Effect of Plasticizer on Oxygen Permeability of Cast Polylactic Acid (PLA) Films Determined Using Dynamic Accumulation Method

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ABSTRACT

Polylactic acid (PLA) is becoming an increasingly important biopolymer for packaging applications. PLA brittleness limits its applicability. This study evaluated PLA properties with increasing amounts of added polyethylene glycol (PEG) plasticizer. Oxygen transmission rate (OTR) of cast films was determined using the newly available Dynamic Accumulation (DA) method. Arrhenius temperature sensitivity of OTR and polymer Permeability was also determined. Permeability of neat PLA is 4.848 ml mm (STP)/m2 s kPa; hence, 4.84 ml mm (STP)/m2 s kPa, 4.07 ml mm (STP)/m2 s kPa and 5.42 ml mm (STP)/m2 s kPa by adding PEG 1 %, 5% and 10% respectively. The main conclusion from this work is increasing PEG will enhance the PLA permeability number but excess PEG in PLA film will decrease the permeability number.

KEYWORDS: *OTR, oxygen transmission rate, dynamic accumulation, PLA, polylactic acid*

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1.0 INTRODUCTION

Polylactic acid (PLA) is a thermoplastic bio-polyester polymer with properties similar to polystyrenethat is also compostable under commercial composting conditions. [1]To the extent that bio-based polymers offer actual or perceived environmental benefits, packaging manufacturers may be able to realize competitive advantage by incorporating bio-polymers into their products.[2] Therefore, interest in PLA for plastic packaging applications is increasing.[3]

Currently, PLA is being commercialized and used as a food packaging polymer.[4] However, PLA is known to be brittle, which limits its applicability. Therefore, plasticizers may be added to enhance ductility and flexibility of PLA based packaging. Plasticizers help to increase polymer chain mobility by decreasing intermolecular forces [5] and hydrogen bonding between polymer chains.[6,7] Plasticizers also affect glass transition temperature and gas permeability.

Oxygen barrier properties of PLA have been reported to be between polyethylene terephthalate and polystyrene.[8,9] A relatively low glass transition temperature permits greater polymer chain mobility at moderate temperatures resulting in higher gas diffusivity and overall permeability.[10]Knowledge of gas transmission properties of packaging materials are critical for a successful package design for many products.[11] Permeation is influenced by solubility of permeant in the film, rate of diffusion of permeant through the film, film thickness, temperature and specific partial pressure difference.[12]

Oxygen transmission rate (OTR) is an important film specification parameter. Film and package OTR are important for determining product shelf life. Until recently, the steady-state method for measuring OTR, as described by ASTM D-3985,[13] has been widely used. However, a new approach based on the principle of dynamic accumulation (DA) has been gaining popularity due to simplicity and relatively low cost.[11] Briefly, DA involves mounting a film between an accumulation chamber and a test gas. For the case of measuring OTR via DA, the accumulation chamber is initially flushed with an inert gas such as nitrogen and the test gas is air or oxygen. Once the accumulation chamber is flushed, it is sealed and oxygen accumulation is monitored over time, typically with a non-destructive oxygen sensor such as those based on florescence quenching (e.g. Oxysense, Dallas, TX). A schematic of a typical DA permeation cell is depicted in Figure 1.

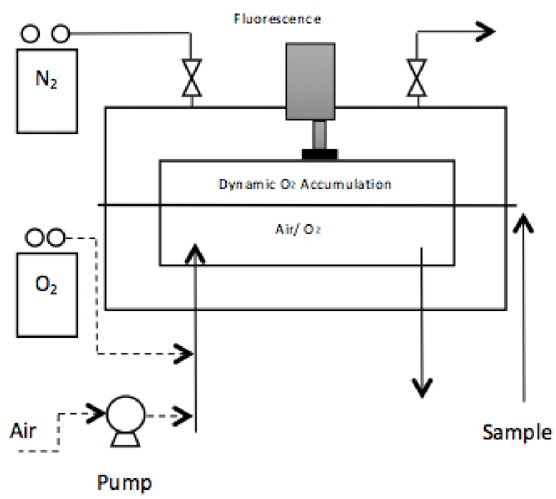

Figure 1. DA permeation cell.

