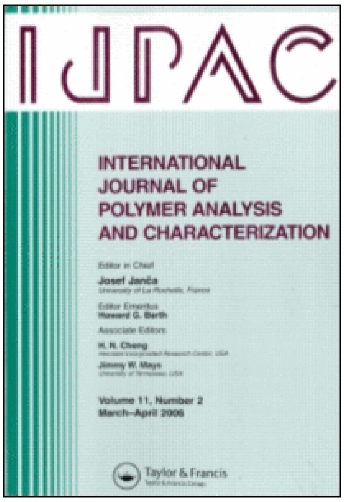

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Influence of Temperature and Mixing Ratio on Water Vapor Barrier Properties of Extrusion-Coated Paper

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Abstract: When making food packages from fiber-based, extrusion-coated materials, water vapor transmission rate (WVTR) of the material is one of the key factors defining the shelf life of the product. The WVTR test is commonly a time-consuming procedure that delays progress in project development. In this study, a calculation method for WVTR-determinations was devised that can reduce the amount of testing and thus enhance the speed of research. Furthermore, the effect of atmospheric conditions on the permeation of water vapor through packaging materials is an important factor in view of the use of food packages all over the world. In this study, it was found that the combined effects of both relative humidity and temperature resulted in an almost linearly increasing WVTR as a function of mixing ratio under the given atmospheric conditions.

Keywords: Water vapor transmission rate; WVTR; LDPE; PP; Mixing ratio; Permeability

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INTRODUCTION

Extrusion coating of paper or paperboard with polyolefin-based coatings is typically used to improve water vapor barrier. Industrial wrappings (paper roll wrapping) and packages (milk carton) are the most typical end uses of extrusion coated products where an enhanced water vapor barrier is required. Normally, a simple LDPE coating (low density polyethylene) with a coating weight of about 10–25 g/m^2 is sufficient for most purposes. However, for demands even better barrier properties have increased in recent years. In other words, there are pressures to design packages that tolerate climatic conditions all around the world.

Naturally, the conditions in the topics are the most demanding, but high temperature and humidity can also exist during transportation. Therefore, today's extrusion coatings must provide better barrier properties. It is well known that extrusion coatings made of polypropylene (PP) and high density polyethylene (HDPE) give an even better water vapor barrier than LDPE. In order to satisfy the most demanding barrier requirements, the coating weights need to be as high as 50–60 g/m^2. However, high coating thickness brings out some technical disadvantages such as curling and excessive stiffness.

The need for a fast and reliable method to measure water vapor transmission rate (WVTR) values of extrusion-coated materials has arisen. To evaluate WVTR values with different coating weights, one must make up a large series of trials in extrusion coating. In addition, scattered WVTR results are difficult to analyze and interpret.

When polymer film has no pores or pinholes, the penetration of molecules through the film occurs with activated diffusion. In activated diffusion the penetration of molecules is a three-stage process[3–7]:

1) Adsorption onto the film's surface
2) Diffusion through the matrix
3) Desorption away from the film's surface

We assume that the polymer film is initially free from penetrants. When one face of the polymer is exposed to a penetrant, there will be accumulation within the film. During a period of time the rate of permeation across the opposite faces will rise from zero to a constant value. This is known as the transient state of permeation. The situation after the constant value is known as the steady state of permeation. The determination of WVTR is based on moisture's steady-state permeation through a film.[3]

Mathematical treatment of transport phenomena starts with Fick's laws of diffusion. Fick's first law states that[3,7,8]

$$J = -D\frac{dc}{dx} \tag{1}$$

where J = diffusion flow or flux through unit area of film; D = diffusion coefficient; c = concentration of penetrant at a certain point of film; x = distance of the point from the high penetrant concentration face of the film.

