Prediction of WVTR with General Regression Models

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ABSTRACT

In this study, general regression models are used to predict moisture barrier properties of extrusion coated papers in different atmospheric conditions. Basically, water vapour transmission rates (WVTR) of different polymers are affected by three factors: coating weight (or squared mass) of a studied polymer, temperature and moisture concentration of surroundings. Regression models find mathematical connections between WVTR and these variables making WVTR analysis even more effective in determining moisture barrier properties of studied polymers. As a result of the study, a practical computer program is established where WVTR of extrusion coated paper is predicted as a function of user-defined temperature, relative humidity and coating weight.

INTRODUCTION

Moisture barrier properties of extrusion coated papers are mainly controlled by the used coating polymers. The general selection of moisture barrier polymers includes low and high density polyethylenes (PE-LD and PE-HD), polypropylene (PP) and polyethylene terephthalate (PET) [1]. Also, some new polymers have recently been introduced for the same purpose. These include cyclo-olefin copolymers (COC), liquid crystal polymers (LCP), nanocomposites etc. [2-5]. Common to the coatings is that they give a specific water vapour barrier for the material depending on the atmospheric conditions and the used coating weights. Water vapour barrier of extrusion coated paper can be measured with different standard methods [6-9] and is specified as water vapour transmission rate (WVTR).

Concerning laboratories, the evaluation of WVTR can be a time consuming procedure. Aiming towards lighter load of testing the target of this study was to establish a mathematical model that is employed as a practical, fast and easy-to-use tool to predict WVTR. Many studies have recently been performed to find prediction models and mathematical expressions for permeability of polymers [10-14]. Also, in terms of food deterioration, many shelf life prediction models have been developed based on the water vapour barrier properties of the package [15-18]. This study represents another expression for WVTR based on regression analysis and computer simulation made for experimental studies. Regression modelling is commonly used in technology when more deterministic models are not efficient due to complexity and disturbances of the problem. Regression analysis establishes sort of a “black-box type” model where the input and output values are not bound to each other with physical laws or scientific facts but the correlation is found via experimental testing and statistical treatment of the results [19].

Mathematical treatment of WVTR starts with Fick’s first law. It states that

\[ J = -D \frac{dc}{dx} \]  

where \( J \) = diffusion flow through unit area of film, \( D \) = diffusion coefficient, \( c \) = concentration of a penetrant and \( x \) = distance of the point from the film surface. Concerning WVTR test, the target is to achieve a steady state phase where the diffusion flow of water vapour doesn’t change over time. In addition, the product \( D*S \) is called the coefficient of permeation (P) and Henry’s law state that \( c = S*p \), where \( S \) = solubility coefficient and \( p \) = partial pressure of the penetrant. As a conclusion, we find a simple mathematical expression for WVTR (equation 3) [20-21].
Practically, there are three external factors affecting WVTR of extrusion coated paper. These are temperature and humidity of surroundings and the thickness of the extrusion coated polymer layer. As equation 3 shows, the thickness of the coating has an inverse proportion to WVTR. The influence of humidity is expressed as a partial pressure difference between the film’s surfaces (p₂-p₁) and the influence of temperature is controlled by the coefficient of permeation (see equation 4: Arrhenius relationship). In addition to these, there are countless polymer dependent factors influencing WVTR; crystallinity, orientation, cross-linking, molecular weight, chemical bonding between the polymer chains etc. Obviously, it is very difficult to isolate and estimate the effect of all these factors separately on WVTR. Due to this problem, it was decided early in the study to set up the prediction models on the three external factors and overcome the diversity of polymers by creating the models separately for each coating.

\[ P = P_0 \exp\left(- \frac{E_p}{RT}\right) \]  

**MATERIALS AND METHODS**

To gain experimental WVTR data for statistical treatment, extrusion coating trials were performed at the pilot-line of TUT/Institute of Paper Converting. The pilot-line included a suitable extrusion station for polymers and a roll-to-roll process for the substrate in order to produce the needed extrusion coated samples. Four extrusion coating polymers were chosen to the study: LDPE (CA7230), HDPE (CG8410), PP (WG341C) and COC (Topas 8007F-400). The polymers were supplied by Borealis except the COC-grade which was delivered by Topas Advanced Polymers. One-side pigment-coated paper, Lumiflex 90 from Stora Enso, was employed as a substrate. The non-pigmented side of the paper was extrusion coated. The substrate was pre-treated with corona equipment (2 kW) to obtain good adhesion with the coating. With COC also flame treatment was employed as an adhesion promoter. 20 set points were produced in the trials, five set points with each polymer, to yield coating weights from about 10 g/m² to 50 g/m².

