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Permeability of silo bag material for carbon dioxide and oxygen

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ABSTRACT

Silo bag or grain bag storage system is a recently developed technology used for temporally storing dry cereal grains, oilseeds and pulses. The silo bag film is made of high and low density polyethylene. The success of this storage system depends on airtightness of silo bags, and permeability of the silo bag film is one of the main parameters that determines the airtightness of the silo bag. Permeability of the silo bag film to carbon dioxide (CO_2) and oxygen (O_2) has not been reported. The stretching of a silo bag during grain loading and storage time of grain (the silo bag film will be exposed to sunlight during storage period) may affect its permeability. Permeability to CO_2 and O_2 of the silo bag film was determined using a specially designed testing unit which had testing and receiving cells separated by the tested silo bag film. The gases were held in the testing (O_2 or CO_2 99.9% purity) and receiving cells (N_2 99.9% purity) for 48 h; and about 1.5 ml gas samples were collected using a 2 ml syringe at 0, 4, 8, 12, 24, 48 h after purging from the receiving cells. The gas samples were analyzed using a gas chromatograph. The permeability of silo bag film at room temperature to CO_2 and O_2 were 21.61 ±1.50 ×10^{-6}, and 1.95 ±0.36 ×10^{-6} $m^3 m\ d^{-1} m^{-2} atm^{-1}$ respectively. The permeability to CO_2 and O_2 was affected by the storage environment and stretching.

Key words: Airtightness, Modified atmospheric storage, Permeability, Silo bags

Permeability of the packaging material is one of the major parameters that determines the success of modified and controlled atmospheric storage of grain and food materials. Permeability is defined as transfer of gas molecules from the stored product to the external environment or from the external environment to the stored product through package material. Permeation rate is the rate at which the gas or vapour passes through the polymer or packaging material. Permeability coefficient is the volume of gas or vapour passing through a unit area of polymer per unit time, with a unit pressure difference across the sample (Delassus, 1997).

Permeability of a film differs from gas to gas and it depends on dimension (dynamic diameter) and shape of gas molecules. For example, for some packaging materials like polyethylene (PE) N_2 has the smallest permeability rate, O_2 has a higher rate, and CO_2 has the highest permeability rate (Cooksey, 2004). The basic theory states that, when the gas molecule has a smaller dynamic diameter, it can easily diffuse through the barrier material resulting with a higher diffusion rate. Commonly, the permeability ratios of a material for N_2, O_2, and CO_2 gases are 1:4:14 (Delassus, 1997). But the size and shape of gas molecules are not the only parameters that affect the permeability. Temperature and humidity also play major roles for permeability of a material to different gases (Cooksey, 2004). For hygroscopic materials like nylon, polyvinyl alcohol and polyvinyl acetate, an increase in relative humidity (r.h.) increases the permeability for gases. But for polyethylene materials (low and high density polyethylene), permeability for N_2, O_2 and CO_2 are unaffected by the change in r.h., because of their excellent water barring capacities. Increase in temperature increases the permeability of a material to different gases, and this linear relationship between temperature and permeability is controlled by the gas transition temperature (T_g) of the material (Delassus, 1997). Permeability of a material increases about

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9% per °C increase in temperature above T_g and about 5% per °C increase in temperature below T_g. When the temperature increases, the gas molecules attain more energy allowing them to easily pass through the packaging materials (Cooksey, 2004). In polythene based films, mechanical stress on the films has less effect on permeability when compared to temperature and humidity (Mrkić et al., 2007). The tensile drawing orientation has significant effect on permeability coefficient of co-extruded low density polyethylene (LDPE) films to O_2 and CO_2 gases (Compañ et al., 1996). Villaluenga and Seoane (2000) reported that, the number of layers of LDPE films did not affect the permeability coefficient of LDPE films to CO_2.