In steady-state diffusion, diffusion coefficient D does not depend on the penetrant's concentration. Thus, Equation (1) can be integrated to give

$$J_s = \frac{D(c_1 - c_0)}{l} \tag{2}$$

where J_S is the steady-state flow, l is the film thickness, and c_1 and c_0 are the concentrations on the film's two faces.[3,8–10]

In many cases it is easier to determine pressures or partial pressures of gas or vapor (p) above the faces of the film, rather than the concentrations. In this situation, Henry's law states that

$$c = Sp \tag{3}$$

where S is the solubility coefficient. This relationship is obeyed only at low penetrant concentrations. By combining Equations (2) and (3), the following equation is obtained:

$$J_s = \frac{DS(p_1 - p_0)}{l} \tag{4}$$

which is the well-known equation of permeation. The product DS is called the coefficient of permeation P, thus[3,8–10]:

$$J_s = \frac{P(p_1 - p_0)}{l} \tag{5}$$

Equation (5) is now in the form of standardized determination of WVTR ($g/m^2/24\,h$). The determination states that:

$$WVTR = \frac{1}{A}\frac{dQ}{dt} = \frac{P(p_2 - p_1)}{L} \tag{6}$$

where Q = mass of the penetrant passing the film; t = permeating time; L = thickness of film; P = coefficient of permeability; A = area of the film; p_2 = partial pressure of water vapor on backside of film; p_1 = partial pressure of water vapor on front side of film ($>p_1$).

Equation (6) supposes that all the penetration through the film occurs by steady-state activated diffusion. In barrier polymers, permeation indeed happens mostly with this mechanism, although polymers always include pin holes and microvoids that increase the permeability. However, the equation works well enough with common semi crystalline plastics.[3,8–11]

Atmospheric conditions have a great influence on WVTR. The strongest factors are temperature and relative humidity (RH), which affect the coefficient of permeability, P, and the partial pressure difference ($p_2 - p_1$) in Equation (6). Typical conditions for WVTR measurements are: normal room (23°C, 50% RH), mild (25°C, 75% RH), and tropical (38°C, 90% RH).[1,2]

The temperature dependence of P, D, and S is controlled by the Arrhenius relationship, as follows:

$$P = P_0 \exp(-E_p/RT) \tag{7}$$

$$D = D_0 \exp(-E_D/RT) \tag{8}$$

$$S = S_0 \exp(-\Delta H/RT) \tag{9}$$

where ΔH is molar heat of sorption, E_D is activation energy of diffusion, and E_p is activation energy of permeation.[5,7–11] These three parameters are connected to one another, as follows:

$$E_p = \Delta H + E_D \tag{10}$$

E_D is always positive and is increased as the molecule size of the penetrant is increased. The partial molar heat of sorption may be expressed as

$$\Delta H = \Delta H_{\text{cond}} + \Delta H_{\text{mix}} \tag{11}$$

where ΔH_{cond} is the molar heat of condensation of the permeant and ΔH_{mix} is the partial molar heat of mixing. For permeant gases, such as H_2, N_2, and O_2, ΔH_{cond} is small comparing to ΔH_{mix}. Therefore, for permeant gases ΔH is always small and positive and the solubility coefficient S increases slightly when temperature increases. For condensable gases, such as SO_2, NH_3, and H_2O, ΔH is negative because of the large and negative ΔH_{cond}. The size of ΔH nearly equals the oppositely signed diffusion energy E_D. Thus, the activation energy of permeation E_p is close to zero, and the WVTR can be considered to be nearly independent of temperature Equation (7).[5,7–11]

The influence of humidity on WVTR is controlled by partial pressure difference $p_1 - p_0$ (1 and 0 represent the opposite faces of the sample). As can be seen from the Equation (6), the moisture content of the conditions studied is directly proportional to WVTR values. Thus, the effect of humidity on WVTR values should be dominant comparing to temperature.[5,7–11]

EXPERIMENTAL

Materials and Sample Preparation

The extrusion-coating polymers in this study were LDPE (CA7230) and PP (WG341C). The PP grade is not purely a homopolymer of PP, but it also contains some ethylene comonomer. The polymers were supplied by Borealis Polymers. The substrate was one-side pigment-coated paper (Lumiflex 90 g/m^2) from Stora Enso. The non-pigment–coated side of the paper was extrusion coated.

Extrusion coatings were applied using the pilot line at Paper Converting Institute (Tampere University of Technology). The pilot line has a co-extrusion station to produce the plastic coatings. The station contains four extruders (screw diameters 60 mm, 40 mm, and 2 × 30 mm), a Cloeren five-layer feed block with Selector Plug^{TM}, and a 700 mm wide T-type die with deckle systems and encapsulations (Cloeren). The encapsulations were used with LDPE in every set point to control the neck-in phenomena. LDPE and PP coatings were produced as monolayers. Line speed in the coating process varied from 40 to 180 m/min to yield coating weights from about 10 to 67 g/m^2. The outputs of the extruders were chosen to give good quality film. Corona discharge equipment was used (at 2 kW power) to maintain a good adhesion between the paper and the coatings all the way through the trials.

