

MOISTURE BARRIER BEHAVIOR OF POLYMER FILMS ON FOOD PACKAGING PLASTIC MATERIALS

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Abstract: *This paper deals with experimental studies on the effect of relative humidity and temperature on plastic films that are currently being used as primary and secondary packaging materials for food products at different environmental conditions. The analysis was done on four plastic films include ethylene vinyl alcohol EVOH, polypropylene and polyethylene bases. The water vapor transmission rates were determined at accelerated conditions of 80% relative humidity and at 40°C temperature as per the ASTM standard. The rate of moisture absorption increases linearly with time until a certain point, after which it becomes constant. The polypropylene film had better moisture barrier properties with good mechanical structural integrity and is the most economical. The multi-layered film of 200 µm showed good results, however, it is not very coherent when posed as a second layer packaging material at accelerated conditions in the stability chamber.*

Keywords: *EVOH, PP, PE, packaging materials, Moisture barrier properties, Water vapor Transmission rate*

ABBREVIATIONS USED

EVOH - Ethylene-vinyl alcohol
PP – Polypropylene
PE – Polyethylene
LDPE – Low Density Polyethylene
LLDPE - Linear Low Density Polyethylene
HDPE – High-density Polyethylene

1. INTRODUCTION

Packaging the food product has contributed greatly to the development of the food industry. It is a complex process that enables food to circulate from the producer to the consumer. The functions of a package are protection, the convenience of use, communication, and containment of packaged products under environments such as those subjected to during the packaging process, storage and distribution. Protective packaging enables products to be transported to the user and has made it possible to centralize production facilities into areas where raw materials are concentrated and therefore take advantage of economies of scale operations (Bijet al. 2015). Product and its package have become interdependent to such a degree that we cannot consider one without the other (Meritainne daet al. 2018, Majidet al. 2018, Kim and Seo 2018, Yun and Dong 2017, Smithet al. 1990).

One of the main problems faced by the food industry is food deterioration by the penetration of moisture, oxygen and to an extent, organic vapors. Factors that influences the deterioration property of the packaged food include moisture, filling gas, temperature, light, and pH. The gas permeability and moisture of the food packaging materials are the most important factors affecting the quality preservation of its contents (Moet al. 2014). Storing food in inappropriate environments accelerates the deterioration and thus there is a need for better preservation of the food. Packaging these food products with the help of suitable polymeric material increases its shelf life considerably and aids in preserving its quality. Packaging material such as polyethylene, polypropylene, polystyrene, vinyl polymers etc, are extensively used by the packaging industry. Plastic films are used for food packaging due to economic considerations and have benefits in physical, chemical, mechanical properties over other packaging materials. One major drawback that affects the texture, color and therefore the sensory quality of the food product is the moisture that tends to penetrate through the film materials. Thus, there is a growing need to find a suitable method to determine the water vapor transmission rate through these plastic packaging films that are highly susceptible and permeable to water vapor (Majid;Ahmad Nayik;Mohammad Dar and Nanda 2018). Food products have considerably less shelf life in regions with high humidity and high temperatures (Abbas et al. 2019). Therefore, it is vital to use a packaging material that can overcome this hurdle (Wikströmet al. 2014). Four sample films were chosen and a complete performance of these plastic films is estimated in order to determine the most suitable material for the packing of food that includes sweetening, coloring and flavoring chemicals. These sample films were chosen on the basis of their prevalence in the current consumer environment and the potential for widespread use. The four films were acquired through industrial sources and are candidates in consideration for food processing and packaging industries.

2. MATERIALS AND METHODS

The most commonly used packaging films that are employed in the industry are Ethylene vinyl alcohol (López-Rubio et al. 2005, Maes et al. 2018), polypropylene and polyethylene bases Films. LDPE/LLDPE film are two different polyethylene resins that have similar properties such as clear translucency, good moisture barriers and fair gas barriers, can be heat sealed, and are strong and highly flexible (Bumbudsanpharokeet et al. 2017). HDPE film, a part of the

polyethylene family, is found in many of the similar applications as LDPE and LLDPE (Butler and Morris 2010, Grewalet al. 2012, Mokwena and Tang 2012). HDPE also tends to be stiffer than other polyethylene films, which is an important characteristic for packages that need to maintain their shape. In addition, HDPE is strong and puncture-resistant has good moisture barrier properties and is resistant to grease and oils. PP film has excellent moisture barrier characteristics, good clarity, high gloss, and good tensile strength. The resin also has a high melting point, which makes it desirable in packages that require sterilization at high temperatures.

