

Grease Resistant Multilayer Polyethylene Films

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ABSTRACT

Barrier properties are important performance requirements for many packaging applications. Sophisticated and automated techniques exist for testing oxygen and moisture transmission rates, however, only a few elementary methods exist for determining a package's resistance to grease permeation. In addition, most grease permeation methods only provide a qualitative measure of grease penetration. As interest grows for incorporating recyclable plastic film structures into packaging for high fat content products, a simple technique is required for determining a film's grease barrier properties and for ranking of different flexible film structures. Hence, a semi-quantitative method to measure grease/oil permeation through multi-layer films has been developed, and the results of several multilayer film structures are presented to delineate the efficacy of different film resins in improving the grease barrier properties of polyethylene multilayer films. The present study shows that it is now possible to develop cost effective and recyclable polyethylene film packaging structures with good grease barrier performance by utilizing certain single site catalyzed bimodal polyethylene (PE) resin architectures.

INTRODUCTION

Grease containing materials such as natural and prepared foods for human consumption, pet foods, liquids, gels and pastes have been packaged in various types of packaging materials in the past including metal cans, glass bottles, wax coated paper, rigid plastic containers and the like. More recently, the trend has been to package these materials in flexible packaging utilizing multilayer films to reduce packaging material to product ratio. This trend is primarily driven by environmental factors including less energy consumption during manufacturing and transportation, and reduction in packaging materials while providing end user (consumer) convenience with flexible films. Various polymeric materials have been used to develop flexible films and multilayer film structures with each layer providing specific functionality. For grease resistance, polymers such as EVOH, nylon, PET, ionomers, EVA, EEA, EAA, PVDC and the like are often considered for one or more layers of the structure and used depending on the application and desired cost of a structure. Although, some of these polymers and their combinations are useful in providing a grease barrier in packaging films, they are often expensive, require a tie layer, and/or the resulting film structures are difficult to recycle after their intended use. Unfortunately, many of the currently used functional barrier polymers containing multilayer films cannot be recycled in existing waste streams and must go to landfill. With growing environmental concerns around the globe and consumer preference to increase recycling of packaging materials, there is a need for grease resistant all polyethylene packaging films. Furthermore, from a manufacturing perspective, there is a need to reduce costs of multilayer film structures by replacing expensive polymers such as EVOH, nylon, PET, ionomers, EVA, EAA and the like with cost effective and/or cheaper polyethylene materials. Until now, all polyethylene films have not been very successful in providing grease resistance for the flexible packaging industry.

Since NOVA Chemicals manufactures a diverse suite of PE resins for the film packaging industry, a study was conducted to look at the grease resistance efficacy of some of the PE resins at their *Centre for Performance Applications* in Calgary, Alberta. In order to do these evaluations, we first looked at any published literature on the methods for measuring grease resistance of flexible films. This research showed that only a few rudimentary laboratory methods exist for determining a package's resistance to grease permeation. In addition, most grease permeation methods only provide a qualitative measure of grease penetration. Before the performance of various multilayer film structures could be assessed and ranked, it was necessary to develop a quantitative method that can discern between different film structures for their efficacy under different conditions (e.g. film structure arrangement, film thickness and service temperature, etc.). The other task was to develop several multilayer film structures utilizing non-PE and PE resins with different molecular architectures manufactured with different catalyst and process technologies, and test them for grease barrier performance. Therefore, the objectives of this work were twofold: (1) develop a semi-quantitative method to measure grease/oil permeation through multilayer films; and (2) develop several multilayer film structures to evaluate their relative efficacy for grease barrier. The goal was to determine if it is at all possible to develop all PE grease resistant film structures that are easily recyclable and cost effective for flexible packaging.

METHOD OF MEASURING GREASE RESISTANCE

A literature search for measuring “Grease Barrier in Food Packaging” revealed that currently there are only a few methods to evaluate grease penetration through flexible plastic films [1 - 4]. A summary for each of these test methods is provided in **Table 1**. All of the published tests involved depositing grease (fat, oil, or fatty acids) on one side of a film and examining under controlled conditions (generally at elevated temperature) for a certain period of time until grease is detected on the opposite side of the film. Either the film was tested by extracting the oil penetrated into the film by gravimetric analysis or tensile strength changes in the film, or the opposite side of the film was tested for surface properties (for changes in coefficient of friction, surface energy, or visual analysis such as staining).