Test Methods

Coating weights of the samples were measured from the 65 cm^2 area circular test pieces with smooth edges. The pieces were cut with Lorentzen & Wettre's circular cutter from the middle of the samples, and they were weighed with an analytical balance.

Water vapor transmission rates were measured from the same test samples as the coating weights. The measurements were made with the cup method according to standard SCAN P22:68.[2] A cross section of the cup method is shown in Figure 1. In the method calcium chloride is placed on the bottom of an aluminum dish. A circular test sample is placed against the dish. The sample is then covered with a cylindrical weight with a bottom area of 50 cm^2 accurately at the middle of dish. The sample is sealed tightly against the dish with hot wax. After the wax is cooled, the weight is removed and the dish is placed into the controlled atmosphere. After stabilization, the daily increase in the weight of the dish was recorded per unit area, and the water vapor transmission rate was expressed as g/m^2/24 h. Five parallel measurements were made per sample.

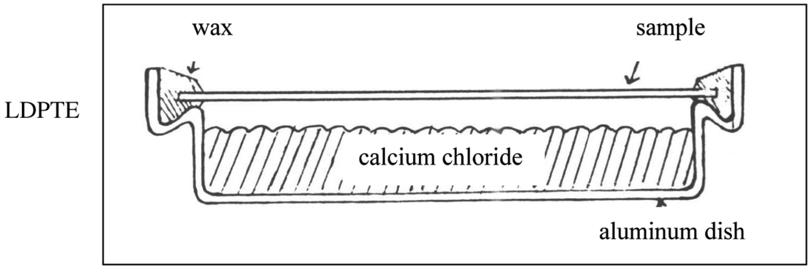


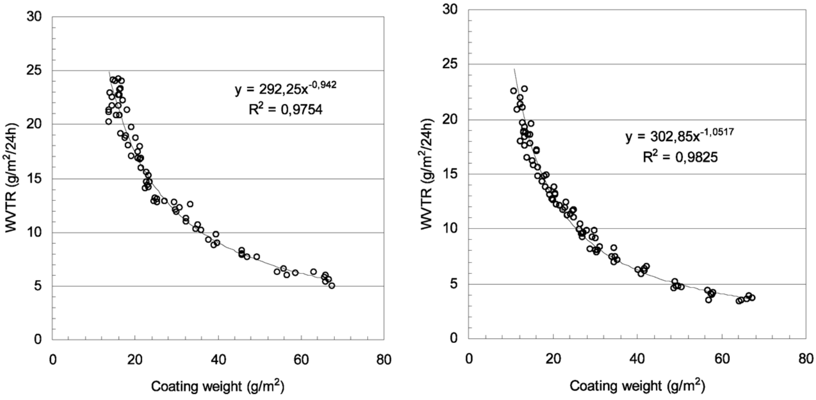
Figure 1. Cross section of WVTR cup method.

RESULTS AND DISCUSSION

WVTR Calculation Model

Various coating weights of LDPE and PP were prepared on top of the paper. Coating weights and WVTR values were determined, and WVTR values as a function of coating weights are shown in Figure 2.

For further studies it was useful to develop a mathematical approach for the plotted results shown in Figure 2. According to the fully developed diffusion flow, WVTR is inversely proportional to the thickness of the barrier layer. On the other hand, because thickness is directly proportional to the coating weight (g/m^2) of the polymer, it can be stated



(a) (b)

Figure 2. WVTR of LDPE- and PP-coated samples in tropical (38°C, 90% RH) conditions as a function of coating weight. The solid lines provide the power law model that fits the data points.

that WVTR is inversely proportional to the coating weight of the polymer. Thus, it can be written:

$$y(x) = Ax^{-1} \tag{12}$$

In Equation (12), y describes WVTR value and x is coating weight, while A is a constant. To cover the extended x-values (i.e., to predict WVTR values with extended coating weights), it is possible to use a computer spreadsheet program (e.g., Microsoft Excel). Such a program must include a statistical predicting model and regression analysis. Also, the model must include the form of Equation (12).

