FLEX BARRIER PROPERTY ENHANCEMENT IN FILM STRUCTURES USING MICROLAYER COEXTRUSION TECHNOLOGY

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Abstract

Microlayer coextrusion is a process in which two or more polymers are extruded and joined together in a feedblock or die to form a single structure with multiple layers. This paper describes a multilayer coextrusion process technology to maintain the gas barrier property of Ethylene Vinyl Alcohol (EVOH) barrier films after flexing.

Introduction

Coextrusion is a common method used for producing multilayer cast and blown films. Coextrusion is a process in which two or more polymers are extruded and joined together in a feedblock or die to form a single structure with multiple layers. This technique allows the processor to combine the desirable properties of multiple polymers into one structure with enhanced performance characteristics. The coextrusion process has been widely used to produce multilayer sheet, blown film, cast film, tubing, wire coating, and profiles [1-6].

Currently films containing metal foil dominate the barrier packaging market with over 15.4 billion dollars in global laminate film sales. Despite the dominance of the foil films which provide excellent unflexed barrier performance at a low price, alternative packaging solutions that maintain barrier performance after flexing, amenable to microwave operation, transparent enough to view the packaged contents inside, and offer sustainability and a lower carbon footprint are highly desirable. Currently, no clear polymer can offer the oxygen barrier performance of foil, in a low carbon footprint, competitive cost solution.

Ethylene Vinyl Alcohol (EVOH) comes the closest to matching the oxygen, clarity and cost parameters. However, flex barrier properties of EVOH barrier films are poor due to the brittle nature of EVOH. EVOH barrier packaging products with an improved flex barrier property may provide an alternative packaging solution in foil dominating liquid packaging markets.

Background

Attempts to maintain flex barrier properties until now have been focused on using metalized layer lamination, coating and/or inorganic particle addition in multilayer structures with seven or fewer layers [7-14]. Recently, G. Medlock and M. Dolgovskij studied EVOH flex crack resistance between conventional EVOH films vs. microlayer EVOH films [15]. Their study demonstrated that microlayer EVOH films yielded superior flex crack resistance compared to films with a single EVOH layer. In addition, they claimed that lower modulus polymers such as PE based ties compared to Nylon resist crack propagation from one EVOH microlayer to another. The number of layers was varied from 7 to 21 layers and the sample went though up to 1,000 Gelbo flexing cycles.

This study and G. Medlock and M. Dolgovskij' study using microlayer technology clearly have advantages over previous art by (i) improving recyclability due to the use of polymer-only systems (i.e., no inorganic/metallic particles), (ii) avoiding an extra step such as lamination, or coating, or chemical vapor deposition, (iii) maintaining transparency, and (iv) allowing microwaving. Furthermore, this study covers larger number of layers up to 35 layers with statistical analysis to confirm the barrier property enhancement with respect to the number of layers.

Experimental

Barrier and tie materials used in this study are listed in Table 1. The barrier resins of choice were EVAL L171 and H171 grades from Kuraray America Inc. The % mol ethylene content, Melt Flow Index, and density information are listed in Table 1. Tie materials were blends of Dow AMPLIFY (Trademark of The Dow Chemical Company) and AFFINITY resins to vary the density from 0.875 to 0.9 g/cc. The skin material was Dow Low Density Polyethylene (LDPE 503A) resin. This resin has a Melt Flow Index of 1.9 g/10 min (190^{o}C/2.16 kg). The core to skin ratio of the film structure was set to 20:80. The overall film thickness was approximately 127 micrometers (5 mils). The design of experiment (DOE) was created using 4 independent variables: number of layers, barrier resin type (% mol ethylene), tie material density, and EVOH/Tie ratio in the core. The detailed DOE is shown in Table 2.

