Improving the Accuracy and Reliability of Models used to Predict Multilayer Film Properties

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ABSTRACT

Multilayer packaging films are becoming increasingly complex due to the expanding number of layers, types of polymers and blend components that a typical structure contains. Designing or modifying today's multilayer films usually requires expensive, time-consuming trials on commercial or pilot film lines. A mathematical model that accurately predicts critical performance properties from component materials and basic principles could potentially reduce trial costs and accelerate structure development. However, developing such a model is very challenging due to the broad range of possible structures and conditions, and the fact that many film properties are non-additive and/or non-linear.

This paper will present an integrated model that calculates many important multilayer film properties along with three case studies that were used to improve the model's accuracy and reliability. The model accurately predicts many properties such as barrier, tear, tensile modulus, layer viscosities and bending resistance for a variety of coextruded packaging films. This paper however, will focus on three case studies where the initial predictions were unreliable due to inaccurate or incomplete starting assumptions. The model's reliability for these general cases was then significantly improved by following a systematic approach for identifying and correcting the primary sources of error. This approach, which can be repeated and implemented to improve multilayer predictions, will be presented along with general modeling recommendations.

INTRODUCTION

Today's packaging films have evolved from relatively simple monofilms and laminates into complex, ultra-thin structures with more layers, types of polymers and a wider variety of blend components than ever before. As this complexity increases, film manufacturers tend to be more cautious when developing radically different films, or even changing existing structures to maximize performance without extensive – and therefore expensive – trials. This caution, while understandable, slows innovation.

An complementary approach for developing innovative and optimizing existing structures is to predict film properties from mathematical models that use component material properties and known relationships. Accurate models could reduce trial expenses, risks and uncertainties associated with changes and ultimately accelerate innovation. Currently, models are rarely used to predict properties in multilayer packaging for the following reasons:

First, most models or calculators focus on a single property while commercial films must simultaneously meet many demanding performance and cost requirements. A calculation that accurately estimates how a material substitution or layer ratio change affects oxygen barrier has limited value if the effect on stiffness, cost, optics and other critical properties is unknown. Second, multilayer film properties are often non-linear and sometimes cannot be extrapolated from basic material properties. Interactions between distinct layers or materials can be difficult to quantify in multilayer films since individual materials do not always retain their properties. Finally, film properties are affected by processing and environmental conditions that are difficult to incorporate into a model. Package designers appreciate the difficulties of accounting for these effects and therefore prefer to rely on empirical data from test films over simulations.

While these obstacles are significant, the potential innovations and cost savings from more accurate simulations favor developing better models. NOVA Chemicals has designed an integrated model that

enables estimation and comparison of many multilayer film properties for different structures. The model was built in a modular framework that enables the addition of new products to a material database as well as new calculations and property predictions.

The accuracy of any model deteriorates as the number of assumptions and interactions increase. This model's flexible format makes it possible to refine equations and algorithms as new relationships, interactions, and discoveries are made using if→then logic statements and non-linear equations as appropriate. This dynamic and iterative approach involving initial estimations from basic assumptions, comparison to actual data, and refinement, allows for continuous improvement of the model's accuracy and reliability.

This paper will review three case studies that demonstrate how multilayer film models can be continuously improved and refined to account for complex relationships and material interactions. In these cases, the initial predictions were inaccurate or significantly different from measured values in actual films. By systematically identifying the sources of error and refining the calculations, the model's accuracy and reliability was improved.

MATERIALS AND METHODS:

The test films used to verify model predictions for these case studies were all coextruded on a on Brampton Engineering blown film line. General structures and die details for the case studies are presented in Table 1 below. Every attempt was made to match commercial production conditions as closely as possible.

