Effects of Temperature and Humidity on the Barrier Properties of Biaxially-oriented Polypropylene and Polyvinyl Alcohol Films

Mo Chen
Graphic Arts College,
Qufu Normal University
chenmoysj@126.com

Yuan Wang
Graphic Arts College,
Qufu Normal University,
wangyuan_0209@126.com

Shijiu Yin
Ecnomics College,
Qufu Normal University
yinshijiu@vip.163.com

ABSTRACT

The goal of this work was to study the effects of relative humidity (RH) and temperature on the barrier properties of biaxially-oriented polyvinyl alcohol (BOPVA) and polypropylene (BOPP) films. The water vapor transmission rate (WVTR) and the oxygen transmission rate (OTR) of the BOPVA and BOPP films were determined with MOCON PERMATRAN-W and MOCON OX-TRAN at 10˚C - 40˚C and 35%-90% RH. The results indicated that RH and temperature had different influence on the WVTR and OTR of the BOPVA and PP films. The OTR and WVTR values of the BOPVA films increase both exponentially with RH. Their WVTR values increase exponentially with temperature, but the OTR values decrease exponentially with the increase of temperature. For the PP films, the relationship between temperature and the WVTR and OTR followed an exponential curve [y=Aexp(x/B)+C], but the WVTR and OTR values were linear with the increase of RH. There was different linear tendency: the WVTR of the BOPP films increased with the increase of RH, the OTR of the BOPP films decreased.

Key Words: *BOPVA Films; BOPP Films; Barrier Property; Water Vapor Transmission Rate; Oxygen Transmission Rate*

1.0 INTRODUCTION

The water vapor transmission rate (WVTR) and the oxygen transmission rate (OTR) are used to calculate the water vapor permeability (WVP) and the oxygen permeability (OP) of packaging materials which affects the shelf life and quality of the product. [1,2] The permeability of packaging materials, [3] especially, the barrier performance of edible films, [4-8] were investigated comprehensively. As equipment in recent years has been continually updated and technology (monoaxially or biaxially extruded) is improved, the performance of film packaging materials is more outstanding, such as biaxially-oriented polyvinyl film now has unexpected barrier performance to oxygen and moisture. As a result it is necessary to determine the barrier properties of these new advanced materials. On the other hand, the updated permeation test equipment with coulometric or infrared sensors are becoming more and more accurate and sensitive. They can provide continuous variation of the test humidity environment by adjusting the partial pressure of water, therefore making them more precise than saturated salt solutions. The effects of temperature and humidity on the barrier performance of the packing materials can be determinated accurately. [9]

Biaxially-oriented polyvinyl alcohol (BOPVA) and polypropylene (BOPP) films are typical polar and non-polar films that are being widely used on food and pharmaceutical packaging materials. Our investigation is aimed to 1) offer more complete water vapor and oxygen permeation data for these films at different RH/temperatures, and compare the results with previous determinations, 2) discuss the potential similarities and the differences of permeation between the non-polar and polar packaging films and 3) investigate the effects of RH and temperature on the transmission rate of water vapor and oxygen on the new BOPVA and BOPP films.

2.0 MATERIALS AND METHODS

2.1 Materials

The biaxially oriented PP films were provided by Alcan Packaging Propack Co., Ltd. (Huizhou, China). The BOPVA films were provided by Nippon Systhetic Chemical Co., Ltd. (Osaka, Japan). The specifications of the selected films are shown in Table 1.

2.2 Methods

2.2.1 Material thickness

The film thickness was measured by DRK204A electric thickness (Deruike Instrument Co. Ltd, Jinan, China). The average thickness of the film at five random locations was adopted as the mean thickness of film.

2.2.2 Measurement of the water vapor transmission rate

The water vapor transmission rate (WVTR) values of the BOPVA and BOPP films were measured at 10°C-40°C with 50% RH or at 23°C with RH between 35%-90%, respectively. All the measurements were performed according to modified ASTM F 1249-90 [10] with PERMATRAN-W 3/33 (Mocon Inc., Minneapolis, USA). The films were cut into uniform hexagon shape with a template and placed in the test cells. The environmental condition was: RH 50±5%, temperature 23±1˚C, and atmospheric pressure. The effective area of water vapor transmission was 50 cm^2. The concentration of the water vapor was held at different levels by rotating the RH pressure regulator. The system was purged by flowing a rapid stream of nitrogen and then the sample was conditioned. In an actual run, the water vapor was introduced into

Films	Processing Method	TS (MD/TD)[a] (MPa)	ELO (MD/TD)[a] (%)	Density (g/cm^3)	Thickness (μm)
BOPP	biaxially oriented	113/102	46/48	0.91	15.0±0.5
BOPVA	biaxially oriented	260/310	71/46	1.20	12.2±0.3
[a] TS and ELO presented tensile strength and elongation at break, respectively; MD, machine direction; TD, transverse direction.					