In this paper, four physically different types of packaging films were used. Three of which contain polyethylene (PE) as its base polymer material and one which contains polypropylene (PP) as its base material. The films supplied by established food packaging industries are used as test sample that satisfies food-grade parameters. Additional materials required are plastic films and PP tubes, heat sealing machine (Generic 12" Hand Impulse Sealer), stability chamber (85% RH, 40°C) (EIE Stability Chamber), desiccator (300 mm), analytical weighing balance (accuracy 0.0001), finished product and food material for packaging.

Water Absorption Measurements without food product

The rate at which water vapor will pass through a material under specified conditions and specimen geometry is termed as Water Vapour Transmission Rate (WVTR). The factors that can affect WVTR values include thickness, resin composition, molecular weight distribution, crystallinity/density, chain length and chain length distribution, chain orientation, polymer blends, additives and coatings (Huet al. 2001, Kuusipalo and Lahtinen 2005, Mokwena et al. 2011).

Prior to testing, the film samples were specimen to standard size 4.5 cm by 9 cm packets (Tock 1983) with the help of a mechanical cutter and sealer. The initial weights of the films were recorded with the help of an analytical balance. The food product sample was then inserted into the respective packets (either with or without PP tube). The arrangement included (i) a product without PP tube in sleeve (placed in the stability chamber), (ii) product with PP tube in sleeve (placed in the stability chamber), (iii) product in PP tube with sleeve outside (placed in the desiccator), and (iv) product in PP tube with sleeve inside (placed in the desiccator). This was followed by the calculation of WVTR for a product in the stability chamber, determination of moisture uptake of raw materials in the stability chamber, and calculation of WVTR for raw materials placed in the stability chamber.

The experiment for measuring water absorption was conducted by taking the initial weights of the packet along with the product placed inside (w_a), and then placing in accelerated conditions inside a stability chamber. Water absorption measurements were taken at a temperature of 40 °C and RH of 85%. Samples were periodically taken out (on

a daily basis), wiped with a paper towel to remove surface water and weighed immediately to obtain final weight, (w_b). Two replicates were used for each measurement time for the films.

Water Absorption Measurements with Food Product

The experiments were repeated with the finished food product under identical conditions. The Loss of Drying test LOD was conducted. The experiment dealt with packing the finished product in separate film bags and placing them in a desiccator for one-week. Petri dishes were taken and their initial weight was noted (w_i). Approximately 5g (recorded weight w_r) of food materials were placed inside the petri dishes and the final weight before LOD studies were recorded (w_1). The petri dishes were then put inside an oven at 105°C for approximately three hours. The dishes were taken out and their weights were recorded with the help of an analytical balance (w_2). Two replicates were used for each measurement and the LOD study was carried out twice. The LOD percentage value was calculated with the help of the following equation:

$$LOD \% = \frac{w_1 - w_2}{w_r} \times 100$$

LOD was performed to ensure that the moisture is the only volatile component present in the samples and the weight loss is not due to any other substances. The LOD experiment was conducted for both the finished product and raw materials. The LOD percentage values for the finished product are shown in Table 1.0 the average loss in value attained was 5.748%

The weight of the finished product placed inside the individual film was recorded (w_a). A solution of Sodium Chloride (6.3N) was prepared by adding 365g of NaCl powder in 1000ml water and poured into the desiccator to enhance the diffusion of water molecules. The samples were subsequently placed inside the desiccator maintained at room temperature and approximately 71% RH. The samples were then periodically taken out, wiped with a paper towel and immediately weighed to obtain final weight (w_b). Two replicates were used for each measurement time for the films.

In this experiment, the product was placed inside PP tubes. There were two sets of samples prepared: one where the sleeves covered the tube and one where the tubes covered the sleeves. For this experiment, an additional blank pouch was also added in order to calculate the water vapor transmission rate and presence. The results obtained were studied and reported. The difference in weights of the samples was recorded and plotted along with time.