Table 1: Coex Structures used for the case studies:

	CASE STUDY	Die Diameter	General Coex Structure Layer Ratio
1	HDPE Barrier Study	4 inch	LLDPE / HDPE / LLDPE 30 % / 40 % / 30%
2	LLDPE Tear Study	6 inch	HDPE/ HDPE / LLDPE 35 % / 40 % / 25%
3	Nylon Relative Humidity (RH) effects	14 inch	Nylon/Tie/PE/Tie/Nylon/tie/PE/PE/Sealant 12% / 10% /10%/ 11% /12% / 11% / 11% / 10% /12%

The test films used in Case Study 3 were converted into water filled pouches on a ROVEMA® vertical-form-fill and seal pouch line with a back fin seal. Pouches were filled with minimal air headspace. The finished pouches were evaluated for leaker rates as a function of packaging line speed using both at-line and aged drop impact tests. Physical and barrier properties of the films used in the pouches were also determined by removing the water and running tests on the non-sealed portions of the films within 20 minutes.

The materials used in the test films are presented below in Table 2. All materials are commercial products with melt indices and densities suitable for co-extruded blown films.

Table 2: Resins used to produce test films

CODE	SUPPLIER	DESCRIPTION	GRADE
LLDPE-1	NOVA Chemicals	Octene LLDPE (1MI, 0.917 density)	SURPASS® FPs117-C
LLDPE-2	NOVA Chemicals	Octene LLDPE with high toughness (0.65 MI, 0.916 density)	SURPASS® FPs016-C
sHDPE	NOVA Chemicals	Octene HDPE with high barrier (1MI 0.966 density)	SURPASS® HPs167-AB
vLLDPE	NOVA Chemicals	Octene LLDPE (0.9 MI, 0.912 density)	SCLAIR® FP112-A
Butene	NOVA Chemicals	Z/N catalyzed butene copolymer	NOVAPOL® PF0118-C
Tie Conc.	DUPONT	LLDPE-based tie concentrate	BYNEL® 41E710
Tie Blend	NOVA Chemicals	Blend resin used with 20% tie concentrate	SURPASS® FPs016-C
PA	BASF	Nylon 6,6-6 Copolymer	ULTRAMID® C40

RESULTS AND DISCUSSION

Case Study #1: Blending Effects - Estimating Permeability in Coex Films with Blended HDPE Layers

The water vapor transmission rate of a multilayer film can be predicted reasonably well from equation 1 below.

Equation 1: Water vapor transmission rate for a multilayer film

$$1 / WVTR = t_1/WVPV_1 + t_2/WVPV_2 + t_3/WVPV_3 + \ldots t_n/WVPV_n$$

Where:
WVTR = Water vapor permeation rate of multilayer film (grams/100in^2-day)
t_n = Thickness of layer n (mils)
$WVPV_n$ = Water vapor permeation value for layer n. (grams-mil/100in2-day)

The permeation value is the transmission rate normalized for a 1 mil film gauge and considered an intrinsic polymer property for the model.

Individual layers that contain blends of different polymers present a special challenge (2). For many polyolefin-polyolefin blends, the permeability of the blended layers can be estimated reasonably well by multiplying the permeation values of the specific polymers by the weight percent used in the blend. For example, the water vapor permeation value (WVPV) of layer *n* can be estimated by weight averaging the WVPV of individual layers using equation 2.

Equation 2: Water vapor permeation value for a blended layer in a multilayer film

$$WVPV_n = (WVPV_a) * (\text{weight fraction a in blend}) + (WVPV_b) * (\text{weight fraction b in blend})$$

Where:
Material a = LLDPE with WVPV of 600 grams-mil/100in2-day
Material b = HDPE with WVPV of 120 grams-mil/100in2-day
Blend Ratio in Layer = 80 % w/w component a, 20 % component b

WVPV for this layer = (600 * 80%) + (120 * 20%) = 504 grams-mil/100in2-day

The above equations predicted transmission rates within 8% of the measured values for a variety of coextruded structures. However, in coex films containing blends of sHDPE with LLDPE in specific layers, the measured water vapor transmission rates were much lower than the model's calculated predictions.