A grain storage silo bag is made of both, high density polyethylene (HDPE) and low donsity polyethylene LDPE; (Fig. 1). Permeability of HDPE film to CO_2 and O_2 at 25°C are 19.0×10^{-8} and 6.5×10^{-8} m^{3}md^{-1}m^{-2}atm^{-1} respectively. Permeability of LDPE film to CO_2 and O_2 at 25°C are 105.0×10^{-8}, and 19.5×10^{-8} m^{3}md^{-1}m^{-2}atm^{-1} respectively (Osborn and Jenkins, 1992). Abalone et al. (2011a) assumed the silo bag filmwas made of 50% of HDPE and 50% of LDPE. Based on this assumption, Abalone et al., (2011a) calculated the equivalent permeability of the silo bag film to CO_2 and O_2 as 3.22×10^{-7} and 9.75×10^{-8} m^{3}md^{-1}m^{-2}atm^{-1} respectively. This calculation might result in error because the mixing ratio of LDPE and HDPE and structure between HDPE and LDPE films might influence the permeability of gases. To the best of our knowledge, the permeability of silo bag film has not been reported so far.

Fig. 1. Silo bag filled with canola

The stretching of silo bag film during loading of grain may affect the permeability of silo bag material. The temperature gradient between inner (grain) and outer (ambient air) parts of a silo bag can change the energy of gas molecules, which may alter the permeability. Silo bag film exposed to solar radiation during the entire storage period might gradually deteriorate. Aged silo bag film might have different permeability than the new film. Changes in permeability of silo bag film will influence the airtightness of silo bags, and airtightness is one of the main factors for the safe storage of grain. The measured permeability of silo bag material is one of the main parameters required for the development of mathematical models to predict the interstitial gas concentration in silo bags. Therefore, permeability of silo bag film should be measured. The objective of this study was to measure the permeability of the new and aged (exposed to the environment for 7 and 10 months) silo bag film to CO_2 and O_2.

MATERIALS AND METHODS

A permeability testing apparatus was designed and fabricated based on the setup used by Villaluenga