Table 1: Published Methods for Measuring Grease Barrier Resistance

Method	ASTM F119-82 [1]	Cheney and Breese [2]	TAPPI T507 cm-09 [3]	Wyser <i>et al.</i> [4]
Title	Standard Method for Rate of Grease Penetration of Flexible Barrier Materials (Rapid method)	Improved Technique for Monitoring the Grease Penetration Through Substrates	Grease Resistance of Flexible Packaging Materials	Novel Method for Testing the Grease Resistance of Plastic-based Dry Pet Food Packaging
Brief description of test	A barrier material is placed between a grease soaked swatch of cloth and frosted glass. A weight is placed on the cloth. The frosted glass is monitored for signs of grease wetting by picking up assembly.	Similar to ASTM standard except monitoring is done with time-elapsd photography and without a weight. Visual aid is used to observe wetting (dots).	For grease-proof, glassine, vegetable parchment or other grease resistant papers and plastic coatings. The tested film separates an oil saturated blotter and a clean blotter. Measure the area of the oil stains on the “clean” blotter after 4 h, at 60°C.	A weight is placed on the fat source which is on the tested film that is placed on a TLC plate. After a set period of time, the TLC plate is inspected under UV light to determine amount of grease penetration.
Measurable	Time to grease penetration	Time to grease penetration	Area of grease stains: Visual observation	Area of grease stain: By UV
Limitations	<ul style="list-style-type: none"> Requires continuous monitoring Significant handling during experiments Uses elevated temperatures (up to 60°C) Large error possible 	<ul style="list-style-type: none"> Difficult to see failure Large error possible 	<ul style="list-style-type: none"> Short time period – may not be sufficient for PE films (developed for paper) Detection of stain potentially difficult Significant error in quantifying 	<ul style="list-style-type: none"> Based on a ranking determined by operator (is/ stained, slightly stained, not stained) Significant error in quantifying
Benefits	Simple experiment with minimal equipment	Little interference with experiment during run so that the expected error is less than that for the ASTM method. Photographic record.	Potential for quantification (stain area)	Simple and clear detection system. Potential for quantification (stain area)

In the method developed by Wyser *et al* [4, 5], the visual staining was measured qualitatively using fluorescent TLC plates which seemed to be the clearest detection type. In this work, we developed this method further so that quantitative ranking of different film structures can be made. Some modifications to the method were made to evaluate the efficacy of different structures and resin types in those structures. Wyser *et al.* also found that chicken fat mixed with oleic acid was the most aggressive grease mixture and resulted in relatively fast grease penetration times (over the course of days at elevated temperatures). In this work, we used lard which is readily available in supermarkets, does not require refrigeration and naturally contains a high level of oleic acid. Some work was also explored with olive oil which was promising, but will not be reported here for the sake of brevity. We also decided to fix the testing time period (at 48 h) instead of periodically checking for grease breakthrough to avoid excessive handling of the test equipment and the risk of spilling grease onto the TLC plate (see **Figure 1** below). Initial tests showed that 48 hours at elevated temperatures was sufficient time to differentiate films with poor grease resistance. In this work, we used computer software to calculate the area stained by the grease instead of visual ranking of the amount of staining. This provided quantification of the degree of grease penetration through a film structure at different conditions.