Film barrier properties can be affected by several factors such as polymer processing effects (i.e. film cooling rates and degree of orientation) (2) and environmental factors such as test temperature and relative humidity. Aubee et al (4) found a barrier synergy in blends of sHDPE with linear polyethylenes which suggests the weighted average assumption of equation 2 will not accurately predict the permeability of sHDPE and LLDPE blends. Figure 1 displays predicted and actual WVP values for sHDPE and LLDPE blends. A non-linear equation was developed from Aubee's data that estimates the WVPV of layers containing sHDPE and LLDPE blends. The non-linear equation accounts for the barrier synergy of blended sHDPE and LLPE layers.
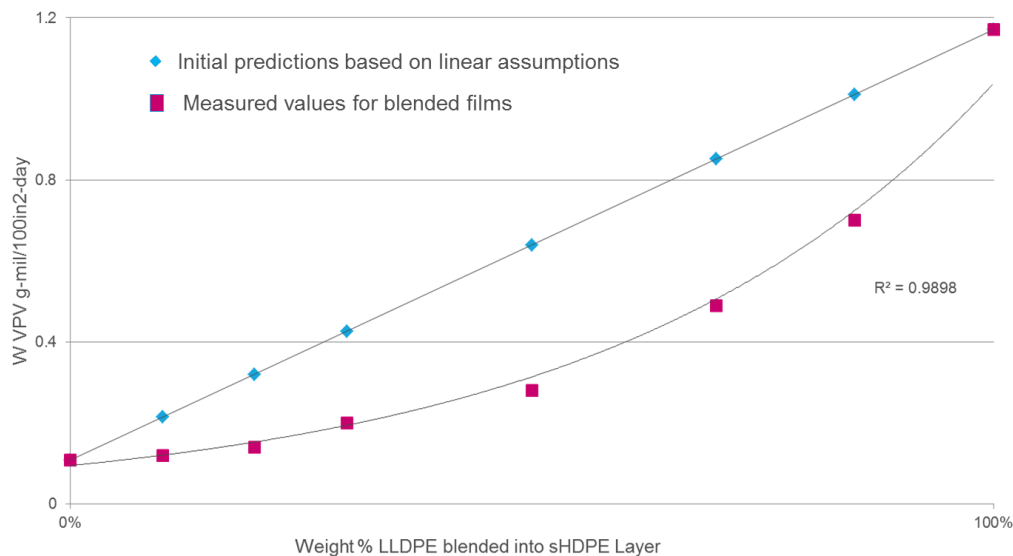
Figure 1: Predicted and actual water vapor permeation values for 1 mil monolayer films made from sHDPE + LLDPE blends

The predicted moisture permeability of films containing blended sHDPE layers was typically within 5 to 8% of the measured value when the exponential equation was substituted for equation 2 in the model. The model was modified to automatically substitute the exponential equation for these sHDPE blends by incorporating an if→then logic statement into the permeability algorithm.

Case Study #2: Layer Interaction Effects - Loss of LLDPE Tear Strength in HDPE Coex Structures

Elmendorf tear strength can be difficult to predict in multilayer films since the tear strength of one layer is influenced by the elastic and tensile properties of adjacent layers. However, prediction errors can be minimized when the fundamental tear mechanism is understood and modeled correctly.

Wu and McCarthy showed that tear values of films containing LLDPE are greatest when the LLDPE layer is able to elongate in a direction perpendicular to the tear propagation line (5). An LLDPE film that can freely elongate absorbs energy at the tear propagation point which increases the apparent tear strength.

When the same LLDPE film is laminated or coextruded next to a stiff material with poor tear strength, the LLDPE elongation can be restricted which effectively lowers its tear strength.

This reduced tear strength is evident in coextruded films containing adjacent layers of LLDPE and HDPE. In HD/LL films, the actual tear values of coex films were much lower than values predicted by adding tear values of equivalent thickness, monolayer films. The predictions were much more accurate when the "zero elongation tear" values for the LLDPEs were substituted for the standard LLDPE tear value in HD/LL coex films.

