Water Vapour Permeability of Poly(lactic acid)/Chitosan Binary and Ternary Blends

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Abstract
In this study, poly(lactic acid) (PLA) containing chitosan and poly(vinyl alcohol) (PVOH) was prepared using melt mixing followed by compression molding. Effects of chitosan and PVOH on the water vapour permeability of the PLA were evaluated. The water vapour permeability (WVP) and water vapour transmission rate (WVTR) of PLA/chitosan blends are higher than the pure PLA, which attributed to the hydrophilicity of chitosan. Incorporation of PVOH improved compatibility and interfacial bonding of PLA/chitosan blends. It was found that the WVP and WVTR of the PLA/chitosan/PVOH ternary blends are lower than that of the PLA/chitosan binary blends.

Keywords*: Poly(lactic acid), Chitosan, Polymer blends, Compatibility, Water vapour permeability*

1 Introduction

The disposal of petroleum-based plastics and the restricted availability of petrochemical resources is a global concern. In recent years, biopolymers have been the focus of academic and industrial research interest from the viewpoint of sustainable development and reducing impact on the natural environment. There are various types of biodegradable polymers such as polyesters, starch, polyhydroxyalkanoates, cellulose etc. Example of biodegradable aliphatic polyesters includes poly(lactic acid) (PLA), poly(glycolic acid) and poly(ε-caprolactone). PLA derived from renewable resources (e.g. corn, sugar beets, wheat) has become popular owing to its sustainability, biodegradability, superior transparency, high modulus and strength. PLA has potential to be used in food packaging, automotive parts, disposable tableware, sutures and drug delivery device [1-7].

Chitin can be found in the exoskeleton of arthropods such as insects, crabs, shrimps, lobsters, and some fungal cell walls [8]. Chitosan is the most abundant organic materials produced by the deacetylation of chitin under alkaline conditions. Chitosan shows good biocompatibility and biodegradability. Additionally, it is worth to mention that the degradation products of chitosan are non-toxic, non-immunogenic and non-carcinogenic [9].

Both PLA and chitosan are biodegradable and suitable for packaging applications. Because of the high cost of PLA, adding chitosan seems to be a possible approach to develop a cost effective PLA blends. However, the incompatibility between PLA and chitosan need to be mentioned [10]. From literature, incorporation of poly(vinyl alcohol) (PVOH) could improve the compatibility between PLA and chitosan. Grande & Carvalho [11] prepared ternary blends of chitosan/PLA/PVOH via oil-in-water emulsion process. The blends of chitosan/PVOH/PLA in the ratio of 1:2:2 and 1:6:1 showed a high level of adhesion between phases. Zhang et al. [12] demonstrated that the dense membranes of chitosan/PVOH/PLA blend can be prepared by casting technique. It was reported that the mechanical properties of the blends are controlled by the PVOH loading.

Permeability is defined as transfer of molecules from the product to the external environment, through package or from the external environment through the package, to the product. Water vapour permeability (WVP) is the measurement of the time rate of water vapour transmission through unit area of flat material of unit thickness induced by unit vapour pressure difference between two specific surfaces, under specified temperature and humidity conditions. This test is to determine the water vapour transmission of materials through which the passage of water vapour may be of importance, such as paper, plastic films, sheet materials, plastics products, and so on [13].

To the best of our knowledge, there is limited study on the water vapour permeability of PLA/chitosan blends. These properties are essential so the PLA blends can be a potential material for food packaging. Water vapour barrier properties are important for maintaining or extending the shelf life of packaged food product as the physical and chemical deteriorations of the packaged food product are related to its equilibrium moisture content. For fresh food it is important to avoid dehydration while for bakery or delicatessen it is important to avoid water permeation [14]. In this study, the water vapour permeability (WVP) properties of PLA/chitosan films with and without PVOH were measured at temperature of 30°C.