The coextrusion line used in this study consists of three 38.1 mm (1.5 inch) diameter, 30:1 L/D or 24:1 L/D single screw extruders. Extruders A and B feed a three layer feedblock coupled with layer multipliers (see Figure 1). A 5 layer structure was created by operating all three extruders without a multiplier (3 core layers+2 skin layers). A four and a two channel multiplier were used to create 19 layer samples (17 core layers+2 skin layers). 17 core layers were calculated by counting double layers as one layer after multiplications. For example, initial 3 layers become 12 layers after flowing through a four channel multiplier. However, 3 internal mating layers during re-stacking process are A-A double layers (Figures 1 and 2). Therefore, actual flow structure has 9 A-B alternating layers. After this flow goes through a two channel multiplier, it has 17 alternating layers (9 x 2 – 1 double layer = 17 alternating layers). In a same way, two four channel layer multipliers were used to create 35 layer samples (33 core layers+2 skin layers). 33 core layers are calculated as follows: 3 X 4 = 12 layers – 3 double layers = 9 alternating layers; 9 X 4 = 36 layers – 3 double layers = 33 alternating core layers).

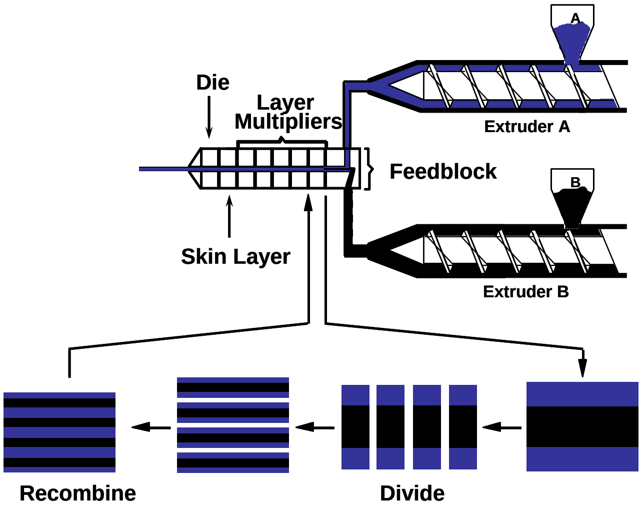


Figure 1. Coextrusion Line Set-up

Figure 2 shows a schematic of the four channel layer multiplier. This multiplier creates 9 alternating layers from 3 layers as described earlier.

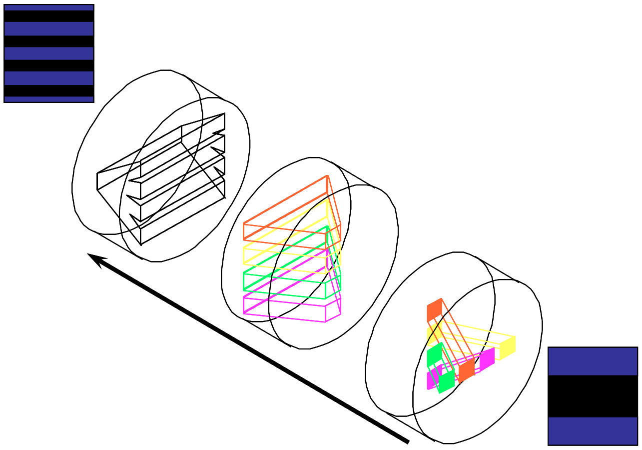


Figure 2. A schematic diagram of the 4 layer Multiplier

The multilayered structures are further sandwiched with two skin layers by another extruder before entering a 304.8 mm (12 inch) coat hanger style die with a 0.559 mm (0.022 inch) die lip gap.

The processing temperatures for all extruders, feedblock, multipliers, and die were maintained at 210^{o}C (410°F) except at the feeding zones of the extruders. The microlayer samples were made of 20% of a core structure containing the alternating microlayers, and 80% of a skin structure equally divided between each side of the core. The core material ratio was varied from 30 vol%/70 vol% to 70 vol%/30 vol% in the core (see Table 2). The overall flow rate was maintained at 27.2 kg/h (60 lb/h).

Film samples were tested for the following physical properties using the ASTM standards listed in the Table 3.

Results

Effect of Flex Cycles on Oxygen Barrier Property

Oxygen transmission rate (OTR) was measured at 23^{o}C and 85% relative humidity before and after flexing (400 Gelbo flex cycles) on the samples with fewer than 2 pin holes in the structure. The compositions and layer numbers of these films are shown in Table 4.

OTR measurements for the sample 17 with 5 layers before and after flexing were included to demonstrate the detrimental effect of flex cycles on the samples with a small number of layers (Table 4). After 400 flex cycles, the 5 layer sample failed the OTR test. The permeation value of 65 cc-mil/100in^2.day is the maximum measureable number by the Dow MOCON unit and is shown in parentheses for the reference.