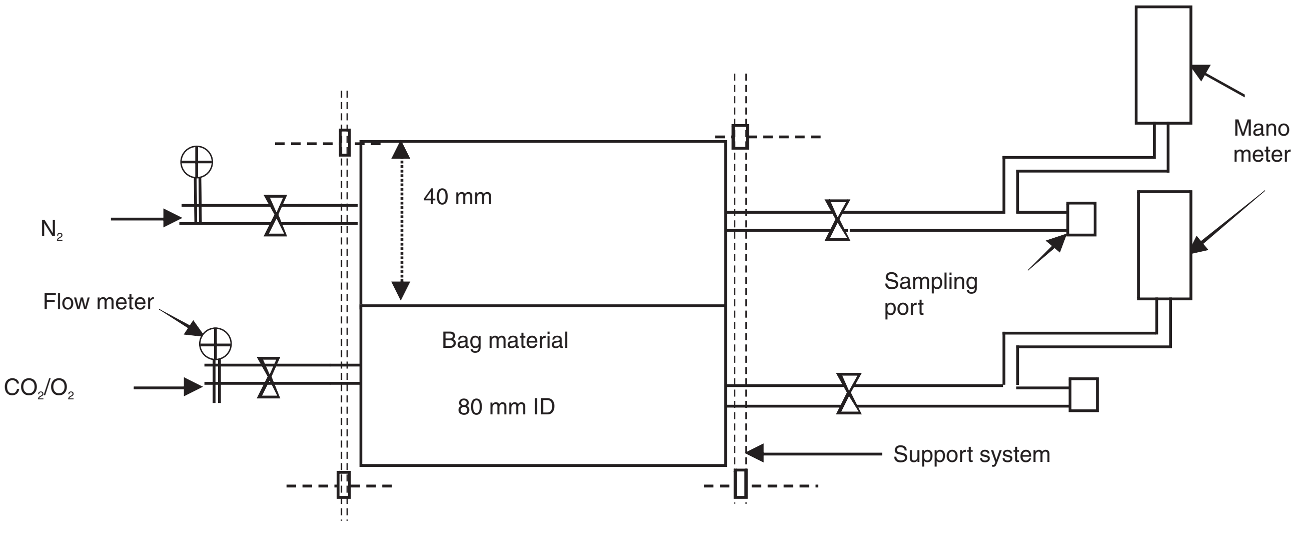

Fig. 2. Schematic view of permeability measurement system

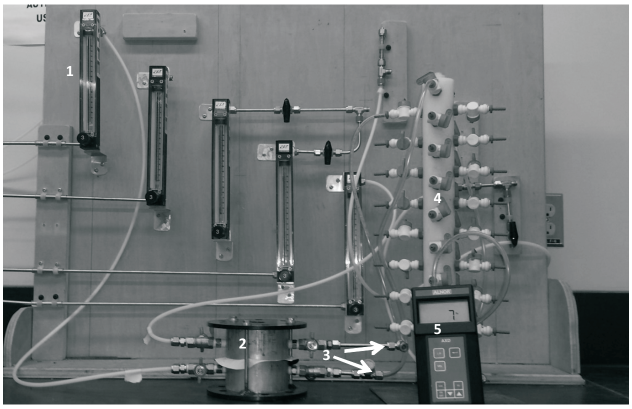

Fig. 3. Permeability testing system (1) flow meter; (2) test cell; (3) gas sampling ports; (4) multiport chamber; (5) micro manometer

and Seoane (2000) for testing the permeability of low-density polyethylene films. Measurement of permeability was carried out in a static phase. The testing apparatus was made up of stainless steel and had two identical cylindrical compartments (Figs. 2 and 3). The internal diameter of the cylindrical compartments was 80 mm and the height of each compartment was 40 mm. The silo bag film was placed between these two compartments. The two compartments were tightened against each other with screws to ensure the airtightness between the two compartments. The airtightness of the compartments was leak-tested using soap water solution at all joints and connections. All the tests were carried out at room temperature (21 ± 1°C).

Testing gas (O_2 or CO_2 with 99.9% purity) was introduced into one compartment and carrier gas ($N_2$with 99.9% purity) was introduced into another compartment. The cells were flushed with the respective gases for 3 min, and outlet valves were closed and then cells were filled with respective gases for 2 min. Inlet gas flow was controlled by a flow meter and a gas flow of 0.3 l/s was maintained during introduction. The gases were held in the testing and receiving cells for 2 days (48 h); and about 1.5 ml of gas samples were collected using 2 ml syringe through the sampling port at 0, 4, 8, 12, 24, 48 h after introduction to the receiving cell. The total volume of each chamber was 201.1 ml, and totally 9 ml of gas samples were collected over 48 h. The collected gas sample was then analyzed using the gas chromatograph (Model: Clarus 420, Perkin Elmer, Woodbridge, ON). The pressures of testing and receiving cells were measured using a micro manometer (Model: AXD 540, ALNOR products, Shoreview, MN). The permeability was calculated using the following equation (Singh and Heldman, 2009; ASTM, 2012):

$$P = \frac{Ql}{At\Delta \mathrm{P}}$$

where, P is the permeability of the material $m^3 m\ m^{-2}\ d^{-1} atm^{-1}$, Q is the amount of O_2 or CO_2 in the receiving compartment (m^3), l is the thickness of the silo bag film (m), A is the area of silo bag film (m^2), t is the time (d) and Δp is the pressure difference between compartments (atm).

The quantity of the O_2 or CO_2 in the receiving chamber (m^3) was calculated from the concentration of O_2 or CO_2 measured in ppm using the gas chromatograph. Permeability was calculated for all five time intervals (0–4, 0–8, 0–12, 0–24, and 0–48 h) and mean of these values was reported. Silo bag has the property of getting stretched upto 10% while loading grain in to the bags using bag loaders. The centre part of the silo bag (especially sides) gets this stretch due to the horizontal pressure exerted by the stored products on the bag film. In tail part, around 3 m of bag film was left to use grain bag extractor equipment for unloading the bags, where bag film did not get stretched. Five types of bag materials were tested with five replicates:

- New material: About 0.2 m × 0.2 m piece of film was sampled before the canola was loaded into the silo bag;
- 7 months stretched: The piece of film was sampled from the side of the silo bag after 7 months of canola storage;
- 7 months-unstretched: The piece of film was sampled from the tail portion of the silo bag after 7 months of canola storage;

Table 1. Permeability of the silo bag film (n=5)