Table 1. LOD% values for each product component

Product Component	LOD %
Sweetening agent 1	7.278%
Sweetening agent 2	0.031%
Flavoring agent 1	0.079%
Coloring agent 1	1.133%
Flavoring agent 2	4.489%
Saccharide Control value (Bizziet al. 2011)	14.0%

Stability Chamber Analysis with Food Product

The product components of the finished product were then placed in the various films and then into the stability chamber. Five product components were provided which included sweetening agents, coloring agents and flavoring agents. The same experimental procedure as the previous one was followed. For this experiment, an additional blank pouch was also added so as to calculate the water vapor transmission rate and permeance. Moisture uptake percentage values are determined and plotted along with time.

TRANSMISSION FLUX ANALYSIS

A critical function of flexible packaging is to maintain the dryness of the food products (potato chips etc.) and moisturizes state of the products (cheese, chewing-gum etc.). Without protective packaging, products will quickly gain or lose moisture until they are at equilibrium with the environmental relative humidity. At this point, crispy products are soggy, and chewy products are hard and dry. WVTR is the standard measurement by which films are compared for their ability to resist moisture transmission. Lower values indicate better moisture protection. With the Water vapor transmission rate testing, effective quality control of food can be guaranteed so as to improve the storage, transportation and shelf life results and prolong the shelf life span of the product. The following calculations were performed for the finished product and its raw materials after being subjected to accelerated conditions for a week. The weight change and transmission rate (flux) can be calculated by the relation

$$Q_t = (T_t - T_i) - (C_t - C_i)$$

where, Q_t = net weight gain of the sample inside the pouch
 T_t = weight of the pouch with a sample at time t
 T_i = the initial weight of the pouch with sample
 C_t = weight of the control pouch at time t
 C_i = the initial weight of the Blank pouch

$$\text{Transmission flux} = \frac{Q_t}{A t}$$

where 't' is taken as one day; A is pouch area

3. RESULTS:

The films obtained were subjected to Fourier-transform infrared spectroscopy (FTIR) analysis for identification of the base materials and determination of its opacity. Further experiments were carried out in the stability chamber for determining the transmission rates for water vapor through the films. This was conducted for two scenarios, the transmission rates were determined without including the food components that are to be packaged follows experiments with food components. Finally, the same experiment was conducted in a stability chamber for ascertaining of the shelf life of the packaged product.

Film Identification

The results obtained from the IR spectroscopy for the four different film samples were analyzed. Film sample A was a slightly translucent film. Film sample B was a translucent film. Film samples C and D were transparent films. The graph below shows the IR spectra for polymer film sample A, the peak curve at 2846.93 ensures the quality of the material. Film A and film B contain polyethylene with the EVOH layer. Film C contains polyethylene without the EVOH layer and film D contains polypropylene material. The IR spectra for polymer film samples A, B, C and D were shown in Figure 1.

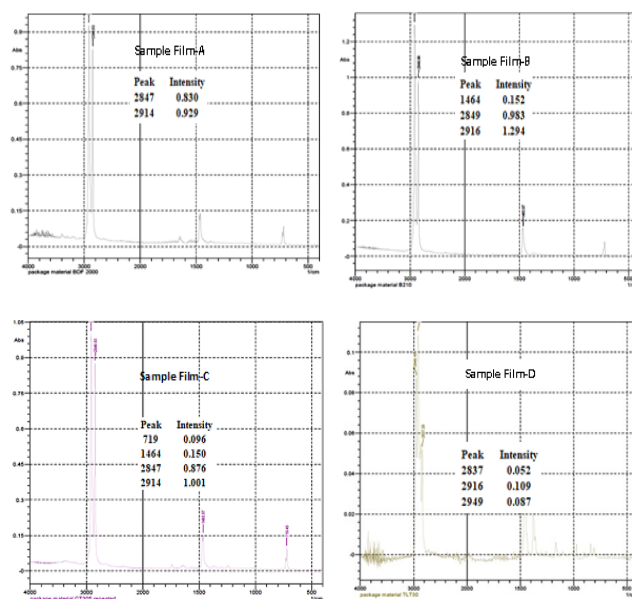


Figure 1. IR spectra for polymer film samples A, B, C and D

The transmission rates for the two cases of WVTR analysis were performed and the results for each film with respect to the food component were tabulated and corresponding bar graphs were generated. Similarly, the results for moisture uptake percentages in a stability chamber were recorded and are presented in graphical form against a time period of 5 days. Finally, the results at different weights and at room

temperature and 71% relative humidity are presented in graphical form in order to accurately decide on the optimal film for application.