2 Experimental

2.1 *Materials*

Poly(lactic acid) pellets (PLA, IngeoTM 3051D) were supplied by NatureWorks LLC® (USA). The specific gravity and melt flow index of PLA are 1.25 and 25 g/10 min., respectively. The glass transition temperature (T_g) and melting temperature (T_m) of the PLA are 60°C and 158°C, respectively. Chitosan powder (practical grade, obtained from shrimp shells) was supplied by Sigma Aldrich (USA). The T_m of chitosan is approximately 105°C. Poly(vinyl alcohol) (PVOH; 99% hydrolyzed, M_w 89,000-98,000 g/mol) was supplied by Sigma Aldrich (USA). Table 1 shows the materials designation and compositions.

Table 1: Materials designation and compositions

Materials designation	**Compositions**		
	PLA (wt%)	**Chitosan (wt%)**	**PVOH (phr)**
PLA	100	-	-
PLA/Chitosan (70/30)	70	30	-
PLA/Chitosan/PVOH-5	70	30	5
PLA/Chitosan/PVOH-10	70	30	10
PLA/Chitosan/PVOH-15	70	30	15

2.2 *Sample preparation*

Prior to mixing, all the materials were dried in an oven at 50°C for 24 h. Melt compounding of PLA and its PLA/chitosan blends was performed by using an internal mixer (Haake PolyDrive, Germany) at 160°C. The rotor speed was set at 50 rpm. Compression molding was performed at 160°C. All the compression-molded PLA specimens (thickness 0.40 mm) were kept in desiccators prior to further testing.

2.3 *Water vapour permeability and water vapour transmission rate determination*

Water vapour permeability (WVP) test was conducted according to ASTM Method E96-00. The test film was sealed as a patch onto a petri dish (diameter 8.0 cm and height 1.5 cm) containing distilled water (Relative Vapour Pressure (RVP) = 1) with 1.3 cm-deep headspace. The petri dish assembly was then placed in a dessicator maintained at room temperature and RVP = 0 by using silica gel. The petri dish assembly was weighed for every hour at first day, and then the weighing was made every day over a 6-day period. By statistical approach, when a straight line adequately fits the weight change vs time plot by linear regression with $r^2 \geq 0.99$, the constant rate of weight change was obtained. Water vapour transmission rate (WVTR) was calculated from the slope of the straight line divided by the test area (see Equation 1). WVTR (g h^{-1} m^{-2}) for each type of film was determined with three individually prepared films as the replicated experimental units.

$$\text{WVTR} = G/tA = (G/t)/A \tag{1}$$

where,

G = weight change (from the straight line), g

t = time when G occurred, h

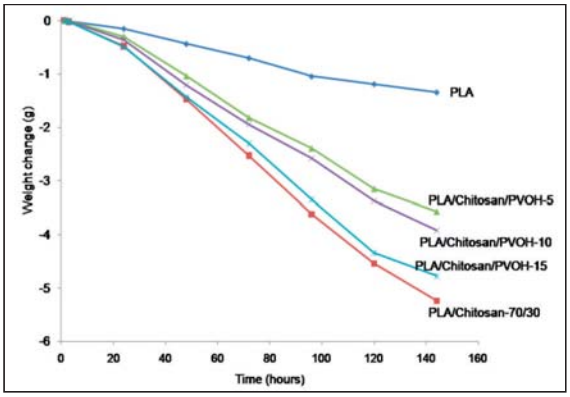

Figure 1: Weight changes of PLA/chitosan blends as a function of exposure time.

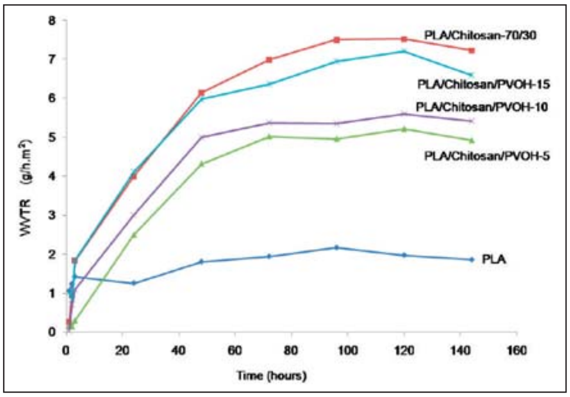

Figure 2: Water vapour transmission rate (WVTR) of PLA and PLA/chitosan blends.