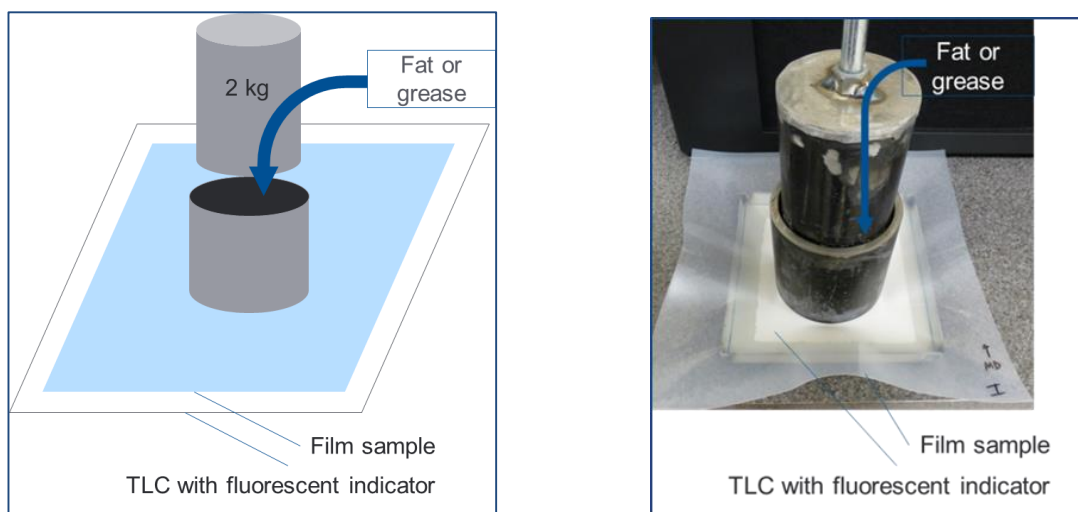


Figure 1: Diagram and photograph of experimental apparatus

In this method, a 20 cm by 20 cm piece of film is placed over a 10 cm by 10 cm thin layer chromatography (TLC) plate in which the silica contains a fluorescent indicator (POLYGRAM® SIL G/UV254 available from Macherey-Nagel GmbH & Co. KG). The TLC plate is contained in a stainless steel tray. A pre-heated stainless steel ring (with an inner diameter of 6 cm) is placed on the film and 2 g of lard is placed inside the ring. A pre-heated 2 kg piston (with an outer diameter of just under 6 cm) is placed inside the ring to apply pressure of approximately 7 kPa onto the film. The apparatus is then placed inside an oven (HP 5890A or Yamamoto CVS602C) at 40°, 50°, 60° or 70°C for 48 hours. The apparatus (**Figure 1**) is removed from the oven and the weight and film are separated from the TLC plate. The plate is photographed (Panasonic LUMIX® DMC-ZS15 camera) in a viewing box with ultraviolet (254 nm) light to determine the relative amount of grease breakthrough for the test film. The grease absorbs light at 254 nanometers and will thus appear as dark regions on the TLC plate. The photograph is uploaded to image processing software (Image J) and the colour image is converted to grey scale. The dark portion of the image from within the ring corresponds to the fraction of grease breakthrough.

A totally grease resistant film would not show any dark area on the TLC plate (and would be reported as having a grease breakthrough value of 0) and a film with no grease resistance would result in a completely stained TLC plate (and would be reported as having a grease breakthrough value of 100). Typical values were between 0 and 60.

Over the course of developing the test method, many sets of films were tested: 9 layer films containing both recyclable and non-recyclable resins; 3 layer films with all PE materials (recyclable); and 9 layer films containing all PE materials (recyclable). The work was further validated using some commercial pet food retail packages available in supermarkets. Each set of films will be discussed individually.

RESULTS AND DISCUSSION

All the materials used in the multilayer films are listed in **Table 2**.

Table 2: Basic Resin Properties

Resin Type	Resin Code	Resin Name	Melt Index, dg/min.	Density, g/cc
Single site octene LLDPE	sLLDPE	SURPASS® FPs016-C	0.65	0.916
Z-N octene LLDPE	o-LLD	SCLAIR® FP120-D	1.0	0.920
Single site bimodal HDPE	sHDPE	SURPASS® HPs167-AB	1.20	0.966
Z-N HDPE	HDPE-1	SCLAIR® 19C	0.95	0.958
Maleic anhydride modified LLDPE	Tie Resin	BYNEL® 41E710	N/A	N/A
Ethylene vinyl alcohol copolymer	EVOH	EVAL® H171B	1.7	1.17
Ethylene acrylic acid copolymer	EAA	PRIMACOR® 1410	1.0	0.938
Zn ionomer	Ionomer	SURLYN® 1650	1.8	0.940
Z-N HDPE	HDPE-2	SCLAIR® 19G	1.20	0.960
Z-N octene VLDPE	o-VLD	SCLAIR® FP112-A	0.90	0.912

SURPASS® FPs016-C and SURPASS® HPs167-AB are single site catalyzed (SSC) sLLDPE and sHDPE resins, respectively, made in NOVA Chemicals' dual reactor Advanced SCLAIRTECH™ solution process. With the single site catalysts, the overall resin architecture essentially consists of two narrow, compositionally uniform molecular weight distributions. Molecular weights for the two reactor components can be controlled virtually independently. Component molecular weight distributions can be moved up or down and the relative proportions of polymer made in each of the two reactors can be adjusted. Details of the proprietary dual reactor solution process for polyethylene manufacturing are provided elsewhere [6, 7]. FPs016-C was used for high toughness, high melt strength and high sealability in the multilayer film structures, whereas, HPs167-AB provides high stiffness and exceptional moisture barrier performance. SCLAIR® FP120-D and SCLAIR® FP112-A are Zeigler-Natta (ZN) catalyzed LLDPE and VLDPE octene copolymers made in NOVA Chemicals' Advanced SCLAIRTECH™ solution process. SCLAIR® 19C and SCLAIR® 19G are ZN catalyzed high density polyethylene resins commercially available from NOVA Chemicals Corporation. BYNEL® 41E710 is a maleic anhydride modified LLDPE that is a commercially available resin from DuPont® and is used in tie layers. EVAL® H171B, an EVOH, is a commercially available resin from Kuraray Company. PRIMACOR® 1410, an EAA, is a commercially available resin from The Dow Chemical Company. SURLYN® 1650 is a Zn ionomer that is a commercially available resin from DuPont®.