The objective of this work was to measure OTR of cast PLA films with increasing concentrations of plasticizer and to obtain Arrhenius temperature sensitivity parameters of OTR for sample films.

2.0 MATERIAL AND METHOD

2.1. MATERIALS

Polylactic acid pellets were purchased from Shenzen Essu Industrial Co.Ltd.. Guangdong, China with molecular weight (M_W) ca. 100,000 g/mol. Chloroform C606-4 HPLC grade, was purchased from Fisher Scientific, USA. Polyethylene Glycol-400 was purchased from Fisher Scientific, USA with average molecular weight 380-420, density 1.13 g/mol.

2.2. PLA FILM CASTING PREPARATION

PLA films were cast from 5% (w/v) weight solution in chloroform using via casting in glass petri dishes. 20 gram PLA were dissolved in 400 ml chloroform and stirred vigorously for 30 minutes at 60oC. Then, PEG was added in concentrations of 0, 1, 5 and 10% (w/w), respectively.

To achieve different film thicknesses, PLA solutions were poured onto glass petridishes in volumes of 5, 10, 15 and 20 ml, respectively. Solutions were dried into films at 35oC for 15 hours. PLA film production were done in three replication each variable. Resultant PLA films were peeled from petri dishes and thicknesses were measured in 5 locations using a micrometer.

2.3. OTR MEASUREMENT

Dynamic accumulation experiments were performed using permeation cells and fluorescence oxygen detection equipment from Oxysense, Inc. (Model 310, Dallas, TX). The oxygen accumulation chamber had a sample area of 16.62 cm^2 and volume 8.3 cm^3. Initially, the cell was purged with more than 10 volumes of industrial grade nitrogen from a compressed gas cylinder. Purging was followed by monitoring oxygen concentration decrease to a constant zero level using the Oxysense Model 310 device. Industrial-grade oxygen (approximately 100%) was used to purge the test-gas chamber. Oxygen concentration in the DA chamber was measured and recorded periodically using the Oxysense Model 310 (Oxysense, Inc). OTR was subsequently calculated as described by Abdellatief and Welt. [11]

OTR measurements were performed at 15, 23 and 35oC using a fabricated bench top environmental chamber equipped with feedback temperature controller. The system was comprised of a Peltier Effect mini-refrigerator (NuCool Model C-RNU-281VS; Haier America Trading, LLC, NY, USA) and a 100 W light bulb controlled by a PID temperature controller (Omega Model CSC32; Omega Engineering, Inc., Stamford, CT, USA). The environmental chamber is capable of maintaining set point ±0.2^{o}C. OTR measurement were replicated in three times.

3. RESULT AND DISCUSSION

3.1. OXYGEN TRANSMISSION RATE

OTR of the PLA films are plotted as a function of thickness (μm) (Figure 2). The OTR number decrease with increasing film thickness. As expected, the film thickness has a role to reduce the PLA film OTR number.

As expected, OTR is a function of film thickness. [12] OTR value of PLA films decrease with increasing of the thickness. As result, the OTR value is higher with a thinner of PLA films. The trend OTR of PLA films show exponentially. Exponential equation prediction of PLA films OTR and thickness is 1640.7 $e^{-0.012x}$.

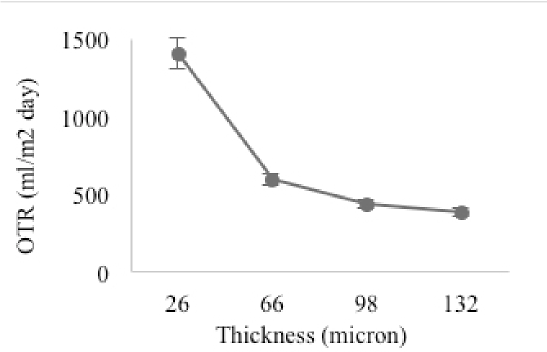

Figure 2. OTR versus PLA film thickness (µm).