Transmission Rate

Water vapor transmission rates of the polymer film samples obtained under identical conditions were shown in Figure 2. The blue, Brown and green colors represent the polymeric material that contains polyethylene as its base material and the yellow color bars represent the polymeric material with polypropylene as its base material.

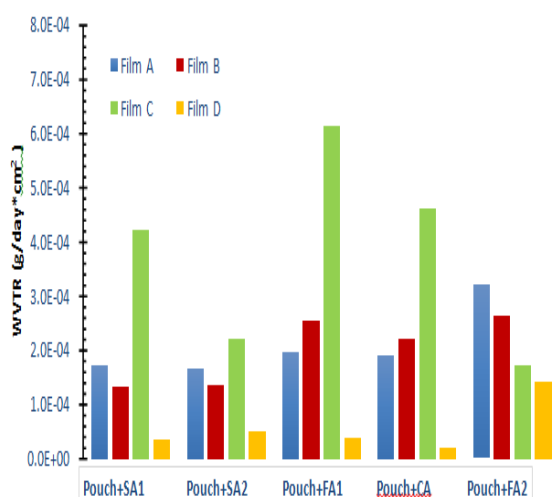


Figure 2. Graphical comparison of Water Vapor Transmission Rates, SA - Sweetening agent; FA - Flavoring agent; CA - Coloring agent

Experimental results are reported for different sweetening agents, flavoring agent and coloring agents. As seen from the graph, the last material which happens to be a flavoring agent is highly hygroscopic in nature. It can be noticed that the polymeric material that shows a high moisture barrier property in accelerated conditions is film D.

Transmission rate analysis with finished product

The moisture uptake percentage values for the given four polymeric films were shown in Figure 3 with respect to the provided final products. The moisture uptake percentage values are calculated by subtracting the initial weight from the final weight and then dividing it by the given sample weight converted to percentage. Different raw materials provided, show different curves that primarily depend on their hygroscopic properties and depend on the level of affinity for the various film samples.

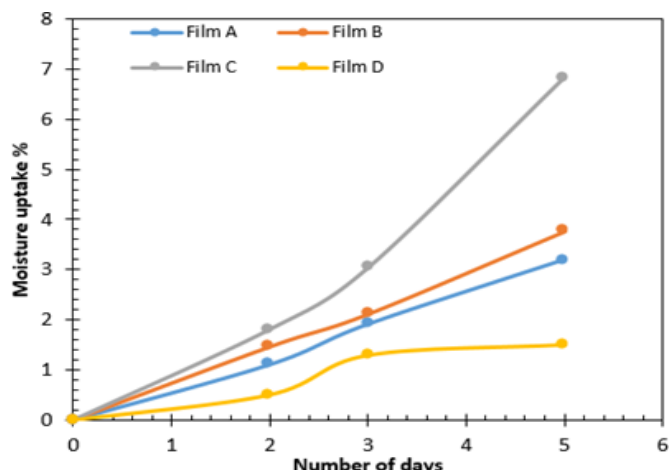


Figure 3. Moisture uptake for SA1 with the finished product

The moisture uptake of the finished product with packaging material at alternative conditions. Figure 4 shows the difference in weights of the finished product along with its films acting as primary and secondary packaging materials placed in the stability chamber at accelerated conditions of 85% RH and 40 °C.

The two charts vary significantly is due to the fact that the secondary packaging material is composed of multi-layered polymer material which has B210 additives. When the product is placed inside a PP tube and is then covered with next packaging material, there could be chances that water which enters the sleeve may remain in the void region between the sleeve and the PP tube. Thus, using a multi-layered plastic film would probably make it comparatively harder for water to evaporate. The moisture uptake of the finished product in poly propylene (PP) tubes with packaging material at alternative conditions. Similar procedure was followed in the desiccator with the product in PP tubes at room temperature and 85% RH. The analysis was performed for the product and Figure 5 shows the difference in measured weights value for the product in PP with sleeve outside and inside respectively placed in the desiccator. Table 2 summarizes the results of the graphical representation and the individual changes as observed.