9-layer Films with Variety of Resins

Several 9-layer coextruded blown films were made on a blown film line manufactured by Brampton Engineering, Brampton, Ontario, Canada. The compositions of the films are shown in **Table 3**. For clarity, the heading “*layer ratio*” refers to the weight % of each layer and the “*skin*” layers are shown as the first and last columns. The 11 films in this group have the *same skin layers* (layer A is made up of sLLDPE and layer I is made up of o-LLD). The core layers (D, middle and F) are made up of either EVOH and the necessary tie layers or EAA (an ethylene acrylic acid co-polymer), or ionomer or o-LLD (a ZN octene LLDPE resin). The intermediate layers (B, C, G, and H) were designed to be the same for each film. They were made up of either o-LLD, sHDPE, a blend of sHDPE with 20% o-LLD, or HDPE-1. The films were named such that the first number represents the number of layers, s indicates that layer A is made of sLLDPE resin, and the resins shown are the core layer followed by the intermediate layer. The grease resistance of these films is reported in **Table 4** and some results are charted in **Figure 2**. The photographs from which the grease breakthrough values are eventually calculated are shown in **Table 5**.

EVOH is universally considered a good grease barrier, so little to no grease penetration for films comprised of EVOH was expected. Films containing EVOH represent typical, non-recyclable, grease-resistant barrier films. The two films with EVOH (**9Ls.EVOH/o-LLD** and **9Ls.EVOH/sHDPE**) indeed showed low grease breakthrough values (1 and 4 %, respectively) despite the relatively high oven temperature at 70°C. Surprisingly, a few films without EVOH showed similarly good grease resistance performance: **9Ls.EAA/sHDPE** and **9Ls.EAA/sHDPE blend**. This was the first evidence collected that showed that the single site catalyzed bimodal sHDPE behaves as a good grease barrier unlike other conventional HDPEs. The film **9Ls.EAA/HDPE-1** (with the ZN catalyzed HDPE) has much higher grease breakthrough value at 70°C than the similar film with sHDPE in the intermediate layers. Without the presence of an HDPE in the film structure, the amount of grease penetration is quite high; see film **9Ls.o-LLD/o-LLD** that, even at lower oven temperatures

(50°C), has comparatively large grease breakthrough values (greater than 10%) as shown in **Table 4** and **Figure 2**. Films **9Ls.EAA/sHDPE** and **9Ls.EAA/sHDPE blend** have equally good grease resistance and may be recyclable in typical consumer waste streams.

Table 3: Composition of 9-Layer Films with Variety of Resins

Film #	Film/Layer Names	A	B	C	D	Middle	F	G	H	I
	Layer ratio (weight %)	15	12	12	8	6	8	12	12	15
1	9Ls.EVOH/ o-LLD	sLLDPE	o-LLD	o-LLD	80% o-LLD + Tie Resin	EVOH	80% o-LLD + Tie Resin	o-LLD	o-LLD	o-LLD
2	9Ls.EVOH/sHDPE	sLLDPE	sHDPE	sHDPE	80% o-LLD + Tie Resin	EVOH	80% o-LLD + Tie Resin	sHDPE	sHDPE	o-LLD
	Layer ratio (weight %)	15	10	10	11	11	11	10	11	11
3	9Ls.EAA/sHDPE	sLLDPE	sHDPE	sHDPE	EAA	EAA	EAA	sHDPE	sHDPE	o-LLD
4	9Ls.Ionomer/sHDPE	sLLDPE	sHDPE	sHDPE	Ionomer	Ionomer	Ionomer	sHDPE	sHDPE	o-LLD
5	9Ls.EAA/sHDPE blend	sLLDPE	sHDPE + 20% o-LLD	sHDPE + 20% o-LLD	EAA	EAA	EAA	sHDPE + 20% o-LLD	sHDPE + 20% o-LLD	o-LLD
6	9Ls.Ionomer /sHDPE blend	sLLDPE	sHDPE + 20% o-LLD	sHDPE + 20% o-LLD	Ionomer	Ionomer	Ionomer	sHDPE + 20% o-LLD	sHDPE + 20% o-LLD	o-LLD
7	9Ls.EAA/ HDPE-1	sLLDPE	HDPE-1	HDPE-1	EAA	EAA	EAA	HDPE-1	HDPE-1	o-LLD
8	9Ls.Ionomer /HDPE-1	sLLDPE	HDPE-1	HDPE-1	Ionomer	Ionomer	Ionomer	HDPE-1	HDPE-1	o-LLD
9	9Ls.EAA / o-LLD	sLLDPE	o-LLD	o-LLD	EAA	EAA	EAA	o-LLD	o-LLD	o-LLD
10	9Ls.Ionomer / o-LLD	sLLDPE	o-LLD	o-LLD	Ionomer	Ionomer	Ionomer	o-LLD	o-LLD	o-LLD
11	9Ls. o-LLD/o-LLD	sLLDPE	o-LLD	o-LLD	o-LLD	o-LLD	o-LLD	o-LLD	o-LLD	o-LLD

