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New developments in MMW*-HDPE resins for moisture-barrier applications

THOMAS J. SCHWAB[1], LINDSAY E. CORCORAN[2]

Food packaging for products such as cereals, cookies and crackers typically needs good moisture-barrier resistance to help maintain freshness and to extend the shelf-life from the supply chain to the grocer and consumer. The moisture-barrier is measured via the water vapour transmission rate (WVTR) where a low value indicates a better barrier. While the moisture-barrier is important, there are additional product requirements for films used in these markets. Here are some examples for box liners:

- *Tear strength*. Tear properties, particularly in the machine direction (MD) of film manufacture, are critical when the consumer initially opens the bag. If the tear strength is not sufficient, then a tear may propagate down the length of the film resulting in product loss.
- *Stiffness/modulus*. The feel of the box liner is generally not a requirement for the consumer; however, it is important during the filling process of the product. If the film used to produce the box liner is not stiff enough, the filling rate efficiency may be sacrificed.
- *Seal strength*. The seal strength to open these types of bags requires delicate balancing. If the seal is too strong, then excessive force is necessary to open the box liner, which may lead to a tear. If the seal strength is too low, then the bag may open too easily, which can lead to concerns about product integrity.
- *Low taste and odour*. For food products, it is important to maintain low organoleptics to minimise any flavour transfer from the package to the product.
- *Film appearance*. The aesthetics of the box liner can portray the product quality to the consumer. Therefore, a film that exhibits imperfections, such as melt fracture, on the surface may lead a consumer to believe the product is inferior.

In order to meet these various product requirements, food companies often choose plastic packaging. Almost all of these plastic packages utilise films that are made of multiple layers of different polymer types. High-density Polyethylene (HDPE) is commonly used to provide the necessary moisture-barrier properties. A variety of sealant materials – such as metallocene linear low-density Polyethylene (mLLDPE), Ethylene-Vinyl Acetate (EVA), ionomer or Polybutene-1 – are used to provide the desired amount of seal strength. In addition, the level of the oxygen barrier may be controlled through the use of Ethylene-Vinyl Alcohol (EVOH) or nylon resins. Finally, other types of HDPE can be included as a layer giving additional toughness to the structure via the coextrusion blown film process to make the films for barrier markets such as cereals, cookies, and crackers.

Current moisture barrier films

Equistar Chemicals (part of the *LyondellBasell* group of companies) supplies a number of HDPE products that historically service the moisture barrier market. Resins such as *Alathon M6210*, *Alathon L5885*, or *Alathon L5485* typically make up the bulk of the structure for films in this market and provide much of the moisture barrier protection. The other film properties described above are also met with these products. In addition, these materials give excellent bubble stability for the blown film process allowing them to run at high film production rates.

Alathon M6020 is another HDPE product currently used in this market. The primary benefit of *M6020* is a further improvement in barrier versus the other current products and is commonly used as a layer in the coextrusion blown film process, but at much lower levels in the structure than *M6210*, *L5885*, or *L5485* due to its lower bubble stability as a result of its higher melt index.

Table 1 gives various mono-layer film properties for these products. The table shows subtle differences between *M6210*, *L5885*, and *L5485*, and *M6020* shows superior WVTR to the other grades. Film properties obtained from testing 64 micron mono-layer blown films except WVTR measured on 32 micron mono-layer blown films.

New developments for moisture barrier films

Resin development efforts by *Equistar Chemicals* led to the creation of a number of new HDPE products offering improved performance for film structures requiring a moisture barrier. For example, these new products may provide the ability to down-gauge the film and/or improve the shelflife of the product. In addition, these products also ap-

***Table 1:* Various mono-layer film properties. As the data shows, there are subtle differences among M6210, L5885, and L5485, and M6020 shows superior WVTR to the other grades. Film properties obtained from testing 64 micron (2.5 mil) monolayer blown films except WVTR measured on 32 micron (1.25 mil) monolayer blown films.**

Test		Method	M6210	L5885	L5485	M6020
Melt index, g/10 min (190C, 2160 g)		ASTM D1238	0.95	0.85	0.85	2.0
Density	[g/cc]	ASTM D2839	0.960	0.958	0.954	0.960
Haze	[%]	ASTM D1003	73	71	66	45
Dart drop at 26"	[g]	ASTM D1709	87	86	92	78
1% MD secant modulus	[psi]	ASTM E111	145,000	138,000	122,000	149,000
MD Elmendorf tear	[g]	ASTM D1922	45	47	50	48
TD Elmendorf tear	[g]	ASTM D1922	410	660	650	160
WVTR	[g-mil/100 si/day]	ASTM F1249	0.32	0.33	0.36	0.28

[1] Applications Development and Technical Support – Polyethylene, *Equistar Chemicals LP*, Cincinnati, OH/USA,
[2] Product Development Engineer, *Equistar Chemicals LP*, Cincinnati, OH/USA.