Table 1. Physical properties of the tested BOPP and BOPVA films

the outer cell. As the water vapor diffused into the inner cell through the film, it was carried by the nitrogen stream to the infrared detector. The detector shown a linear response to the concentration of the water vapor in the carrier gas. The resulting signal which was calibrated using standard NIST films (WVTR, g m^{-2} d^{-1}) was continuously recorded. Every reported value is the average of the three testing values.

2.2.3 Measurement of the oxygen transmission rate

The film oxygen transmission rate was determined according to ASTM D 3985-81 [11] standardized test method. All test parameters were set as following: conditioning for one hour, RH (the penetrant chamber, 50%; the carrier chamber, 0%), temperature (23.0°C), and flow rate was set at 10 standard cubic centimetre per minute (sccm). The effective area of the sample was 50 cm^2. For each test, we only changed one parameter such as temperature (ranging from 10°C to 40°C) or RH (ranging from 30% to 90%). The purity of O_2 was more than 99.95%. Diffusion cell was subsequently purged with a carrier gas mixture of 98% N_2 and 2% H_2. When the oxygen flux had stabilized to the coulometric sensor, oxygen transmission was considered to have reached steady state. The oxygen transmission rate (OTR, cm^3 m^{-2} d^{-1}) value was directly given by the oxygen transmission testing system. Each test was repeated four times, and an average OTR was calculated.

3.0 RESULTS AND DISCUSSION

3.1 WVP values and OP values of the BOPVA and BOPP films

According to definition, the oxygen permeability (OP) and the water vapor permeability (WVP) values of the packaging materials could be calculated by multiplying the oxygen transmission rate (OTR) or the water vapor transmission rate (WVTR) by the film thickness and dividing by oxygen or water vapor partial pressure difference from both sides of the membrane. For some WVP and OP values, the original data or the results after the conversion from previous reports, [3,12,13] were analyzed. It could be seen that OP values [6.75×10^{-11}, $(5.71\text{-}11.4)\times10^{-9}$, $3.14\times10^{-11}$$cm^3$ mm $m^{-2}s^{-1}Pa^{-1}$ at 23˚C, 50%RH] of PP films and WVP values [3.15×10^{-6} g mm $m^{-2}s^{-1}Pa^{-1}$ at 23˚C, 50%, 1.45×10^{-7} g mm $m^{-2}s^{-1}Pa^{-1}$, 23˚C, 85%, 3.66×10^{-9} g mm $m^{-2}s^{-1}Pa^{-1}$, 40˚C, 90%] of PVA films had certain differences with our data [$(1.56\text{-}1.69)\times10^{-10}$ cm^3 mm m^{-2} s^{-1} Pa^{-1}, $(1.45\text{-}1.65)\times10^{-11}$ g mm m^{-2} s^{-1} Pa^{-1} at 23˚C, 50%RH]. It may be because there exist differences in test condition, PP and PVA grade, density, processing method between batches. The other results of present study for the BOPVA and BOPP films permeation [$(3.07\text{-}4.66)\times10^{-14}$ cm^3 mm m^{-2} s^{-1} Pa^{-1} for O^2, $(1.70\text{-}1.77)\times10^{-10}$ g mm m^{-2} s^{-1} Pa^{-1} for water vapor at 23˚C, 50%RH] agreed with earlier reports. [3,12,13]

The transmission permeability of the films can be easily obtained from their transmission rate. For comparative study, this paper only analyzed the effects of RH and temperature on the transmission rate of water vapor and oxygen of the BOPVA and BOPP films.

3.2 Effect of RH on the WVTR of the BOPVA and BOPP films

The WVTR values of the BOPP and BOPVA films at 23˚C and different RH were shown in Figure 1. It can be seen that increasing RH increases the WVTR values of the tested films.

It is generally accepted that for Fickian materials (or those that obey Fick's Law), permeation is linear with concentration for all concentration ranges. As expected, the WVTR values of the BOPP films, within certain range, were proportional to the relative humidity. Similar results have been reported for the PE films. [14] Unlike the BOPP films, the relationship between RH and the WVTR of the BOPVA films followed an exponential grow curve as shown in Figure 1. The WVTR values increase with the increase of RH because hydrogen bonds form between the hydroxyl groups of the BOPVA chain segments and water. Water in the films acts as a plasticizer and swells the films. The water vapor diffused more readily across the swollen membrane than the drier films. The swelling rate of the BOPVA films accelerated with the increase of relative humidity. Thus, when RH > 70%, the WVTR values of the BOPVA films were increasing rapidly.

