at 99% RH, 25 °C for 72 hr

**Gas Permeability**

The accumulation of carbon dioxide and depletion of oxygen to beneficial levels by the application of modified atmosphere packaging (MAP) is known to extend the post-harvest life of many horticultural products. An equilibrium modified atmosphere is established inside the package when the O₂ transmission rate (O₂TR) of the packaging film is matched to the O₂ consumption rate of the packaged commodity. The respiration of the living plant tissue results in the production of CO₂ which diffuses through the packaging film dependent on the CO₂ transmission rate (CO₂TR) of the film. The applied packaging film is selected based on the film O₂TR and CO₂TR required to obtain a desirable equilibrium modified atmosphere. From Figure 3, it was evident that O₂TR and CO₂TR of the LLDPE/starch films ranged from 9,600 - 21,400 cm³m⁻²·d⁻¹ and 27,800 - 54,300 cm³m⁻²·d⁻¹ at atmospheric pressure, respectively. The O₂TR and CO₂TR reached to maximum at 20% starch and then continuously dropped when the starch content exceeded 20%. The ratio of CO₂ to O₂ permeation coefficients of the film is defined as permselectivity (β). The β values of the LLDPE/starch films were between 2.5 and 2.9, implying high permeability of CO₂. The high permeability of CO₂ is due to high diffusivity and solubility comparing to O₂. High diffusivity of CO₂ could be due to lower kinetic diameter (3.3 Å for CO₂ and 3.46 Å for O₂). Work by Asira et al. indicated that high permeable films possessing O₂TR, CO₂TR, and β values of 12,000 - 16,000 cm³m⁻²·d⁻¹ atm, 35,000 - 45,000 cm³m⁻²·d⁻¹ atm, and 2.8 - 2.9, respectively could successively extend shelf life of Chinese broccoli without a sign of withering. This is also in good agreement with Al-Ati and Hotchkiss’s work which suggested that packaging films with β values lower than those commercially available (ca. 4 - 8) would further optimize O₂ and CO₂ concentration in MAP (modified atmosphere packaging) of respiring produce, particularly highly respiring and minimally processed produce.

![Figure 3](image_url2)  
**Figure 3.** Gas transmission rate of the LLDPE/starch films

**Water Vapour Transmission**

Effect of starch content on water vapour transmission rate (WVTR) of the LLDPE/starch blend films is shown in Table 2. WVTR of the studied films ranged approximately from 31 to 63 g.m⁻².d⁻¹. From the literature, films with moderate
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Water transmission rate (50 - 100 g.m\(^{-2}\).d\(^{-1}\)) can be used for packaging of fresh produce to control their moisture evaporation and enhance their shelf life.\(^{(14)}\) Because the thickness of the films varied, the WVTR was normalized to film thickness (\(l\)) to obtain the specific water vapour transmission rate (\(\mathcal{R} = \text{WVTR} \times l\)) with units of g.mm.m\(^{-2}\).d\(^{-1}\).\(^{(8)}\) The \(\mathcal{R}\) values increased from 0.92 g.mm.m\(^{-2}\).d\(^{-1}\) in plain LLDPE film to 2.59 g.mm.m\(^{-2}\).d\(^{-1}\) in the LLDPE/starch blends. The more starch content, the higher \(\mathcal{R}\) value it tends to be. This increase is due to two-phase morphology of LLDPE/starch blends, which provides passages for moisture to penetrate through the surface. The incorporation of starch in the LLDPE matrix reduces the intermolecular force between the LLDPE, resulting in enhancing the void contents in the blend films. This phenomenon was confirmed by the results from SEM.

**Table 2.** Water vapour transmission rate (WVTR) and specific water vapour transmission rate (\(\mathcal{R}\)) of the LLDPE/cassava starch blend films

<table>
<thead>
<tr>
<th>Starch content (%)</th>
<th>WVTR (g.m(^{-2}).d(^{-1}))</th>
<th>Thickness (mm)</th>
<th>(\mathcal{R}) (g.mm.m(^{-2}).d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>31.25 ± 0.92</td>
<td>0.0295</td>
<td>0.92 ± 0.04</td>
</tr>
<tr>
<td>10</td>
<td>52.23 ± 2.43</td>
<td>0.0327</td>
<td>1.71 ± 0.08</td>
</tr>
<tr>
<td>20</td>
<td>60.51 ± 2.43</td>
<td>0.0350</td>
<td>2.12 ± 0.08</td>
</tr>
<tr>
<td>30</td>
<td>63.02 ± 1.68</td>
<td>0.0357</td>
<td>2.25 ± 0.03</td>
</tr>
<tr>
<td>40</td>
<td>59.04 ± 5.04</td>
<td>0.0438</td>
<td>2.59 ± 0.26</td>
</tr>
</tbody>
</table>

**Film Morphology**

It is well known that PE and TPS could form immiscible blends because of the high interfacial tension between a non-polar polymer and a highly polar one. So it is very necessary to study the morphology structure of the immiscible blends to understand many properties. Surface morphology of the LLDPE films blended with various contents of starch before and after kept at 99% RH, 25°C for 72 h was examined using SEM (Figure 4). It can be observed that LLDPE film had smooth surface, whereas the blend films showed a specific morphology, rough surface with many air voids, although starch particles seemed to be well embedded in the LLDPE matrix. The surface roughness tends to be associated with starch content, the higher starch content, the more surface roughness. The air gaps visible in the films may be due to moisture content at high starch concentration. The evaporation of moisture created air voids which could not escape from the films.\(^{(15)}\) This result was well supported by work of Raj et al. which revealed that voids were developed in melt extruded LDPE/starch films but no voids were observed in solution cast films.\(^{(14)}\) Comparison micrographs of the blend films before and after conditioning, a notable difference is small drop-like particles, which is presumably presence of starch particles entrapped on the surface swelling after the films exposed to moisture.

**Figure 4.** SEM micrographs of the LLDPE blended with (a) 10%, (b) 20%, (c) 30% and (d) 40% starch before and after conditioning at 99%RH, 25°C for 72 hr
Conclusions

Various starch contents ranging from 10 to 40% in LLDPE were extruded into films. It was found that all studied properties were greatly affected by starch content. Peleg model was useful to fit moisture absorption data and determine absorption rate and moisture capacity of the blend films. Mechanical properties obviously decreased with the increase of starch content particular when the blend films absorbed moisture. Good promise in gas and water vapour transmission properties for fresh produce packaging was shown. SEM study revealed that the LLDPE/starch system possessed two-phase morphology with micro-voids affecting the film properties.

Acknowledgments

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References