G/t = slope of the straight line, g/h
A = test area (petri dish mouth area), m^2

After WVTR value of sample was obtained, the WVP (g $Pa^{-1}s^{-1}m^{-1}$) can be calculated by using Equation 2.

$$WVP = [WVTR/S(R_1-R_2)] \times d \qquad (2)$$

where,
S = vapour pressure (Pa) at test temperature, Pa
R_1 = RVP in the desiccators
R_2 = RVP in the permeation cell
d = film thickness

3 Results and Discussions

Figure 1 shows the weight change of the PLA/chitosan blends as a function of time. It can be seen that the weight change of PLA and its blends decreased with exposure time. The constant rate of weight change was found at 48 h and onwards. The constant rate of weight change for all the PLA/chitosan blends was obtained by linear regression with $r^2 > 0.99$ (see Table 2).

Figure 2 shows the water vapour transmission rate (WVTR) of the PLA/chitosan blends. Initially, for all the PLA/chitosan blends, their WVTR were increased rapidly. According to Hu et al. [15], it is common that for a solid polymer, the water vapour transmission follows a simple mechanism: water vapour permeates the film by sorbing at the entering face, dissolving and rapidly establishing equilibrium, diffusing through the film, and desorbing at the exit face. Thus, it is reasonable that the WVTR of the PLA/chitosan blends was increased rapidly at the beginning, and after that achieved an equilibrium state. Additionally, from Figure 2, one may observe that the WVTR of the PLA/chitosan blends became slower after 4 h and much slower after 48 h. Probably this multiple slowing down could be explained by sorbing at and swelling of hydrophilic components in the entering face during first 4 h, then in volume (up to 48 h), and finally equilibration and desorbing on the exit face. Note that in this study the equilibrium was achieved at approximately 120 h.

Table 2: Linear regression for the weight change measured from water vapour permeability test. (Note: The r^2 values for all the formulation studied comply with the ASTM E96-00, i.e., the constant rate of weight gain was obtained by linear regression with $r^2 \geq 0.99$)

Materials designation	Y = mX + C	r^2
PLA	Y = - 0.009 X + 0.017	0.990
PLA/Chitosan (70/30)	Y = - 0.038 X + 0.163	0.994
PLA/Chitosan/PVOH5	Y = - 0.026 X + 0.113	0.994
PLA/Chitosan/PVOH10	Y = - 0.028 X + 0.108	0.996
PLA/Chitosan/PVOH15	Y = - 0.035 X + 0.134	0.993

Table 3 presents the WVTR at 120 h of the PLA/chitosan blends. The WVTR of the PLA increased up to 74% in the presence of chitosan. This is attributed to the hydrophilicity of chitosan. According to Zhang et al. [12], the WVTR of chitosan membrane can be as high as 140.6 g/h.m^2. Thus, the increase in WVTR of PLA/chitosan (70/30) is expected. However, it is worth to mention that the WVTR of PLA/chitosan/

PVOH blends are lower than that of PLA/chitosan. Adding of PVOH had reduced the WVTR of PLA/chitosan blends to 26-31%, depending on PVOH content. Recall that PVOH can act as a good compatibilizer for PLA and chitosan [16]. We suggest that the reduction of WVTR of PLA/chitosan/PVOH blends is due to the improved compatibility and interfacial bonding of the phases.

Table 3: Water vapour transmission rate (WVTR) of PLA and PLA/chitosan blends. (Note: data taken at 120 h)

Materials designation	**WVTR (g/h·m^2)**
PLA	1.97
PLA/Chitosan (70/30)	7.52
PLA/Chitosan/PVOH-5	5.22
PLA/Chitosan/PVOH-10	5.60
PLA/Chitosan/PVOH-15	7.20

From Table 3, it can be observed that the WVTR of PLA/chitosan blends was affected by the PVOH content. Although the WVTR of PLA/chitosan/PVOH-15 was lower than that of PLA/chitosan (70/30) blend, the WVTR of PLA/chitosan blends increased with the increasing of PVOH content. This can be due to the excessive PVOH amount in PLA/chitosan blend. PVOH can acts as compatibilizer for PLA/chitosan, however its hydrophilicity behaviour still persist. Thus, the free PVOH functional group (e.g., -OH) may interact with water and thus increase the WVTR of the PLA/chitosan blend.