Serial No	Silo bag film	Permeability to CO_2 ($m^3 md^{-1} m^{-2} atm^{-1}$)[a]	Permeability to O_2 ($m^3 md^{-1} m^{-2} atm^{-1}$)[a]
1	New (un-stretched)	$21.61 \pm 1.50 \times 10^{-6A}$	$1.95 \pm 0.36 \times 10^{-6A}$
2	7 months un-stretched	$23.04 \pm 2.04 \times 10^{-6A,B}$	$2.49 \pm 0.24 \times 10^{-6A,B}$
3	7 months stretched	$23.38 \pm 3.72 \times 10^{-6A,B}$	$2.54 \pm 0.31 \times 10^{-6A,B}$
4	10 months un-stretched	$29.20 \pm 3.40 \times 10^{-6A,B}$	$3.54 \pm 0.80 \times 10^{-6B,C}$
5	10 months stretched	$30.70 \pm 2.47 \times 10^{-6B}$	$3.79 \pm 0.33 \times 10^{-6C}$

[A,B,C]The same character after the permeability value in the column indicated no significant difference using Tukey's MRT at $\alpha<0.05$ level

- 10 months-stretched: The piece of film was sampled from the side of the silo bag after 10 months of canola storage;
- 10 months-unstretched: The piece of film was sampled from the tail portion of the silo bag after 10 months of canola storage.

RESULTS AND DISCUSSION

Permeability of new silo bag film to CO_2 was $21.64 \pm 0.54 \times 10^{-6}$ $m^3md^{-1}m^{-2}atm^{-1}$. After 7 and 10 months, the CO_2 permeability of the silo bag film (un-stretched), which was filled with canola and exposed to solar radiation during the storage period, was $23.04 \pm 0.24 \times 10^{-6}$ and $29.20 \pm 0.40 \times 10^{-6}$ $m^3md^{-1}m^{-2}$ atm^{-1} respectively. After 10 months on the field, permeability to CO_2 of stretched and un-stretched bag film was $29.20 \pm 0.40 \times 10^{-6}$ and $30.70 \pm 1.04 \times 10^{-6}$ $m^3md^{-1}m^{-2}atm^{-1}$ respectively. There was a significant difference in the CO_2 permeability between new and 10 months-stretched film (Table 1).

Permeability to O_2 of new and 10 months un-stretched on the field was $1.95 \pm 0.36 \times 10^{-6}$ and $3.79 \pm 0.33 \times 10^{-6}$ $m^3md^{-1}m^{-2}atm^{-1}$ respectively. After 10 months on the field, permeability to O_2 of stretched and un-stretched bag film was $3.54 \pm 0.80 \times 10^{-6}$ and $3.79 \pm 0.33 \times 10^{-6}$ respectively. There were significant differences in the O_2 permeability between new and 10 months on the field films (Table 1).

Guisheng et al. (1995) demonstrated that the permeability of polymer materials could change and was dependent on several factors like the temperature, relative humidity, and properties of polymer materials. Galic and Cikovic (2001) reported that water activity of food inside a packaging material also affected the permeability of the polymer material. The polymer would swell under high water activity, increasing the diffusion of gases through it. Mujica-Paz and Gontard (1997) also reported that relative humidity had a larger role in change of permeability to O_2 and CO_2 of wheat gluten films, when compared to the effect of temperature. In our study, permeability measurement tests were conducted at the room temperature (21 ± 1°C); however, the silo bags were placed on the field for 10 months. During that storage period, the film was exposed to environmental factors (such as temperature, precipitation, snow and UV radiation) which might have caused the change of permeability to O_2.