The statistical computer program used in this study used a power law model that is based on Equation (13):

$$y = Ax^{B} \tag{13}$$

In the chosen model, the variable B illustrates the exponent –1 in Equation (12). In practice, the theory of steady-state activated diffusion Equation (6) is somewhat a generalization, and therefore it needs some support from the chosen model. It can be considered that

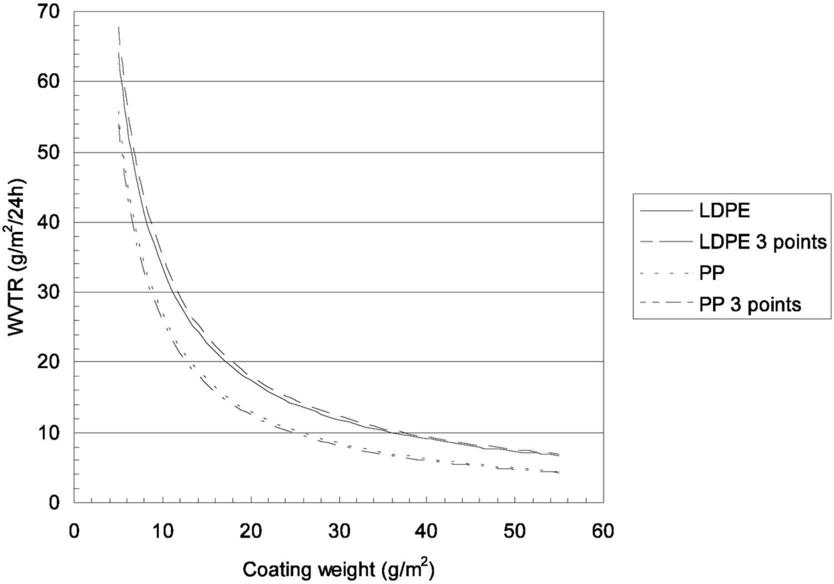


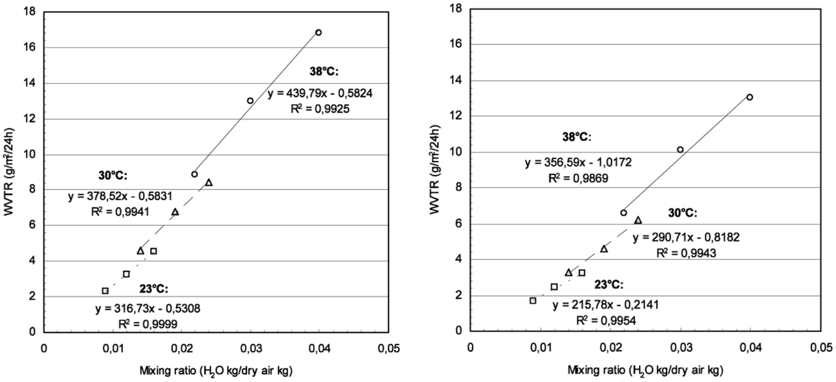
Figure 3. WVTR and power law regression lines of LDPE- and PP-coated samples using three coating weights compared to reference regression lines (see Figure 2). Regression equations and R^2 values for the three point cases were: LDPE ($y = 313{,}84 \times^{-0{,}9523}$; $R^2 = 0{,}9856$) and PP ($y = 294{,}64 \times^{-1{,}0553}$; $R^2 = 0{,}9883$).

the variable B gives more flexibility for the curve to follow the measured dot series, which almost fits the activated diffusion theory but not completely. Therefore, the predicting model used can be considered to be valid.

We discussed that all of the data points measured with the WVTR and coating weight tests can be described with Equation (13) (Figure 2). In addition to the trend lines, the fitted regression equations and R^2 values are also shown. The regression equations in Figure 2 can be used to calculate WVTR in coating weights other than those made in the extrusion coating trials of this study.

Reliability of WVTR Calculation Model

To speed up research, it is important to reduce the amount of test points in extrusion coating trials and WVTR analysis. Thus, the question is whether the WVTR calculation model is reliable with a smaller amount of test points. This can be tested by examining more closely the results of LDPE and PP coatings. Considering the whole dot series, the trend lines were reliable because they followed the dot series through existing x-values. Basically, three points are needed to define the shape of a curve in a xy-scatter plot. Therefore, three coating weights of the results were chosen (approximately 15, 30, and 45 g/m^2). With five parallel WVTR measurements, the computer program had 15 data points total to produce the curve. The power law regression trend lines generated are shown in Figure 3.