Decreasing OTR value of PLA films show a significance difference between 26 microns and 66 microns. OTR value reduced 2.4 times. Hence, PLA film thickness from 66 micron to 132 micron effected decreasing OTR value 1.6 times.

3.2. POLYETHYLENE GLYCOL EFFECT

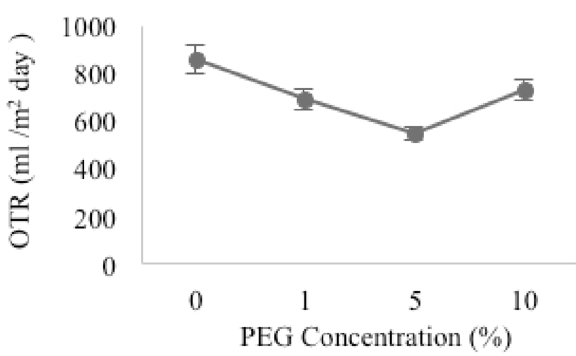

Figure 3. PEG concentration on OTR value.

Plasticizer is commonly added to PLA to improve flexibility and reduce brittleness. OTR of PLA films are plotted as a function of plasticizer (PEG) concentration in Figure 3.

Addition of PEG plasticizer caused OTR to decrease up to plasticizer concentrations of about 5%, after which, OTR increased. The decrease in OTR with initially increasing plasticizer is likely due to increased polymer crystallinity made possible by the presence of plasticizer. Hence, the count of crystallinity intensity of PLA-PEG showed increasing by XRD analysis. The count of crystallinity intensity neat PLA is 1500, otherwise PLA with addition PEG 1%, 5% and 10% are 1600, 2500 and 2000, respectively.

3.3. TEMPERATURE EFFECT

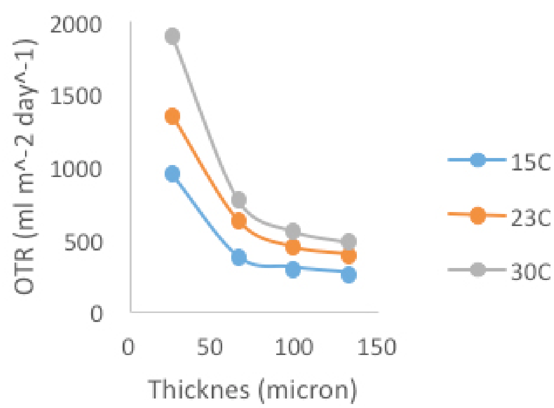

Figure 4. Oxygen Transmission rate (OTR) value PLA film as function of thickness & temperature.

As expected, OTR increase with increasing temperature. The trend of decreasing OTR on PLA film among temperature treatment show a similar pattern. OTR of PLA films are plotted as a function of temperature and thickness in Figure 4.

Related to the graph, the OTR trend is exponentially among temperature gradient. Lower OTR number explain amount less oxygen is less to through pass the PLA film. As result, lower OTR number in PLA film shows a good barrier properties from oxygen penetration. It clears, temperature 15oC result a best temperature condition of PLA film to prevent from oxygen permeation. Energy activation of PLA film surrounding different temperature in Figure 5.

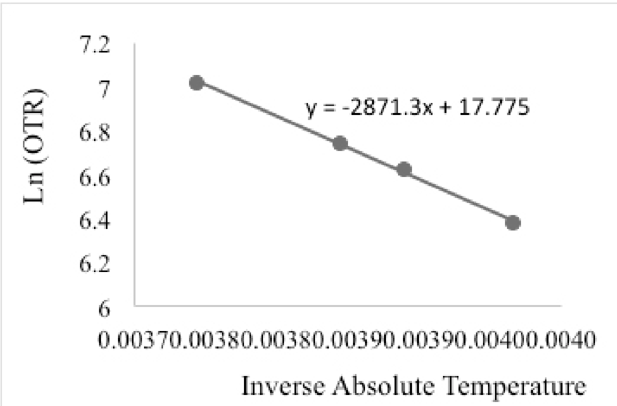

Figure 5. Arrhenius temperature sensitivity parameters.