The zero elongation tear value was obtained by applying an adhesive tape to both sides of the LLDPE film and running a standard Elmendorf tear test. The adhesive tape has low MD tear strength and, if sufficiently bonded, will restrict the elongation of the LLDPE film at the tear propagation point. Figure 2 shows how the MD tear of LLDPE films is reduced when the TD elongation is incrementally restricted by tape. Zero elongation tear values were typically 30 to 50% lower than standard tear values for the monolayer LLDPE films. Similar to the previous case, the model was modified to substitute zero-elongation tear values for LLDPE layers next to HDPE or other stiff, low tear layers by incorporating if→then logic statements into the tear algorithm.
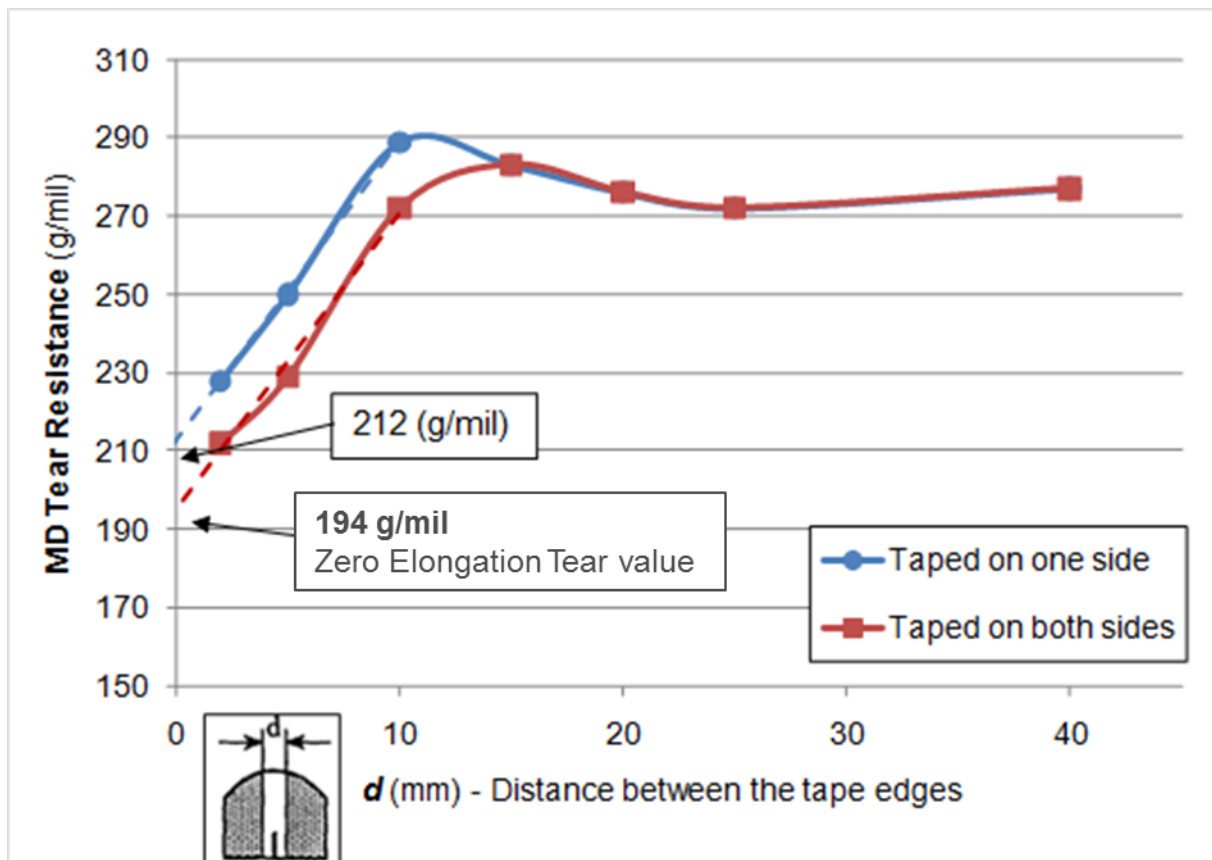

Figure 2: Restricted and zero elongation tear results for 1 mil monolayer LLDPE. MD tear is presented as a function of the gap distance between laminated tapes.

Case Study #3: Environmental Effects - Relative Humidity Effects in Polyamide Coex Films

Two environmental factors that must be considered when modeling multilayer film properties are temperature and relative humidity (RH). Temperature affects most physical properties and can be difficult to model if the polymer undergoes morphological transitions in the solid state (i.e. rubbery to glassy transition). In general, RH will have little effect on polyolefin properties but can significantly change the barrier and physical properties of hygroscopic polymers such as ethylene vinyl alcohol (EVOH) and polyamide homo- or copolymers (PA).