(a) (b)

Figure 4. WVTR of 20 g/m^2 (calculated value, as explained in text) LDPE- and PP-coated paper as a function of mixing ratio. Linear regression trend line curves, their equations, R^2 values, and temperatures are shown in the figure.

Figure 3 indicates only minor deviations between the corresponding curves. This proves that it is possible to introduce a power law regression equation based on only three separate coating weights, which can be used to calculate WVTR in other than measured coating weights. It can also be stated that the reliability is good if at least five parallel WVTR measurements are used and the coating weights used are not too close to each other. Optimally, the difference between coating weights should be about 10–15 g/m^2 and the lowest coating weight should be about 10–15 /m^2.

R^2 value describes the degree of relatedness between two variables. R^2 value is the square of the coefficient of correlation, and it is also called the regression coefficient. R^2 value varies between 0 and 1, which tells how well the actual data fit the predicted model. If R^2 value is 1, the model is perfectly matching with actual data. In this study, R^2 value does not describe the reliability of the WVTR calculation model. Instead, R^2 value indicates the accuracy of analyses, stability of extrusion coating, coating homogeneity, human errors, and other experimental errors.[12–16]

Test Conditions for Assessing the Influence of Humidity and Temperature on WVTR

Table I shows the measurement conditions used, and Table II presents the results for LDPE- and PP-coated samples. The regression equations and R^2 values were determined in a manner similar to that shown in Figure 2.

It is difficult to interpret the results from the trend-line curves shown (for example) in Figure 2. Therefore, the WVTR value was calculated to the exact coating weight of 20 g/m^2, as illustrated in Table III. The trend line curve equations (from Table II) were used to calculate the WVTR values at the coating weight of 20 /m^2.

Table III indicates that temperature had a great influence on WVTR. For example, with PP, a rise of 7°C in temperature increased the WVTR more than an increase of 40% in relative humidity. On the other hand, it is known that the mixing ratio increases with temperature. Table IV

Table I. Conditions used in WVTR measurements

	1. Conditions	2. Conditions	3. Conditions
Test series 1	23°C, 50% RH	23°C, 70% RH	23°C, 90% RH
Test series 2	30°C, 50% RH	30°C, 70% RH	30°C, 90% RH
Test series 3	38°C, 50% RH	38°C, 70% RH	38°C, 90% RH

Table II. Regression results and R^2 values for PP (top) and LDPE (bottom) at each measurement condition

Condition	Trend curve equation for PP	R^2 value
23°C, 50%RH	$y = 63{,}611\, x^{-1{,}2103}$	0,9186
23°C, 70%RH	$y = 36{,}525\, x^{-0{,}904}$	0,9300
23°C, 90%RH	$y = 65{,}091\, x^{-1{,}0043}$	0,9824
30°C, 50%RH	$y = 40{,}97\, x^{-0{,}8393}$	0,8958
30°C, 70%RH	$y = 49{,}342\, x^{-0{,}7936}$	0,8989
30°C, 90%RH	$y = 78{,}691\, x^{-0{,}847}$	0,8969
38°C, 50%RH	$y = 114{,}85\, x^{-0{,}954}$	0,9838
38°C, 70%RH	$y = 186{,}82\, x^{-0{,}9737}$	0,9851
38°C, 90%RH	$y = 248{,}47\, x^{-0{,}9834}$	0,9894
Condition	Trend curve equation for LDPE	R^2 value
23°C, 50%RH	$y = 47{,}337\, x^{-1{,}0056}$	0,9924
23°C, 70%RH	$y = 57{,}328\, x^{-0{,}9574}$	0,9562
23°C, 90%RH	$y = 121{,}2\, x^{-1{,}0962}$	0,9740
30°C, 50%RH	$y = 93{,}637\, x^{-1{,}0036}$	0,9676
30°C, 70%RH	$y = 171{,}7\, x^{-1{,}0789}$	0,9786
30°C, 90%RH	$y = 233{,}97\, x^{-1{,}1099}$	0,9829
38°C, 50%RH	$y = 142{,}24\, x^{-0{,}9262}$	0,9738
38°C, 70%RH	$y = 187{,}15\, x^{-0{,}89}$	0,9696
38°C, 90%RH	$y = 270{,}6\, x^{-0{,}9271}$	0,9834

shows the mixing ratios at the conditions used. The mixing ratio is defined as the mass of water vapor divided by the mass of dry air.