Table 2 Weight difference (gm) with sleeve outside and inside

Film Sample	Weight Difference (Sleeve Outside)				Weight Difference (Sleeve Inside)			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Film A	0.002	0.003	0.0035	0.0038	0.0015	0.0035	0.0055	0.006
Film B	0.0005	0.002	0.002	0.0025	0.0005	0.0018	0.002	0.0025
Film C	0.001	0.002	0.0025	0.003	0.0005	0.0015	0.0018	0.002
Film D	0.001	0.0015	0.0018	0.002	0.001	0.0022	0.0022	0.003
No sleeve (control)	0.0025	0.009	0.010	0.0118	0.0025	0.009	0.01	0.0118

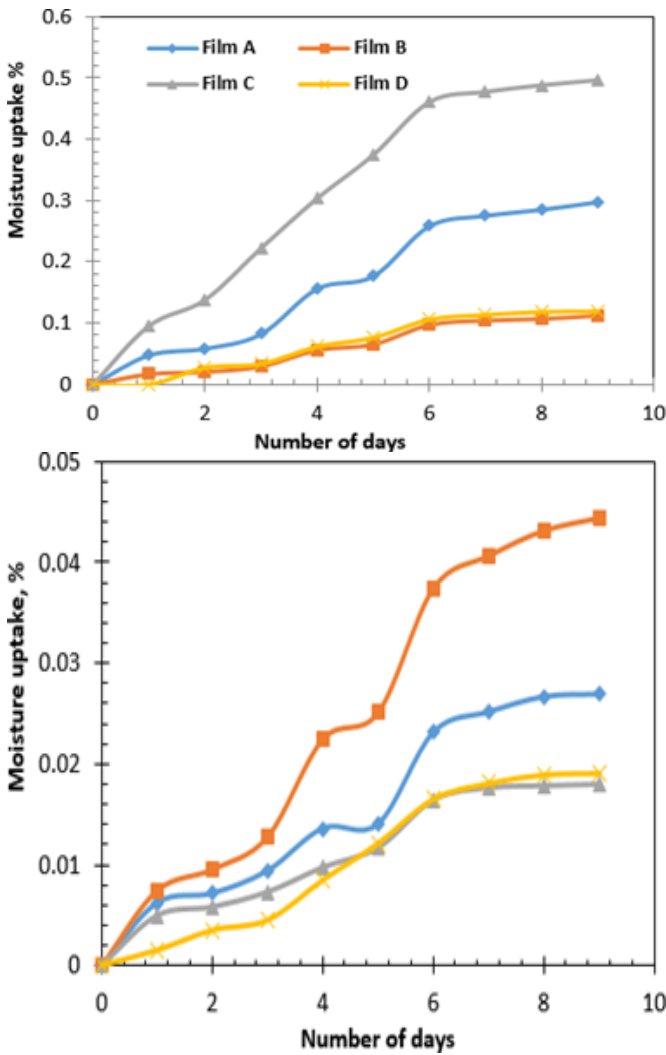


Figure 4. The moisture uptake of films with PP (a) and without PP (b)

The solubility and diffusion coefficient of any barrier materials decides the permeability property. Crystallinity is associated with the diffusion parameter, while polarity is associated with the solubility coefficient. The polarity is usually determined by the kind of functional group attached to the main polymer. The polyethylene and polypropylene are non-polar, but polyvinyl alcohol is polar due to the hydroxyl (OH) group. Non-polar materials are usually a better barrier against water and other polar molecules, but they are poor barriers for non-polar molecules such as organic flavors. On the other hand, polar polymers are not a good barrier against water, but they are better barriers against non-polar organic compounds. The ratio of amorphous to crystalline solid state of the polymer barrier also affects WVTR. The more crystalline a material, the less permeable, is due to the rigidity of the structure.