The impact of RH was apparent in coextruded films containing polyamide in the outer skin and core layers. Film samples conditioned for 72 hours at 30% RH prior to testing had less overall elasticity; higher stiffness or modulus, lower impact strength, and lower elongation at yield than identical films conditioned at 50% RH. Similar films converted into pouches under different RH conditions also showed notable differences: films manufactured in high RH environments had fewer leakers at fast converting line speeds and better drop impact resistance.

These property differences are likely due to the plasticization of the PA layers in higher RH environments. As Figure 3 shows, the secant modulus of polyamide decreases in higher RH environments. Secant modulus and other property changes in hygroscopic polymers can be modeled if the equilibrium RH is known. The equilibrium RH of specific layers in a multilayer film can be estimated reasonably well from the known RH inside and outside the package and the moisture permeability of other layers (8). These property estimations are particularly helpful when designing multilayer structures for liquid products.
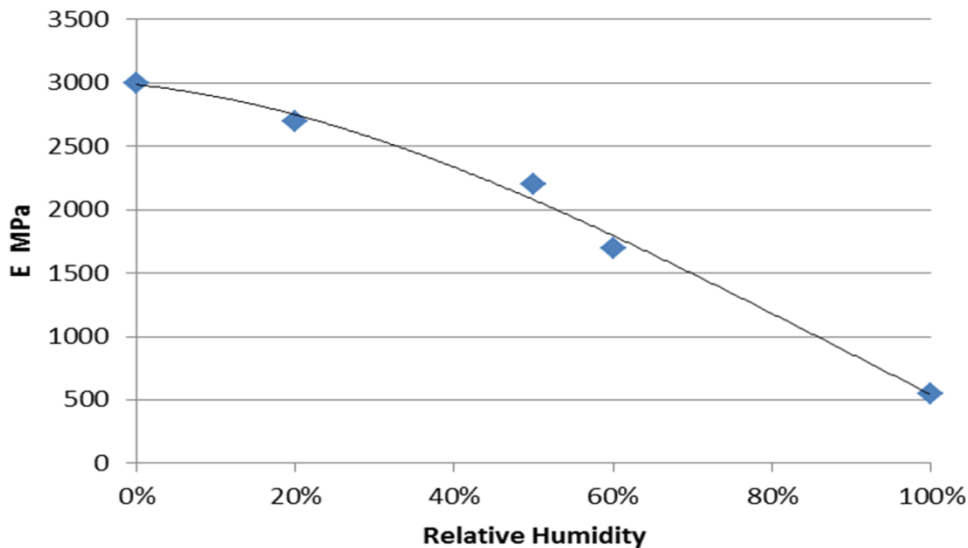
Figure 3: Secant modulus vs. ambient relative humidity for 1 mil monolayer films of polyamide copolymer

The RH effects in coextruded films containing PA copolymer were evaluated in three test films with the following structure:

PA / Tie / PE1 / Tie / PA / Tie / PE2 / PE3 / Sealant

The control film contained a 0.916 density LLDPE in both PE1 and PE2 layers. Test film 1 contained a low MVTR sHDPE in PE1 layer and LLDPE in PE2. Test film 2 contained the sHDPE in PE2 layer. All

test films were converted into water filled pouches with minimal headspace and tested for package integrity.

Figure 4 presents the predicted RH values for individual layers in the two test films in a package exposed 100% RH inside and 40% ambient RH outside. The model predicts that the equilibrium RH of the middle PA layer will be much higher if the sHDPE is in the exterior coex layers (88% RH) than in the interior layers (51%). In these cases, the sHDPE layer is expected to trap moisture in the PA core layer or prevent or moisture from permeating into the PA core layer.

Table 3 presents puncture, secant modulus, and oxygen permeability properties of the three film types that were used in water filled pouches. The test films for these evaluations were obtained from the front panels of water-filled pouches after the pouches were aged for 72 hours. The measured values for secant modulus and oxygen barrier generally corresponded well with model predictions.