According to Figure 4, the effect of mixing ratio on WVTR is strong and has an almost linear correlation to increasing WVTR. At higher mixing ratios the temperature is also naturally higher due to saturation,

Table III. Calculated WVTR (in g/m^2/24 h) for PP and LDPE at the coating weight of 20 g/m^2

	50%RH	70%RH	90%RH
PP			
23°C	1,69	2,43	3,21
30°C	3,32	4,57	6,22
38°C	6,59	10,1	13,1
LDPE			
23°C	2,33	3,26	4,54
30°C	4,63	6,78	8,42
38°C	8,87	13,01	16,83

Table IV. Mixing ratios at the WVTR measurement conditions used

Conditions	Mixing ratio (kg of water/kg of dry air)
23°C, 50%RH	0,009
23°C, 70%RH	0,012
23°C, 90%RH	0,016
30°C, 50%RH	0,014
30°C, 70%RH	0,019
30°C, 90%RH	0,024
38°C, 50%RH	0,022
38°C, 70%RH	0,030
38°C, 90%RH	0,040

Results apply to 1 bar air pressure.

which limits the highest possible mixing ratio at each temperature. The consequence of this can be observed in Figure 4, where the increased temperature also shifts the level of permeation at higher mixing ratios. Therefore, it is obvious that the combined influence of both increasing temperature and mixing ratio causes higher permeation rates.

However, if we look at the regression for the trend lines at each temperature, there is a very good linear correlation (R^2 equals almost 1) between WVTR and mixing ratio. According to the curves, the strong correlation between WVTR and temperature mentioned earlier is not quite the absolute truth, because as the temperature is raised, the mixing ratio is also increased at the given relative humidity.

Table V. WVTR dependence on temperature at fixed mixing ratios

Mixing ratio (H_2O kg/dry air kg)	WVTR and RH (in parentheses)		
	23°C	30°C	38°C
LDPE			
0,014	3,90 (80)	4,72 (50)	—
0,016	4,54 (90)	5,47 (58)	—
0,022	—	7,74 (82)	9,09 (50)
0,024	—	8,50 (90)	9,97 (52)
PP			
0,014	2,81 (80)	3,25 (50)	—
0,016	3,24 (90)	3,83 (58)	—
0,022	—	5,58 (82)	6,83 (50)
0,024	—	6,16 (90)	7,54 (52)

WVTR units are in $g/m^2/24\,h$ and RH units in %. Values with italic font are calculated using the equations in Table II.

The WVTR results in Table V provide a comparison between corresponding temperatures at fixed mixing ratios. These results have also been calculated for 20 g/m^2 samples. The idea is that the fixed results are interpolated on the basis of two consecutive relative humidities. According to Table V, a rise in temperature considerably increases the water vapor permeation.

CONCLUSIONS

It is possible to create a simple model using power law regression to calculate the water vapor transmission rate of extrusion-coated samples. With the modeling, only three set points with different coating weights are needed to evaluate WVTR values of all coating weights. Here are the preconditions for modeling: the three coating weights preferably about 10–15 g/m^2 apart from each other, lowest coating weight of about 10–15 g/m^2, and at least five parallel WVTR measurements per coating weight.

The WVTR results of LDPE- and PP-extrusion coatings indicate that increasing the mixing ratio (water mass per dry air mass) results in an almost linearly increasing water vapor permeation rate. The theoretical rationale for this is that the permeability of a condensing vapor, like water vapor, is mainly controlled by vapor concentrations on the opposite faces of the sample. Another explanation for this phenomenon is that the driving force for the permeating water molecules passing through the sample strengthens due to the increasing partial pressure gradient between the opposite faces of the sample.

Because of the linear correlation between the mixing ratios and WVTR values, it can be stated that temperature has only a small effect on WVTR. However, in a closer analysis the increasing temperature led to increasing permeation rate among the studied extrusion coatings. This can be explained by the Arrhenius relationship between coefficient of permeability and temperature where the balance of activation energy of diffusion and heat of solution play a vital role.

In future studies the role of mixing ratio and temperature will be examined more carefully. The target is to create a prediction model for the water vapor transmission rate, where mixing ratio, temperature, and also the thickness of the coating are the input.

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