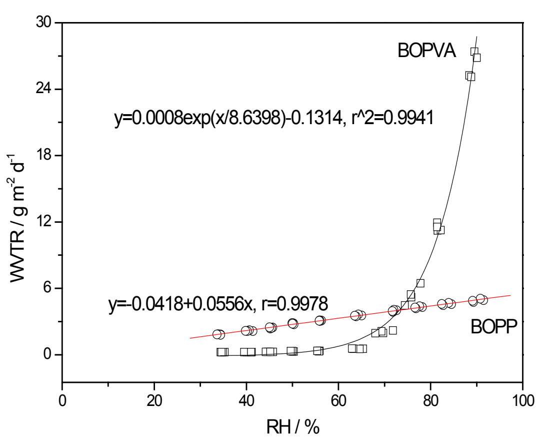


Figure 1. WVTR values of the BOPVA and BOPP films with different RH at 23˚C

3.3 *Effect of temperature on the WVTR of the BOPVA and BOPP films*

At fixed RH (50%), a change in the temperature of system caused a variation in WVTR values of the BOPVA and BOPP films. In addition the higher the temperature, the more water vapor could permeate through the tested films.

The relationship between the WVTR of the BOPVA and BOPP films and temperature can be represented with an exponential function (Figure 2). The results show that the effect of temperature on the WVTR values of the BOPP films was more noticeable than that of the BOPVA films. This was mainly due to the polarity of polymer chains. There was greater intermolecular force in polar BOPVA films. When the temperature was between 10˚C and 40˚C, an increase in temperature had less influence on chain relaxation of the BOPVA films than that of the BOPP films.

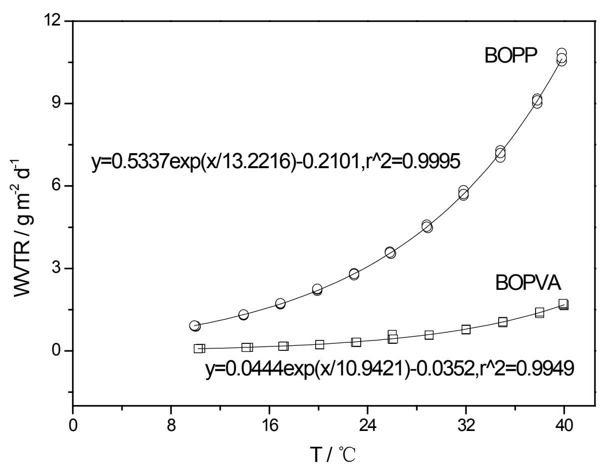
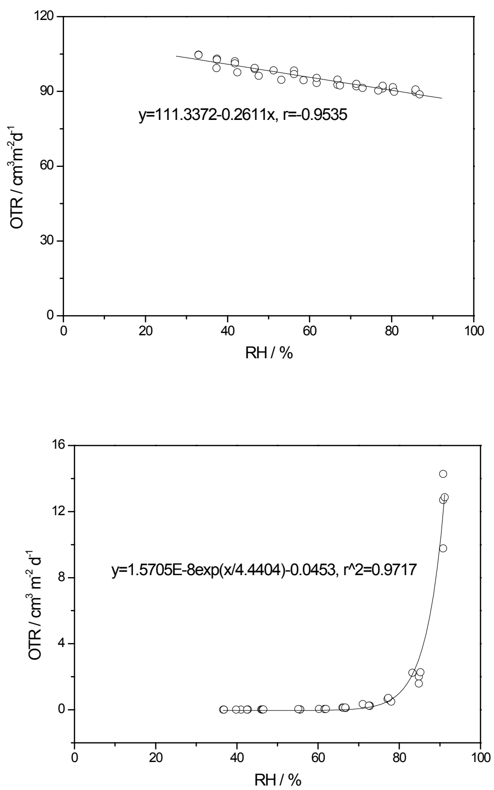


Figure 2. WVTR values of the BOPVA and BOPP films from 10˚C to 40˚ C at 50% RH

3.4 *Effect of RH on the OTR of the BOPVA and BOPP films*

The OTR values of the BOPVA and BOPP films at 23˚C and different RH were shown in Figure 3. The variation in OTR values of the BOPVA and BOPP films with increasing RH can be seen. There was a good fit (r^2>0.95) of the experimental data with the mathematical model. The results of correlation analysis shown that RH and the OTR values of the BOPVA films are exponentially correlated, but there is a liner decreasing trend for the BOPP films. At high humidity, the swelling relaxation of polymer chain leads to exponentially increasing OTR values of the BOPVA films. On the contrary, the BOPP films containing water have no significant swelling phenomenon. The decreasing OTR values of the BOPP films with the increase in RH is a result of lower oxygen solubility in the adsorbed water of the BOPP films.