The OTR measurements on the four higher number of layer samples (sample #: 5, 7, 9, & 11) demonstrate that the flex barrier property was maintained after 400 Gelbo flexes (Table 3). % OTR change before and after flexing with respect to the number of layers is shown in Figure 3. The samples 5 and 11 data were used for 19 and 35 layer cases, respectively, and the permeation value of 65 cc-mil/100in^2.day was used to calculate % OTR change for the 5 layer case. As depicted in Figure 3, the 19 and 35 layer samples maintained the flex barrier property after flexing but the 5 layer sample lost the barrier property. The OTR measurement data on the samples 5 (19 layers) and 11 (35 layers) before and after flex cycles are shown in Figures 4 and 5, respectively.

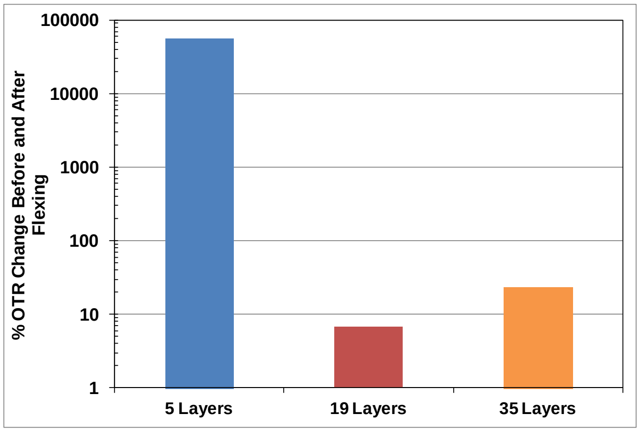


Figure 3. % OTR Change Before and After Flex

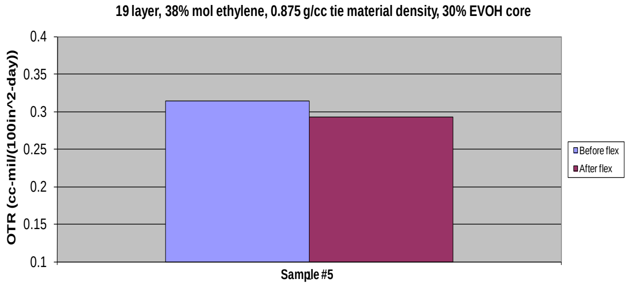


Figure 4. OTR Data of Sample 5 (19 layers) Before and After Flex Cycles: (a) Before and (b) After

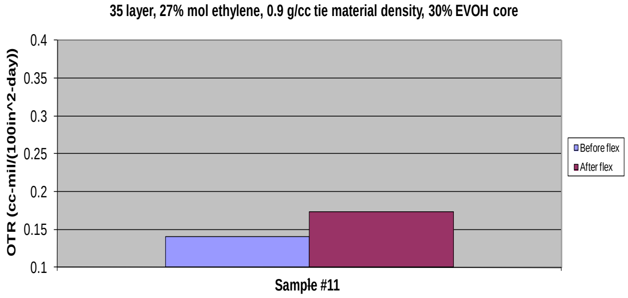


Figure 5. OTR Data of Sample 11 (35 layers) Before and After Flex Cycles: (a) Before and (b) After Flex

The AFM images before and after flex cycles, as shown in Figures 6 and 7, were taken to demonstrate that most of the EVOH (light layers) survived after flexing for both 19 and 35 layer samples.

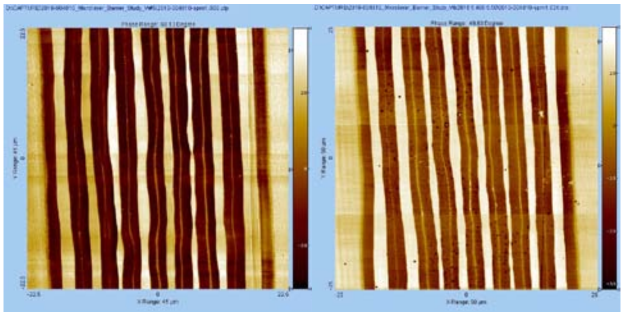

(a) (b)