Activation Energy (Ea) of 23.869 kJ/mol and pre-exponential factor (k_o) of 5.243 x 10^7.Fig 4. Temperature effect on Oxygen Transmission rate (OTR) value as shown via Arrhenius Plot. The following Arrhenius equation (Equation 1) can be used to predict OTR of this film at any absolute temperature (Kelvin):

$$OTR = e^{\left(\frac{-2871}{T\,(K)}+17.775\right)} \quad ....(1)$$

3.3. PERMEABILITY

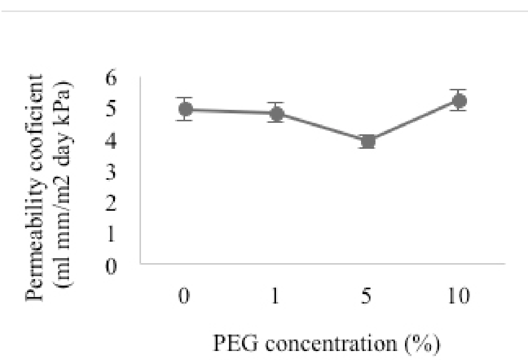

Figure 6. PLA film PEG concentration on permeation coefficient.

OTR is a sample specific measurement. Using the thickness of the film and conditions of the test, OTR may be converted into a more general permeation coefficient, $\bar{P}$. Figure 6 shows $\bar{P}$ of PLA with increasing concentrations of plasticizer. As with Figure 3, a reduction in permeation coefficient at 5% plasticizer is likely due to increased crystallinity resulting from greater chain mobility. At 10% plasticizer, permeation coefficient increases. Permeation coefficient of PLA film is also influenced by temperature. Arrhenius temperature sensitivity on permeation coefficient of PLA is shown in Figure 7.

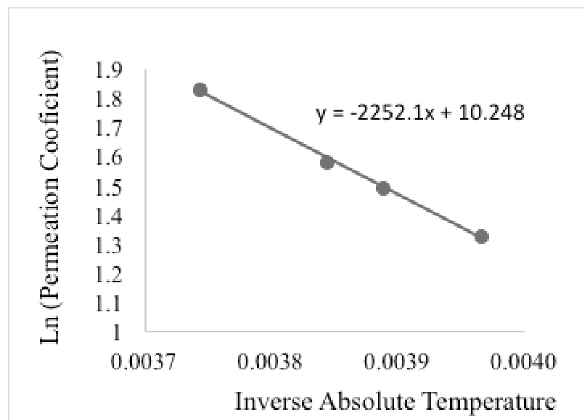

Figure 7. Arrhenius temperature sensitivity on $\bar{P}$.

As expected, $\bar{P}$ increased with increasing temperature. Figure 6 provides Arrhenius temperature sensitivity parameters, Activation Energy (Ea) of 10.3kJ/mol and pre-exponential factor (k_o) of 2.828 x 10^4. The Ea for oxygen permeation is closely 11.1 kJ/mol [8]) and below 28.4 kJ/mol [4]). Equation 2 can be used to estimate $\bar{P}$ at any absolute temperature (Kelvin).

$$\bar{P} = e^{\left(\frac{-2252.1}{T\,(K)}+10.268\right)} \quad ......(2)$$

4.0 CONCLUSIONS

Oxygen barrier properties of PLA samples were actually improved up to about 5% PEG plasticizer. Improvement in barrier properties were likely due to enhanced crystallization made possible by the presence of plasticizer. Beyond 5% plasticizer, however, oxygen barrier properties decreased. As expected, OTR and permeability coefficients showed Arrhenius temperature sensitivity. Arrhenius parameters were provided in order to permit estimation of OTR or permeability coefficient of cast PLA films at any temperature.

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