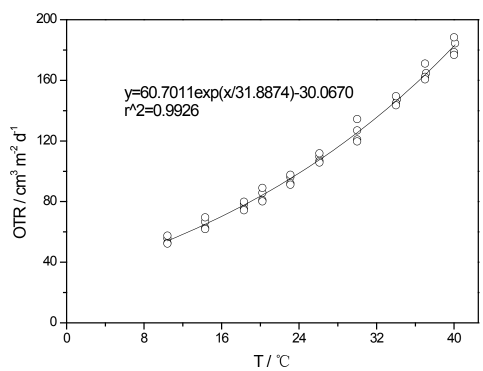
(a) BOPP films (b) BOPVA films

Figure 3. OTR values of the BOPVA and BOPP films measured at different RH and 23˚C

3.5 Effect of temperature on the OTR values of the BOPVA and BOPP films

The OTR values of the BOPVA and BOPP films at temperature range of 10˚C-40˚C and 50% RH are shown in Figure 4. The exponential equations were used to fit the experiment data, resulting in a good fit (r^2>93%). The permeation behavior of the BOPVA and BOPP films was different under the conditions of changing temperature. The higher temperature resulted in higher non-polar chain relaxation, therefore, the OTR values of the BOPP films significantly increased. Similar results have been reported for PE films. [4,15] BOPVA films, possessing strong intermolecular forces at reasonably low humidity (less than the inflection point of the curve in Figure 1), showed the lower solubility of oxygen in water offset the weak relaxation of polar chain, so that the whole system had a lower oxygen transmission rate. This result showing the negative effect of temperature on the OTR was similar to that obtained by Myers. [16] This indicated good similarity of these films, even though the BOPVA films came from different batches.

Research is needed to investigate and quantify the effect of temperature on the OTR values of the BOPVA films in high relative humidity condition. Such information would aid efforts in tailoring the polar films for specific food packaging applications.



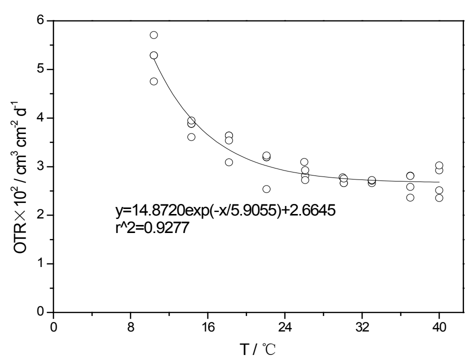


Figure 4. OTR values of the BOPVA and BOPP films measured at different temperature, ca. 50% RH

4.0 CONCLUSIONS

The results of present study for the BOPVA and BOPP films permeability [$(3.07\text{-}4.66)\times10^{-14}$, $(1.56\text{-}1.69)\times10^{-10}$ cm^3 mm m^{-2} s^{-1} Pa^{-1} for O_2 permeation, $(1.45\text{-}1.65)\times10^{-11}$, $(1.70\text{-}1.77)\times10^{-10}$ g mm m^{-2} s^{-1} Pa^{-1} for water vapor permeation at 23˚C, 50%RH] were similar to those provided by the supplier.

The water vapor transmission rate (WVTR) values and oxygen transmission rate (OTR) values of the BOPVA and BOPP films were determined under different RH and temperatures. For the BOPVA films, the OTR and WVTR values both increase exponentially with RH. Their WVTR values increase exponentially with temperature, but the relationship between the OTR values and increasing temperature decreases exponentially. The WVTR and OTR values of the BOPP films increased exponentially with temperature, but they were linear with the increase of RH. There are opposite linear tendency between WVTR and OTR with humidity: the WVTR of the BOPP films increased with the increase in RH and the OTR of the BOPP films decreased.

RH and temperature have different impacts on the barrier properties of the BOPVA and BOPP films. For the BOPP films, the effect of temperature on their permeation behavior is more significant. For the BOPVA films, RH has much larger effect on their WVTR and OTR values.

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