Coating weights and WVTRs of the extrusion-coated paper samples were measured from 65 cm² circular test pieces. Each sample passed through both measures in order to attach certain coating weight and WVTR values to each other. The coating weights were measured with an analytical balance by subtracting the influence of base paper from the result. The WVTRs were measured according to the standard test method SCAN P22:68 [6]. The advantage of the “cup method” is it’s capability to measure a large number of samples simultaneously. In the method a sample is placed against an aluminium dish containing calcium chloride. The sample is then covered with a cylindrical weight having bottom area of 50 cm². Hot wax is drizzled around the cylinder to seal the sample tightly against the dish. After the wax is cooled, the cylinder is removed and the dish is placed into the controlled atmosphere. After stabilization, the daily increase in the weight of the dish is measured and the WVTR is expressed as g/m²/24h.

For the coatings produced in the trials, the exact WVTRs for 20 g/m² coating weights were measured with the help of a power law of regression. A coating weight and a WVTR-value measured from the same sample form a dot in a xy-scatter plot; x-axis = coating weight and y-axis = WVTR. By using the power law of regression, a continuous curve can be formed between all the dots and the regression equation expressing WVTR as a function of coating weight can be drawn. In this study, 5 different coating weights were performed with each coating. With 4 parallel WVTR measures and 5 coating weights per coating totals 20 data points in each atmospheric condition to produce the regression trend lines for each coating. Figure 1 shows an example of creating one of the trend lines (LDPE in standard conditions 38°C and RH 90%).
In the study, WVTRs of samples were measured in 16 atmospheric conditions in order to achieve enough variables for regression analysis. By producing four sets of samples, each sample went through four conditions. Table 1 shows the conditions used in the WVTR test. Following the general practice, the conditions are defined as temperature and relative humidity.

Table 1: Conditions used in WVTR measurements

<table>
<thead>
<tr>
<th>Series</th>
<th>1. conditions</th>
<th>2. conditions</th>
<th>3. conditions</th>
<th>4. conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td>23°C 50% RH</td>
<td>30°C 50% RH</td>
<td>38°C 50% RH</td>
<td>45°C 50% RH</td>
</tr>
<tr>
<td>Series 2</td>
<td>23°C 63% RH</td>
<td>30°C 63% RH</td>
<td>38°C 63% RH</td>
<td>45°C 63% RH</td>
</tr>
<tr>
<td>Series 3</td>
<td>23°C 77% RH</td>
<td>30°C 77% RH</td>
<td>38°C 77% RH</td>
<td>45°C 77% RH</td>
</tr>
<tr>
<td>Series 4</td>
<td>23°C 90% RH</td>
<td>30°C 90% RH</td>
<td>38°C 90% RH</td>
<td>45°C 90% RH</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

WVTR results

Applying the described procedures the WVTRs of the 20 g/m² LDPE, HDPE, PP and COC coatings were measured in the study. As an example, table 2 shows the results of LDPE coating. The results are further illustrated in the figure 2.

Table 2: WVTR results of 20 g/m² LDPE coating in 16 different atmospheric conditions (WVTR unit: g/m²/24h)

<table>
<thead>
<tr>
<th></th>
<th>50% RH</th>
<th>63% RH</th>
<th>77% RH</th>
<th>90% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>3,03</td>
<td>3,45</td>
<td>4,30</td>
<td>4,89</td>
</tr>
<tr>
<td>30°C</td>
<td>5,11</td>
<td>6,86</td>
<td>8,16</td>
<td>9,74</td>
</tr>
<tr>
<td>38°C</td>
<td>9,41</td>
<td>12,13</td>
<td>15,37</td>
<td>19,08</td>
</tr>
<tr>
<td>45°C</td>
<td>14,74</td>
<td>18,92</td>
<td>25,73</td>
<td>32,59</td>
</tr>
</tbody>
</table>
According to the results, the influence of temperature on WVTR appears to be more effective than the influence of RH. However, there are two problems with this expression concerning variable interactions and modelling. Firstly, relative humidity does not define the absolute water concentration of surroundings. It only defines the percentage of the mass that would be present in an equal volume of saturated air at a specific temperature. The second problem is that it is difficult to find an accurate mathematical expression between the variables. For example, the graph of figure 2 is established via smoothing procedures and lacks a specific mathematical expression. To comply with these problems, we replace relative humidity with mixing ratio which represents the absolute humidity of surroundings. Mixing ratio ($\omega$) is defined as the ratio of the amount of water (kg) and the amount of dry air (kg) in the atmosphere [22]. The mathematical expression of it is as follows:

$$\omega = \frac{m_h}{m_i} = \mu \frac{p_h}{p_i} = \mu \frac{p_h}{p - p_v}$$  \hspace{1cm} (5)

where $\mu = M_h / M_i = 18.015/28.964 = 0.6220$, $p = \text{normal air pressure} = 1 \text{ bar}$ and $p_v = \text{vapour pressure of the conditions.}$ Furthermore, the definition of relative humidity is

$$RH = \frac{p_h'}{p_v'}$$  \hspace{1cm} (6)

where $p_h'$ is saturated vapour pressure. Saturated vapour pressure is a function of temperature and can be found from standard tables of humid air. By uniting the equations 5 and 6, mixing ratio can be expressed as a function of relative humidity and temperature as follows:

$$\omega = \mu \frac{p_h'(T)}{p/RH - p_v'(T)}$$  \hspace{1cm} (7)
Consequently, the definition of atmospheric conditions can be made via temperature and absolute humidity, and the WVTR results can be analysed in a different perspective. Figure 3 shows a WVTR vs. mixing ratio diagram of 20 g/m² LDPE coating. According to the diagram, the effect of mixing ratio on WVTR is strong, almost linear. Temperature influences slightly on the slope of the straight WVTR vs. mixing ratio -line. Furthermore, the shape of the curve indicates that the system is most likely suitable for regression estimation. Same observations are found with the other coatings, too. These findings are a backbone to the new prediction model.

![WVTR vs. mixing ratio](image)

**Figure 3:** WVTR as a function of mixing ratio for 20 g/m² LDPE coating

**Model development**

We define temperature, mixing ratio and coating weight as independent variables ($x_1$, $x_2$ and $x_3$, respectively) and WVTR as a dependent variable ($y$). The first step of the model development is to find a regression model that estimates WVTR of a 20 g/m² coating as a function of atmospheric conditions ($x_1$, $x_2$). In the study, several first- and second-order models were tested to obtain the target. Equation 8 shows an example of a second-order model including all possible terms.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2$$  \hspace{1cm} (8)

To solve the $b_i$-values ($i = 1-5$) and to test the reliabilities of the models, we enter the results of table 3 into a spreadsheet or statistical computer program; 16 WVTRs as a function of temperature and mixing ratio for each coating. Note that with a common spreadsheet program, the second-order model must be changed into a first-order to obtain results. For example, the equation 8 is changed into a first-order by taking three more variables into use as follows:

$$x_4 = x_1x_2$$  \hspace{1cm} (9)

$$x_5 = x_1^2$$  \hspace{1cm} (10)

$$x_6 = x_2^2$$  \hspace{1cm} (11)

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_4 + b_4x_5 + b_5x_6.$$  \hspace{1cm} (12)

Commonly, computer programs test the suitabilities of regression models on different problems via reliability indicators. The most important reliability indicators are sum of squares of residuals (SSE), variance ($S^2$), standard error (S) and coefficient of determination ($R^2$). In this study, the models were decided on the basis of
standard errors. Table 3 shows a list of the models tested in the study and the corresponding S-values. The lowest S-value indicates the best accuracy of the model. Note that with different polymers, the most accurate model is not the same one.

Table 3: Standard errors of the tested regression models

<table>
<thead>
<tr>
<th>Model</th>
<th>Std error LDPE</th>
<th>Std error HDPE</th>
<th>Std error PP</th>
<th>Std error COC</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂</td>
<td>0.897</td>
<td>0.590</td>
<td>0.590</td>
<td>0.649</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂</td>
<td>0.689</td>
<td>0.435</td>
<td>0.355</td>
<td>0.447</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁²</td>
<td>0.908</td>
<td>0.589</td>
<td>0.623</td>
<td>0.626</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₂²</td>
<td>0.353</td>
<td>0.203</td>
<td>0.234</td>
<td>0.310</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.440</td>
<td>0.298</td>
<td>0.295</td>
<td>0.346</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.284</td>
<td>0.162</td>
<td>0.223</td>
<td>0.323</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.291</td>
<td>0.170</td>
<td>0.232</td>
<td>0.331</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.519</td>
<td>0.463</td>
<td>0.434</td>
<td>0.313</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.410</td>
<td>0.238</td>
<td>0.214</td>
<td>0.313</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.660</td>
<td>0.520</td>
<td>0.320</td>
<td>0.310</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂ + b₃X₁X₂ + b₄X₁² + b₅X₂²</td>
<td>0.476</td>
<td>0.286</td>
<td>0.278</td>
<td>0.316</td>
</tr>
<tr>
<td>y = b₀ + b₁X₁ + b₂X₂</td>
<td>0.782</td>
<td>0.627</td>
<td>0.483</td>
<td>0.303</td>
</tr>
</tbody>
</table>

As the bᵢ-values are now solved by the computer, the WVTRs of 20 g/m² coated papers can be predicted in different atmospheric conditions. Figure 4 shows an illustrative 3D surface – WVTR as a function temperature and mixing ratio for 20 g/m² LDPE coating. The figure shows also the 16 data points of the measured values and the reliability indicators of the regression model. According to the graph, mixing ratio has clearly greater influence on WVTR than temperature at the tested condition frame. The reliability indicators reflect good accuracy of the model.