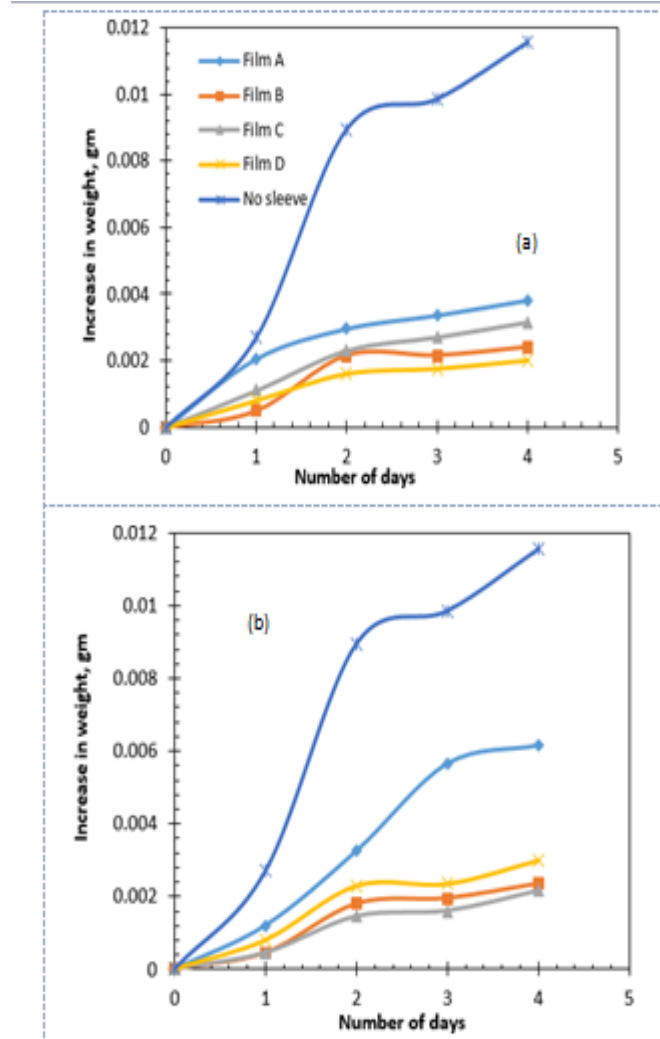


Figure 5. The difference in weight of the product with sleeve (a) outside and (b) inside

The results indicate that multi-layered packaging makes for better efficiency and can confirm that more layers would deter evaporation. However, the inclusion of a PP tube gives differing results under set conditions and the properties of the finished product also influence the overall efficiency of the packaging.

4. CONCLUSION

Packaging is indispensable to the food industry and polymeric packaging is the most efficacious method available. Therefore, getting an insight into the characteristic properties of polymeric materials is vital to make a selection conducive to packaging. From the above results, it can be readily stated that polypropylene shows maximum efficiency with this particular product. However, the polyethylene film with nine layer also shows good results, although it is not very consistent when subjected to a second packaging material (PP tubes) at accelerated conditions. This could arise from the fact that when the product is placed inside a PP tube and covered with a sleeve made up of a polymeric material

with many layers, there could be chances that water which enters the sleeve may remain in the void region between the sleeve and the PP tube. Thus using a nine layered plastic film would probably make it comparatively harder for water to evaporate than using a seven layered material. Moreover, as the results obtained from moisture uptake of SA 1 indicate, it can be concluded that the inclusion of B210 additives and multilayered packaging significantly affects moisture uptake and are primary factors contributing to corresponding evaporation rates.

In explaining the results with respect to the EVOH layer present in two of the plastic films, it can be concluded that although EVOH is highly hydrophilic in nature and tends to absorb substantial amounts of moisture when placed in RH environments, the multi-layered polymeric material did exhibit good results and that is because of the many layers of polyethylene that are present which protects the EVOH layer from contact with moisture. However, if we look at the other EVOH containing material, we can deduce that the number of polymeric layers protecting the EVOH layer is much lesser when placed in the stability chamber.

It was also found that during experimentation the polypropylene material (Film D) is easy and most convenient for physical handling, cutting, and mechanical sealing. Film C, the PE material without the EVOH layer, was harder to seal at high temperatures as it tended to melt very easily. The other two PE materials (Film A and Film B) were comparatively better and could withstand high sealing temperatures. It was found that polypropylene is comparatively more economical than polyethylene. In conclusion, Film D is the most appropriate as a secondary packaging material as it provides chemical, mechanical and economic efficiency. The selection for the most appropriate packaging was achieved through the analysis of experimental results and known physical attributes. Further research into structural properties and analysis of the base material can aid in corroborating the macroscopic features with the microscopic characteristics.