Figure 3 shows the WVP of PLA and PLA/chitosan blends as a function of time. Initially, the WVP of PLA increased slightly, and it can be seen that the WVP of PLA became almost constant after 48 h. Meanwhile, the WVP of PLA/chitosan blends increased rapidly at the first 48 h. After that, the increment in WVP of the PLA/chitosan films became slower and they achieved equilibrium at 120 h. As can be observed in Figure 3, PLA/chitosan (70/30) shows the highest WVP among all the formulation studied. From Table 4, it can be seen that the incorporation of chitosan into PLA had increased the WVP of PLA profoundly. The WVP of PLA is approximately 0.47 x 10^{-10} g/Pa.h.m. It is commonly known that the WVP of chitosan is relatively high. Adding 30% chitosan increase WVP of PLA to 1.91 x 10^{-10} g/Pa.h.m. Again, this is attributed to the hydrophilicity of chitosan and the incompatibility of PLA/chitosan blend.

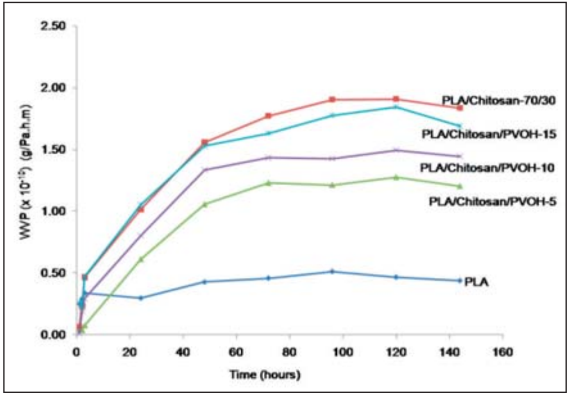

Figure 3: Water vapour permeability of PLA and PLA/chitosan blends.

Similar to the trend of WVTR the WVP of PLA/chitosan blends decreased by the addition of PVOH (c.f. Table 4). This can be due to the improved compatibility of the PLA/chitosan in the presence of PVOH. In other words, PVOH increase the interfacial interaction between PLA and chitosan. Consequently, the PLA/chitosan/PVOH sample is less susceptible to the water vapour, and the outcome is, reduced WVP. However, one may notice that PVOH content influences the WVP of PLA/chitosan blends. Though in overall, the WVP of PLA/chitosan/PVOH is lower than that of PLA/chitosan, increasing the PVOH content increased the WVP value slightly. Adding 5 phr of PVOH reduced the WVP of PLA/chitosan blend from 1.91 x 10^{-10} to 1.28 x 10^{-10} g/Pa·h·m. However, the WVP of PLA/chitosan/PVOH-15 recorded 1.85 x 10^{-10} g/Pa·h·m. This can be related to the hydrophilicity nature of PVOH. Accordingly, higher PVOH content promotes higher water vapour permeability. Thus, although PVOH can be served as compatibilizer for PLA/chitosan blends, its amount should be controlled as far as water vapour permeability is concerned.

Table 4: Water vapour permeability of PLA and PLA/chitosan blends. (Note: data taken at 120 h)

Materials designation	**WVP (g/Pa·h·m)**
PLA	0.47 x 10^{-10}
PLA/Chitosan (70/30)	1.91 x 10^{-10}
PLA/Chitosan/PVOH-5	1.28 x 10^{-10}
PLA/Chitosan/PVOH-10	1.49 x 10^{-10}
PLA/Chitosan/PVOH-15	1.85 x 10^{-10}

4 Conclusions

The water vapour transmission rate (WVTR) and water vapour permeability (WVP) of the PLA was increased by the incorporation of chitosan. This is due to the hydrophilicity of chitosan. On the other hands, adding 5 phr and 10 phr of PVOH was success to reduce the WVP and WVTR of the PLA/chitosan (70/30) blend. This is because of the enhanced interfacial interaction between PLA and chitosan in the presence of PVOH (especially in 5 phr and 10 phr PVOH content). However, it should be taken into the consideration that higher loading of PVOH (i.e., 15 phr) will slightly increase the WVP and WVTR value of the PLA/chitosan blends.

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