Table 4: Grease Breakthrough Test Results

Grease Breakthrough Values %					
Film Number	Film Names / Oven Temperature (°C):	70	60	50	40
1	9Ls.EVOH/o-LLD	1			
2	9Ls.EVOH/sHDPE	4			
3	9Ls.EAA /sHDPE	4	1	0	0
4	9Ls.Ionomer /sHDPE	16			
5	9Ls.EAA /sHDPE blend	5			
6	9Ls.Ionomer /sHDPE blend	12			
7	9Ls.EAA /HDPE-1	25	0	0	0
8	9Ls.Ionomer /HDPE-1	26			
9	9Ls.EAA /o-LLD	44			
10	9Ls.Ionomer / o-LLD	60			
11	9Ls. o-LLD/o-LLD	45	20	12	0

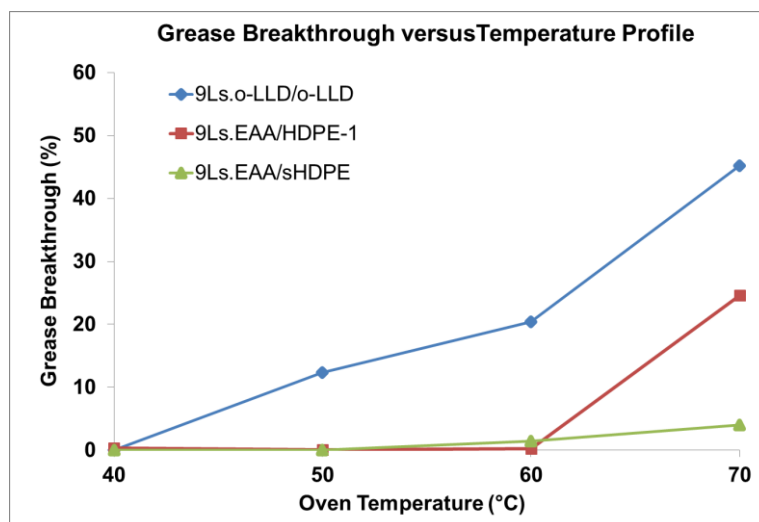

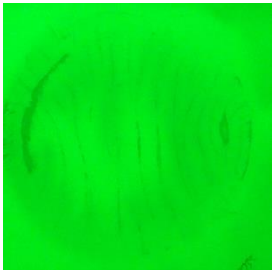
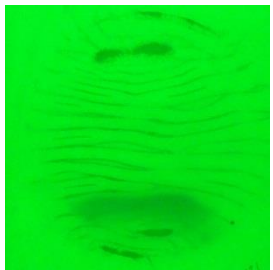
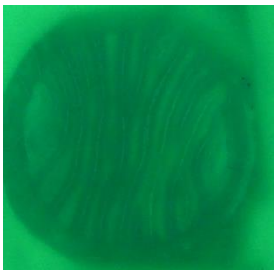


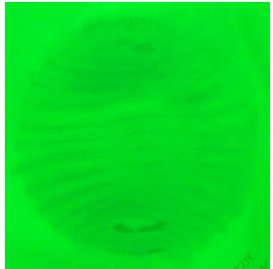
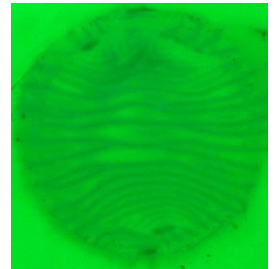

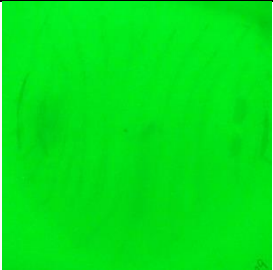
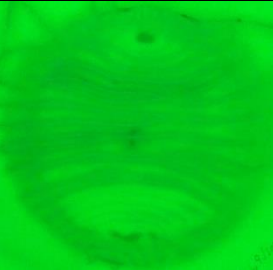


Figure 2: Temperature profiles of selected 9-layer films with SSC resin in Layer A

Table 5: Photographs of TLC plates under UV light after 70°C test is completed.