Figure 6. AFM Images of Sample 5 (19 layers) Before and After Flex Cycles: (a) Before and (b) After

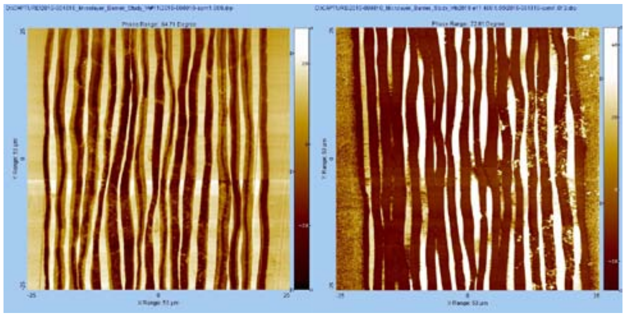

(a) (b)

Figure 7. AFM Images of Sample 11 (35 layers) Before and After Flex Cycles: (a) Before and (b) After Flex

Effect of Layer Number on Pin Holes

Flex durability of our samples has been tested according to ASTM F392-93. The flexing action consists of a twisting motion followed by a horizontal motion, thus, repeatedly twisting and crushing the film. After 400 cycles of Gelbo flexes, physical holes through the structure were measured by a color dye penetration method and the average numbers of pin holes with respect to the number of layers are shown in Figure 8.

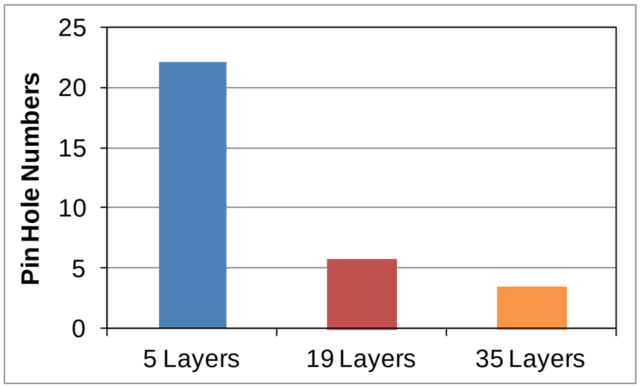
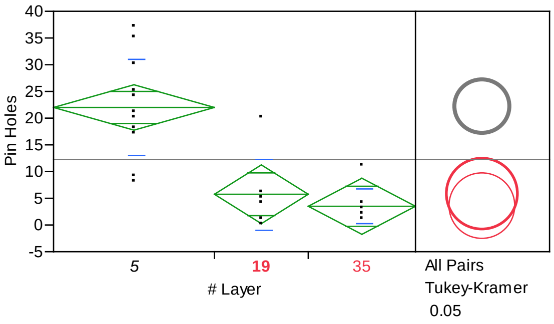


Figure 8. Pin Hole Numbers with respect to Number of Layers

The data was analyzed with a commercially available statistical software (JMP, SAS institute Inc.). Figure 9 clearly demonstrates that the pin hole numbers statistically decrease with the number of layers (a Tukey-Kramer test with confidence = 95%). This is possibly due to: (i) better flexibility of a brittle EVOH barrier resin in thinner layers [16], and (ii) longer tortuous path for the dye to travel through even if some layers were broken in 19 and 35 layer samples [17, 18].

The effect of individual layer thickness of Polyethylene terephthalate (PET) and Polycarbonate (PC) microlayer films on large strain deformation mechanism was studied earlier [16]. As the thickness of individual polymer layers decreases, a transition in deformation mechanism from two-component behavior to one-component-like behavior was observed. Therefore, it is possible to improve the film toughness by decreasing EVOH layer thickness in the EVOH/PE based tie material microlayer system.

A Cussler-Fredrickson model for permeation of small molecules through polymer films filled with impervious particles or crystalline lamellae describes that high content of impermeable particles or crystalline lamellae, high aspect ratio, and high angle of particles/lamellae to the permeation direction (i.e., more perpendicular to the permeation direction) gives less overall permeation of gas molecules. For the EVOH microlayer case, EVOH can be viewed as particles/crystals in the model to decrease the overall permeation due to longer tortuous path [17, 18].