Model: WVTR=b₀+b₁Temp+b₂Mix+b₃Temp*Temp+b₄Mix*Mix
z=-(6,9493)+(,427809)*x+(203,756)*y +(-,00454)*x*x+(5101,53)*y *y

![Reliability indicators](image)

SSE = 0.857234
S = 0.279160
S² = 0.077930
R² = 0.999216

Figure 4: WVTR as a function of temperature and mixing ratio for 20 g/m² LDPE coating

The next step of the prediction model development is to add the influence of coating weight on WVTR. As discussed earlier, coating weight has an inverse proportion on WVTR. Thus, the model for WVTR of a monolayer coated paper can be written:
\[ y = \frac{20}{x_3} \left( f(x_1, x_2) \right) \]  

(13)

where the \( f(x_1, x_2) \) is the best fitted polynomial from the table 3. Furthermore, with the help of a theoretical approach, total barrier performance of a multilayer extrusion coated paper can be estimated. Provided all the \( P_i \)-values of the layers are independent of pressure and concentration and there are no barriers to diffusion due to interfacial phenomena between layers, permeability of a multilayer film obeys the equation

\[ \frac{L_{tot}}{P_{tot}} = \frac{L_2}{P_1} + \frac{L_2}{P_2} + \frac{L_3}{P_3} \]  

(14)

where \( L_1, L_2 \) and \( L_3 \) are the thicknesses of layers and \( P_1, P_2 \) and \( P_3 \) are the corresponding permeabilities. When using specific atmospheric conditions (equation 3, WVTR test), the partial pressure difference of water vapour between the films surface stays as a constant. Thus, the total WVTR of a multilayer structure can be calculated with the help of separate layers as follows

\[ \frac{1}{WVTR_{tot}} = \frac{1}{WVTR_1} + \frac{1}{WVTR_2} + \frac{1}{WVTR_3} \ldots \]  

(15)

Note that if the equation 15 holds true, the order of the layer structure doesn’t affect the total WVTR value. However, when any \( P_i \) is pressure dependent, the equation 15 is no longer valid and the use of the model for multilayer estimation gives inaccurate results [23].

As the final outcome, the study represents a new Labview-based computer program which is employed as a practical and versatile tool for WVTR estimation. In the program, the user defines the atmospheric conditions of the WVTR estimation and the structure of the extrusion coated paper to be measured. Among others, the program plots the WVTR value of the desired case, draws a 3D-graph illustrating WVTR of the structure in all climatic conditions and shows the WVTRs of the selected structure in standard atmospheric conditions (23°C, 50% RH, 25°C 75% RH and 38°C 90% RH). Note, that the program is at it’s best when the chosen temperatures and relative humidities are close to the ones used in the experimental tests. Especially in hot conditions, the barrier behaviours of polymer matrices tend to change comparing to the predicted ones. In addition, the fact is that when leaning on statistical findings, there are no guarantees for the model to work outside the frames of experiments. At this point, the frames of the model for accurate estimations are 20-50 °C and 45-95 % RH. In the future, the plan is to widen the frames by executing further experimental tests in more demanding atmospheres.

CONCLUSIONS

It is possible to create a simple and accurate prediction model that estimates water vapour barriers of extrusion coated papers as a function of temperature, relative humidity and the layer structure of the coating. The root of the model is in the linear correlation between WVTR and mixing ratio (mixing ratio representing the absolute humidity of atmosphere). Temperature has a regular influence on the slope of the WVTR - mixing ratio line and also a small-scale interference on the interception of the line. At first, the prediction model is established for a single 20 g/m² extrusion coating by using the best fitted second-order regression model to describe WVTR as a function of temperature and mixing ratio. With the help of theoretical approach, the influences of coating weight and multi-layer structure are introduced into the model. As a result of the study, a practical, fast and easy-to-use computer program is established that can effectively predict WVTRs of user-defined extrusion coated paper products as long as the selected polymers are treated with the statistical procedures introduced in the text.
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REFERENCE