9Ls.EVOH/o-LLD	9Ls.Ionomer / sHDPE	9Ls.EAA / HDPE-1	9Ls.Ionomer /o-LLD
			
9Ls.EVOH/sHDPE	9Ls. EAA /sHDPE blend	9Ls.Ionomer / HDPE-1	9Ls.o-LLD/o-LLD
			
9Ls.EAA /sHDPE	9Ls.Ionomer /sHDPE blend	9Ls.EAA /o-LLD	
			

3-Layer Films with All PE Resins

All PE three layer co-extruded films (having an A/B/C layer structure) were prepared on a blown film line manufactured by Brampton Engineering at the NOVA Chemicals' "Centre for Performance Applications" using the following conditions: 2.5:1 Blow Up Ratio (BUR), 102 mm (4 inch) die, 0.89 mm (35 mil) annular die gap and 45.4 kg/h (100 lbs/h) output rate. The straight feed extruder screws had 38.1 mm (1.5 inch) diameter and a length/diameter (L/D) ratio of 24/1. Typical extrusion temperatures on this line are 177 to 238 °C. Screw speed is in the range of 35 to 50 revolutions per minute (RPM). The blown film bubble is air cooled. The total thickness of the films was 89 microns (3.5 mils). Each skin layer was made up of 25% of the total film thickness. The core layer was made up of the remaining 50% of the film thickness. The polymers used in this evaluation are shown in **Table 6**.

These films were prepared to verify the ability of sHDPE to act as a good grease barrier in 3 layer films as well. The three co-extruded blown films were prepared with o-LLD in the skins. The films differed only in the content of the core layer. Commercial single site catalyzed sHDPE was used in the core of film **3L.sHDPE**. Films **3L.HDPE-2** and **3L.o-LLD** contained cores of HDPE-2 resin and o-LLD resin, respectively.

Results of the grease barrier testing for these films at all temperatures are provided in **Table 7** and in **Figure 3**. The film containing single site catalyzed sHDPE in the core layer, **3L.sHDPE**, achieved the best grease barrier with low breakthrough values even at the higher temperatures. As previously seen, films containing only LLDPE (e.g. **3L. o-LLD**) have very poor grease barrier performance with high breakthrough values (greater than 15 % at 50°C).

Table 6: Composition of 3-Layer Films

Film/Layer Names	A (25%)	B (50%)	C (25%)
3L.sHDPE	o-LLD	sHDPE	o-LLD
3L.HDPE-2	o-LLD	HDPE-2	o-LLD
3L. o-LLD	o-LLD	o-LLD	o-LLD

Table 7: Grease Breakthrough Test Results for 3-Layer Films

Oven temperature (°C):	Grease Breakthrough Values %			
	70	60	50	40
3L.sHDPE	9	1	1	2
3L.HDPE-2	39	16	3	0
3L.o-LLD	50	24	16	2

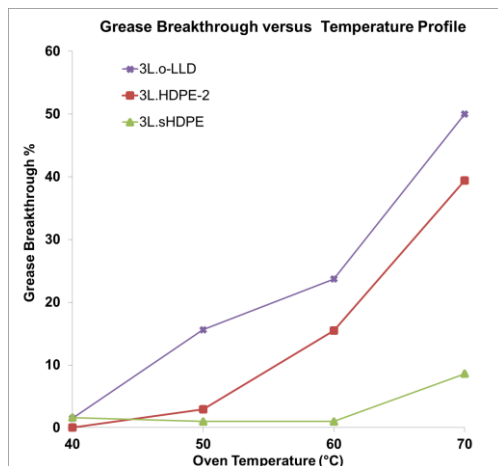


Figure 3: Grease Breakthrough profiles of 3-layer films (48 hours)

The physical properties of these 3- layer all PE recyclable films are shown in **Table 8**. It is seen from this table that the film structure comprising of the single site catalyzed sHDPE resin also has significantly higher film stiffness in addition to the great grease barrier properties. High film stiffness is a pre-requisite in many film applications such as “Stand- up- pouches” (SUPs) that also require excellent moisture and grease barrier properties. It should be noted that the 3-layer film structures shown here are for the illustrative purposes only, and are not optimized to achieve certain package requirements.

Table 8: Physicals Properties for 3-Layer Films

Sample Details	3L.sHDPE	3L.HDPE-2	3L.o-LLD
1% Sec Modulus - MD (MPa)	790	560	208
1% Sec Modulus - TD (MPa)	938	714	222
2% Sec Modulus - MD (MPa)	585	437	171
2% Sec Modulus - TD (MPa)	695	545	181
Tensile Break Strength - MD (MPa)	40.2	38.4	41
Tensile Break Strength - TD (MPa)	38.3	33.7	44.6
Elongation at Break - MD (%)	923	939	888
Elongation at Break - TD (%)	929	895	956
Tensile Yield Strength - MD (MPa)	21.6	18.9	10.3
Tensile Yield Strength - TD (MPa)	23.8	20.9	10.6
Tensile Elongation at Yield - MD (%)	10	12	16
Tensile Elongation at Yield - TD (%)	8	9	17
Dart Impact (g)	172	354	1040
Elmendorf Tear - MD (g)	207	252	1698
Elmendorf Tear - TD (g)	455	630	2090

9-Layer Films with All PE Resins

Encouraged by the results achieved so far, some new 9-layer coextruded blown films with “All PE resins” were made on a co-extrusion line (manufactured by Brampton Engineering) similarly to the aforementioned 9-layer group of films in Table 3. The films in this group have the same skin layers (layer A is made up of o-LLD and layer I is made up of o-VLD which represents the sealant layer). The compositions of these films are shown in **Table 9**. These films were designed to be used in some food packaging or heavy duty sack (HDS) applications without lamination to other films. Primarily, we tested the capability of the films for grease resistance at a thickness of 152 microns (6 mils), but other film properties were also tested.