Level		Mean
5	A	22.083333
19	B	5.714286
35	B	3.500000

Figure 9. Effect of Layer Number on Pin Hole Numbers

Effect of Barrier Resin Type and Content

The extensive statistical analysis was performed to see the effect of barrier resin type (% mol ethylene) and content on barrier and mechanical properties. The expected trends were observed; better oxygen barrier property was observed with the samples containing the 27% mol ethylene content barrier resin. Increasing the barrier resin content improved better the barrier property. Machine and cross direction mechanical properties such as tensile strength and yield stress increased with higher EVOH contents in microlayer samples while ultimate elongation decreased. The samples with the 27% mol ethylene content barrier resin behaved stiffer compared to the ones with 38% mol content.

Conclusions

This study describes a process technology to maintain or improve gas barrier property of EVOH barrier films after flexing. EVOH and MA-g-PE multi- and microlayer samples with 5, 19, and 35 layers were produced in a coextrusion line. Flexing was performed using a Gelbo flexing tester (400 flexes). After flexing, pin hole tests were performed on the film and only those with fewer than 2 pin holes were re-tested for OTR measurements. The clear trend of pin hole numbers decreasing after 400 Gelbo flexes was observed as the number of layers increased. The OTR measurements on these films demonstrated that thin EVOH barrier resin can improve flex crack resistance of the film. This proves that for a given amount of barrier resin, the flex barrier property can be increased dramatically by microlayering. This flex barrier improvement in microlayers is possibly due to: (i) better flexibility of a brittle barrier resin in thinner layers, and (ii) longer tortuous path for gas molecules to travel through the structure even if there are some broken layers. In addition, mechanical properties of these microlayer films were measured and evaluated statistically to understand the general trend.

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Table 1. Oxygen Barrier, Tie, and Skin Resin Properties

Name	% mol ethylene	MI (190°C/2.16 kg)	Density (g/cc)
Barrier Resins			
EVOH L	27	4 (210 °C)	1.2
EVOH H	38	1.7	1.17
Tie Resins			
Maleic Anhydride Grafted PE	-	1.3	0.875
Polyolefin Plastomer	-	3	0.902
Polyolefin Elastomer	-	3	0.875
Skin Resin			
LDPE	-	1.9	0.923

Table 2. DOE Table

Experiment	Number of Layers	Barrier Resin Type (% mol ethylene)	Tie Material Density (g/cc)	EVOH:Tie Core Ratio
1	19	27	0.875	30:70
2	19	27	0.875	70:30
3	19	27	0.9	30:70
4	19	27	0.9	70:30
5	19	38	0.875	30:70
6	19	38	0.875	70:30
7	19	38	0.9	30:70
8	19	38	0.9	70:30
9	35	27	0.875	30:70
10	35	27	0.875	70:30
11	35	27	0.9	30:70
12	35	27	0.9	70:30
13	35	38	0.875	30:70
14	35	38	0.875	70:30
15	35	38	0.9	30:70
16	35	38	0.9	70:30
17	5	27	0.875	30:70
18	5	27	0.875	50:50
19	5	27	0.875	70:30
20	5	27	0.9	30:70
21	5	27	0.875	50:50
22	5	27	0.9	70:30
23	5	38	0.875	30:70
24	5	38	0.9	50:50
25	5	38	0.875	70:30
26	5	38	0.9	30:70
27	5	38	0.9	50:50
28	5	38	0.9	70:30

Table 3. Film Property Tests and Methods

Film Property	***Test Method***
Flex Durability	ASTM F392-93
Oxygen Gas Transmission Rate	ASTM D3985-05
Tensile Properties	ASTM D882
Dart Impact (A)	ASTM D1709

Table 4. OTR Measurements Before and After 400 Gelbo Flexes

Sample #	# Layer	Barrier Resin Type (% mol ethylene)	Tie Material Density (g/cc)	OTR before Flex (cc-mil/100in^2.day)	OTR after Flex (cc-mil/100in^2.day)
5	19	38	0.875	0.31	0.29
7	19	38	0.9	0.28	0.26
9	35	27	0.875	0.59	0.65
11	35	27	0.9	0.14	0.17
17	5	27	0.875	0.12	Failed (65*)

*65 cc-mil/100in^2.day is the maximum permeation value by the Dow MOCON unit