Most of the packaging films (low density polyethylene, polyvinyl chloride, and polypropylene) used in modified atmospheric packaging have 3 to 7 times higher permeability for CO_2 than O_2 (Mattos et al., 2012). The tested silo bag material is combination of HDPE and LDPE and permeability to CO_2 was 8 to 11 times higher than the permeability to O_2. The mix ratio of HDPE and LDPE might be the reason for the higher permeability to CO_2. Abalone et al., (2011a) estimated equivalent permeability of the silo bag film based on the permeability of HDPE and LDPE to CO_2 and O_2 (considering that the film was made with 50% of each PE type). The estimated equivalent permeability to O_2 and CO_2 was lesser than the value measured in our study. The difference in permeability to O_2 and CO_2 values might have been caused by the assumption made to calculate equivalent composition. The measured permeability values were higher than the permeability values reported by Osborn and Jenkins (1992). Abalone et al. (2011b) reported that, even a small perforation in a silo bag had a significant effect on permeability to the gases (increase of 27 for CO_2 and 90% for O_2 for a perforation of 1 mm diameter per m of silo bag) and they also reported that, filling and sealing of silo bags also had significant effects on permeability to O_2 and CO_2. The greatest change on permeability during storage in this study was of 42% for CO_2 and 94% for O_2, indicating that the change of permeability during 10 months of exposure to the environment is in the same order than that produced by a small perforation.

CONCLUSION

At room temperature (21°C), permeability of new silo bag film to CO_2 and O_2 were $21.61 \pm 1.50 \times 10^{-6}$ and $1.95 \pm 0.36 \times 10^{-6}$ $m^3md^{-1}m^{-2}atm^{-1}$ respectively. Permeability to CO_2 and O_2 of un-stretched silo bag film kept on the field under Canadian Prairie conditions after 10 months was $29.20 \pm 3.40 \times 10^{-6}$ and $3.54 \pm 0.80 \times 10^{-6}$ $m^3md^{-1}m^{-2}atm^{-1}$ respectively. Exposure to the environment and stretching of bags while loading the grain into silo bags had significant effects on the film permeability to CO_2 and O_2.

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REFERENCES

Abalone R, Gastón A, Bartosik RE, Cardoso L, Rodríguez JC (2011a). Gas concentration in the interstitial atmosphere of a wheat silo-bag. Part I: Model development and validation. Journal of Stored Product Research **47**: 268–275.

Abalone R, Gastón A, Bartosik RE, Cardoso L, Rodríguez JC (2011b) Gas concentration in the interstitial atmosphere of a wheat silo-bag. Part II: Model sensitivity and effect of grain storage conditions. Journal of Stored Product Research **47**: 276–283.

ASTM (2012) ASTMD1434: Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting. ASTM International, West Conshohocken, PA.

Compañ V, Ribes A, Díaz-Calleja R, Riande E (1996) Permeability of co-extruded linear low-density polyethylene films to oxygen and carbon dioxide as determined by electrochemical techniques. Polymer **37**: 2243–2250.

Cooksey K (2004) Important factors for selecting food packaging materials based on permeability. Ph.D. Dissertation, Clemson University, Clemson, SC.

Delassus P (1997) Barrier polymers. In: Brody A, Marsh KS (eds) Encyclopedia of Packaging Technology. John Wiley and Sons, New York, pp 71–77.

Galić K, Ciković N (2001) Permeability characterisation of solvent treated polymer materials. Polymer Testing **20**(6): 599–606.

Guisheng F, Incarnato L, Di Maio L, Acierno D (1995) Discussion about the use of relative values of permeabilities between two gases for high molecular weight polymers. Polymer **36**(22): 4345–4346.

Mattos LM, Moretti CL, Ferreira MD (2012) Modified atmosphere packaging for perishable plant products. (*In*) Dogan F (Ed.) Polypropylene, InTech, Rijeka, Croatia, pp 95–110.

Mrkić S, Galić, K, Ivanković M (2007) Effect of temperature and mechanical stress on barrier properties of polymeric films used for food packaging. Journal of Plastic Film and Sheeting **23**: 239–256.

Mujica-Paz H, Gontard N (1997) Oxygen and carbon dioxide permeability of wheat gluten film: effect of relative humidity and temperature. Journal of Agricultural and Food Chemistry **45**: 4101–4105.

Osborn KR, Jenkins WA (1992) Plastic Films: Technology and Packaging Applications. CRC Press LLC, Boca Raton, FL.

Singh RP, Heldman DR (2009) Packaging concepts. In Introduction to Food Engineering. Academic Press, Burlington, MA, pp 745–769.

Villaluenga J, Seoane B (2000) Permeation of carbon dioxide through multiple linear low-density polyethylene films. European Polymer Journal **36**: 1697–1702.