The right column in table 3 shows off-line and aged drop impact resistance for water filled pouches. While off-line results were similar for all three film types, the drop impact resistance of aged samples showed differences. The drop height of the control pouch increased significantly with aging while the pouches containing sHDPE changed less with aging. In these pouches, the sHDPE layer may have had a stronger influence on the drop impact resistance than the core PA layer. It is also notable that the aged drop height of pouches made with test film 2 decreased slightly while pouches made with test film 1 increased. This result was unexpected since test film 2 was expected to have higher relative humidity in the PA core layer which would increase the PA layer's elasticity and impact properties.

Figure 4: Predicted relative humidity of specific layers in similar coex structures with HDPE

Test Film 1: HDPE in exterior coex layer

Test Film 2: HDPE in interior coex layer
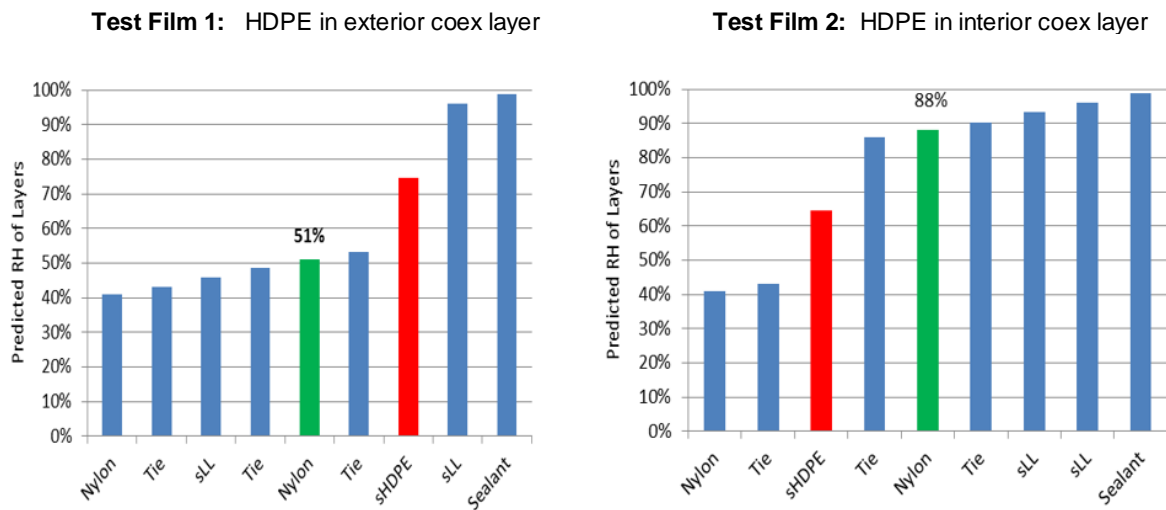
Table 3: Properties of Films used in Water Filled Pouches

Structure	Film Puncture (J/mm)	2% MD Secant Modulus (MPa)	Oxygen Permeability (cc/100in^2-day-atm)	Drop height failure – F50 (feet)	
				Off-line	Aged
Control (no HDPE) PA/tie/LLDPE//PA/tie/LLDPE/seal	57	450	4.2	9.4	18.3
Test Film 1 PA/tie/LLDPE/tie/**PA**/tie/**sHDPE**/seal	48	684	3.37	10.7	13.0
Test Film 2 PA/tie/**sHDPE**/tie/**PA**/tie/LLDPE/seal	62	634	3.62	10.0	9.2

CONCLUSIONS

Many multilayer film properties are difficult to predict or model since they are affected by material and layer interactions, environmental, processing and many other factors that can lead to prediction errors. However, the accuracy of basic models can be improved by continuously comparing model predictions to measured properties for specific structures, identifying the root cause of the difference and modifying the equations or algorithms to capture new discoveries. To do this, the models should be built in a platform that allows designers to easily incorporate new discoveries, relationships and materials.

Predictive models should not be used as a substitute for multilayer film trials, only as a general tool for identifying or screening materials, optimizing layer and blend ratios and predicting general trends.

ACKNOWLEDGEMENTS

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