Table 9: Composition of 9-layer Films with All PE Resins

Film	A	B	C	D	Middle	F	G	H	I
Layer ratio	15	12	12	8	6	8	12	12	15
9L.EVOH/ o-LLD	o-LLD	o-LLD	o-LLD	o-LLD + 20% tie	EVOH	o-LLD + 20% tie	o-LLD	o-LLD	o-VLD
Layer ratio	11	11	10	11	11	11	10	10	15
9L.sHDPE / sLLDPE / sHDPE	o-LLD	sHDPE	sLLDPE	sLLDPE	sHDPE	sLLDPE	sLLDPE	sHDPE	o-VLD
9L. sLLDPE / sHDPE	o-LLD	sHDPE	sLLDPE	sLLDPE	sLLDPE	sLLDPE	sLLDPE	sHDPE	o-VLD
9L. o-LLD /sHDPE	o-LLD	sHDPE	o-LLD	o-LLD	o-LLD	o-LLD	o-LLD	sHDPE	o-VLD
9L.HDPE-1/ sLLDPE / HDPE-1	o-LLD	HDPE-1	sLLDPE	sLLDPE	HDPE-1	sLLDPE	sLLDPE	HDPE-1	o-VLD

For comparison of the “All PE Resins” 9-layer film structures in terms of their grease barrier performance and physical properties, film **9L.EVOH/o-LLD** was used due to the recognized grease barrier properties of EVOH. Film **9L.sHDPE/sLLDPE /sHDPE** was designed for use in HDS and food packaging applications with overall good toughness from sLLDPE, and grease (and moisture) barrier properties from sHDPE, respectively. The barrier and stiffness were optimized by placing the sHDPE in separated layers (B, Middle and H) to take advantage of the I-beam effect for increased bending stiffness [8]. Film **9L.sLLDPE /sHDPE** contains one less layer of sHDPE than **9L.sHDPE /sLLDPE/sHDPE** in order to determine how little sHDPE is required for good grease barrier performance. A slightly higher density version of the structure is film **9L.o-LLD /sHDPE** in which sLLDPE is replaced by o-LLD in layers C and G. Film **9L.HDPE-1/ sLLDPE /HDPE-1** was made to validate the inferior grease barrier performance of HDPE-1 versus sHDPE (comparing against a similar film structure **9L.sHDPE /sLLDPE /sHDPE**). The grease resistance of these 9-layer “All PE Resins” film structures is depicted in **Figure 4**.

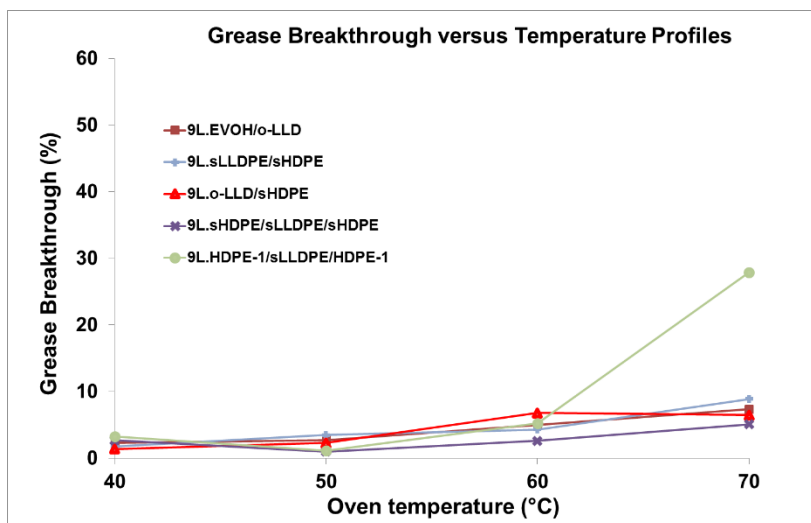


Figure 4: Temperature profile of 9-layer films with All PE Resins (48 hours)

All of the 9-layer films (in **Table 9**) containing single site catalyzed bimodal sHDPE performed very well for grease barrier throughout the entire temperature profile range with grease breakthrough values of less than 10%. Particularly good performer was **9L.sHDPE / sLLDPE /sHDPE** which showed the best grease barrier at all temperatures tested. The grease barrier performance of these films was similar to **9L.EVOH/o-LLD** which is not an easily recyclable film structure. Film **9L.HDPE-1/ sLLDPE /HDPE-1** had lower grease barrier at higher temperatures (e.g. 70°C). Film **9L.sLLDPE /sHDPE** which only contains 21 weight % of sHDPE also achieved good grease resistance performance compared to the film **9L.HDPE-1/ sLLDPE /HDPE-1** that has 50% higher amount of HDPE resin in the film than **9L.sLLDPE /sHDPE**. From these data, it appears that a sHDPE layer with thickness > 1.2 mils may provide good grease barrier performance in the “All PE multilayer film structures” that can be recycled.