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REFERENCES

- [1] Abbas, M., Buntinx, M., Deferme, W. and Peeters, R. (2019) (bio)polymer/zno nanocomposites for packaging applications: A review of gas barrier and mechanical properties. *Nanomaterials* 9: 10, 1494, doi: 10.3390/nano9101494.
- [2] Biji, K. B., Ravishankar, C. N., Mohan, C. O. and Srinivasa Gopal, T. K. (2015) Smart packaging systems for food applications: A review. *Journal of Food Science and Technology* 52: 10, 6125, doi: 10.1007/s13197-015-1766-7.
- [3] Bizzi, C. A., Barin, J. S., Hermes, A. L., Mortari, S. R. and Flores, É. M. M. (2011) A fast microwave-assisted procedure for loss on drying determination in saccharides. *Journal of the Brazilian Chemical Society* 22: 2, 376, doi: 10.1590/s0103-50532011000200026.
- [4] Bumbudsanpharoke, N., Lee, W. and Ko, S. (2017) A comprehensive feasibility study on the properties of lDpe-ag nanocomposites for food packaging applications. *Polymer Composites* 39: 9, 3178, doi: 10.1002/pc.24325.
- [5] Butler, T. and Morris, B. (2010) *Pe-based multilayer film structures vol., vol. edn.* isbn:9780815520214.
- [6] Grewal, R., Sweesy, W., Jur, J. S. and Willoughby, J. (2012) *Moisture vapor barrier properties of biopolymers for packaging materials vol 1107.* Acs symposium series, vol 1107, edn. American Chemical Society. isbn:9780841227880.
- [7] Hu, Y., Topolkarayev, V., Hiltner, A. and Baer, E. (2001) Measurement of water vapor transmission rate in highly permeable films. *Journal of Applied Polymer Science* 81: 7, 1624, doi: 10.1002/app.1593.
- [8] Kim, D. and Seo, J. (2018) A review: Breathable films for packaging applications. *Trends in Food Science & Technology*, doi:
- [9] Kuusipalo, J. and Lahtinen, K. (2005) Influence of temperature and mixing ratio on water vapor barrier properties of extrusion-coated paper. *International Journal of Polymer Analysis and Characterization* 10: 1-2, 71, doi: 10.1080/10236660500346057.
- [10] López-Rubio, A., Lagarón, J. M., Hernández-Muñoz, P., Almenar, E., Catalá, R., Gavara, R. and Pascall, M. A. (2005) Effect of high pressure treatments on the properties of evoh-based food packaging materials. *Innovative Food Science & Emerging Technologies* 6: 1, 51, doi: 10.1016/j.ifset.2004.09.002.
- [11] Maes, C., Luyten, W., Herremans, G., Peeters, R., Carleer, R. and Buntinx, M. (2018) Recent updates on the barrier properties of ethylene vinyl alcohol copolymer (evoh): A review. *Polymer Reviews* 58: 2, 209, doi:
- [12] Majid, I., Ahmad Nayik, G., Mohammad Dar, S. and Nanda, V. (2018) Novel food packaging technologies: Innovations and future prospective. *Journal of the Saudi Society of Agricultural Sciences* 17: 4, 454, doi: 10.1016/j.jssas.2016.11.003.
- [13] Meritaine da, R., de Souza, M. M. and Prentice, C. (2018) *Biodegradable films: An alternative food packaging vol, edn.* Elsevier. doi:10.1016/b978-0-12-811516-9.00009-9.
- [14] Mo, C., Yuan, W., Lei, W. and Shijiu, Y. (2014) Effects of temperature and humidity on the barrier properties of biaxially-oriented polypropylene and polyvinyl alcohol films. *Journal of Applied Packaging Research* 6: 1, 40, doi: 10.14448/japr.01.0004.

- [15] Mokwena, K. K. and Tang, J. (2012) Ethylene vinyl alcohol: A review of barrier properties for packaging shelf stable foods. *Critical reviews in food science and nutrition* 52: 7, 640, doi: [16]Mokwena, K. K., Tang, J. and Laborie, M.-P. (2011) Water absorption and oxygen barrier characteristics of ethylene vinyl alcohol films. *Journal of Food Engineering* 105: 3, 436, doi: 10.1016/j.jfoodeng.2011.02.040.
- [17] Smith, J. P., Ramaswamy, H. S. and Simpson, B. K. (1990) Developments in food packaging technology. Part ii. Storage aspects. *Trends in Food Science & Technology* 1, 111, doi: 10.1016/0924-2244(90)90086-e.
- [18] Tock, R. W. (1983) Permeabilities and water vapor transmission rates for commercial polymer films. *Advances in Polymer Technology* 3: 3, 223, doi: 10.1002/adv.1983.060030304.
- [19] Wikström, F., Williams, H., Verghese, K. and Clune, S. (2014) The influence of packaging attributes on consumer behaviour in food-packaging life cycle assessment studies-a neglected topic. *Journal of Cleaner Production* 73, 100, doi:
- [20] Yun, X. and Dong, T. (2017) *Fabrication of high-barrier plastics and its application in food packaging* vol., vol, edn. Elsevier.