The film physical properties of the multilayer compositions (in **Table 9**) are shown in **Table 10**. It is interesting to see from this Table that the 9-layer “All PE Film Structures” shown here also have high film stiffness, tensile break strengths, and film toughness (Dart Impact, Puncture Resistance and Tear Strengths) that are generally required in many of the food packaging, SUPs and HDS applications. Again, it should be noted that the 9-layer film structures shown here are for the illustrative purposes only, and have not been optimized to achieve any particular package requirements. Package designers may find many other combinations depending on the need and application.

Pet Food Packaging Films

Retail pet food packages were collected to further validate the test method. The grease breakthrough results for these packages are provided in **Table 11**. The brand names of the packages are not reported here; however, the structures of these packages are described in **Table 11**. Due to limited supply of materials, we could only test at one temperature for each film and a testing temperature of 60°C was selected. All the packages performed very well with only Package 2 showing some grease penetration on the TLC plates. However, grease staining was not visible on the film specimen.

Table 10: Film Physical Properties of 9-layer Films with All PE Resins (6.0 mil Films)

Film/Property	9L.EVOH/ o-LLD	9L.sHDPE / sLLDPE / sHDPE	9L.sLLDPE /sHDPE	9L.o-LLD / sHDPE	9L.HDPE-1/ sLLDPE / HDPE-1
1% Secant Modulus - MD (MPa)	417	543	422	449	426
1% Secant Modulus - TD (MPa)	433	599	470	500	498
2% Secant Modulus - MD (MPa)	340	417	326	343	325
2% Secant Modulus - TD (MPa)	353	460	360	385	381
Tensile Break Strength - MD (MPa)	20.6	33.2	36.2	35.3	40.8
Tensile Break Strength - TD (MPa)	18.7	35.1	35.4	39.2	38
Elongation at Break - MD (%)	619	871	906	926	978
Elongation at Break - TD (%)	571	898	901	980	953
Tensile Yield Strength - MD (MPa)	14.5	16.9	14.4	15	15.4
Tensile Yield Strength - TD (MPa)	14.4	17.7	15.1	16	15.9
Tensile Elongation at Yield - MD (%)	14	12	13	13	16
Tensile Elongation at Yield - TD (%)	15	11	13	12	12
Dart Impact (g)	738	1008	1056	960	978
Puncture (J/mm)	53	77	74	70	80
Elmendorf Tear - MD (g)	1242	1224	1788	1914	1746
Elmendorf Tear - TD (g)	2070	1824	2376	2916	1746

Table 11: Grease Breakthrough Test Results for Retail Pet Food Bags at Oven Temperature of 60°C

Package #	Film Composition	Grease Breakthrough values %
1	PET / ink-adhesive / PET / adhesive / LLDPE-LDPE	2
2	Contains 3 paper layers HDPE / HDPE / HDPE / EVA (~30% VA)	8
3	PET glued to paper and PP glued to other side of paper	1
4	PET / ink-adhesive / metalized PET / PU adhesive / LDPE / EP copolymer / LDPE	0
5	Nylon glued to paper and PP glued to other side of paper	1
6	PET / ink-adhesive / metalized PET / adhesive / butene LLDPE	1
7	PET / PU adhesive / LLDPE / LLDPE-TiO2 / LLDPE	0

CONCLUSION

A relatively quick semi-quantitative method for evaluating the grease resistance of multilayer packaging films was developed. It was found that films containing EVOH or PET can provide typical, non-recyclable, grease-resistant barrier films. Conventional HDPE resins may also provide some level of grease resistance at lower service temperatures (e.g. < 50°C). However, single site catalyzed bimodal sHDPE resins can be used in co-extruded multilayer PE film structures as an effective grease resistant layer at service temperatures up to 70°C. It was also shown that it is possible to develop all PE grease resistant film structures that have excellent physical properties, are easily recyclable and cost effective for the flexible packaging industry.

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KEYWORDS

Grease Resistance, Polyethylene, PE, Food Packaging Film, Heavy Duty Sacks, Stand-up Pouch, SUP, Recyclable Plastic Film, Multilayer Film, Multilayer Structure Single Site Catalyst, sHDPE, HDPE, LLDPE, and VLDPE

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