*MMW = medium molecular weight

pear to have other potentially useful properties such as improved optics and MD tear. The following four sub-sections discuss in more detail how these new HDPE products might be used to create added downstream benefits and value.

Improved moisture barrier

In some cases, the packaging for products has limitations on the amount of possible down-gauging due to the required level of WVTR to meet targeted shelf life specifications. With new HDPE resin design and the use of nucleation technologies, further improvements in moisture barrier may be achieved.

Nucleation of HDPE occurs by adding an organic salt to the resin. Under the proper processing conditions the salt can change the way that crystal growth in the polymer takes place during cooling. The resulting change in crystal orientation is believed to create a more torturous path for water vapour molecules to travel through blown films, thereby leading to improvements in WVTR. Depending on the HDPE product, improvements of WVTR by as much as 30% have been demonstrated compared to the un-nucleated version of the HDPE.

Test		Method	M6020	M6010SB
Melt index (190C, 2160 g)	[g/10 min]	ASTM D1238	2.0	1.15
Density	[g/cc]	ASTM D2839	0.960	0.960
Haze	[%]	ASTM D1003	45	35
Dart drop at 26 inches	[g]	ASTM D1709	78	66
1% MD Secant modulus	[psi]	ASTM E111	149,000	134,000
MD Elmendorf tear	[g]	ASTM D1922	48	46
TD Elmendorf tear	[g]	ASTM D1922	160	280
WVTR	[g-mil/100 si/day]	ASTM F1249	0.28	0.25

***Table 2:* Comparison of mono-layer film properties of M6020 and M6010SB. Film properties obtained from testing 64 micron (2.5 mil) mono-layer blown films except WVTR measured on 32 micron (1.25 mil) mono-layer blown films.**

Test		Method	M6210	L5885	L5485	M5410
Melt index (190C, 2160 g)	[g/10 min]	ASTM D1238	0.95	0.85	0.85	1.15
Density	[g/cc]	ASTM D2839	0.960	0.958	0.954	0.954
Haze	[%]	ASTM D1003	73	71	66	26
Dart drop at 26 inches	[g]	ASTM D1709	87	86	92	105
1% MD Secant modulus	[psi]	ASTM E111	145,000	138,000	122,000	122,000
MD Elmendorf tear	[g]	ASTM D1922	45	47	50	58
TD Elmendorf tear	[g]	ASTM D1922	410	660	650	260
WVTR [g-mil/100 si/day]	ASTM F1249	0.32	0.33	0.36	0.36	

***Table 3:* Comparison of mono-layer film properties of M6210 with L5885, L5485, and M5410. Film properties obtained from testing 64 micron (2.5 mil) mono-layer blown films except WVTR measured on 32 micron (1.25 mil) mono-layer blown films.**

The development of *Alathon M6010SB* utilises new resin design and nucleation resulting in improved moisture barrier properties compared to *M6020*. In addition, the haze of *M6010SB* is lower than *M6020*, resulting in improved contact clarity. The lower melt index of *M6010SB* (1.15 versus 2.0) gives additional melt strength to the film structure. As a result, the layer distribution of *M6010SB* may be increased to give a further benefit to WVTR with minimal effects to bubble stability and output.

Table 2 compares mono-layer film properties of *M6010SB* and *M6020*. Film properties obtained from testing 64 micron mono-layer blown films except WVTR measured on 32 micron mono-layer blown films.

Improved toughness

As described above, insufficient toughness, primarily MD tear, is a critical property for many end-use applications. As the film gauge is reduced, the importance of higher MD tear increases because there is less material to provide tear strength. This leads film producers to look for resin choices that offer improved toughness.

To respond to this need *Alathon M5410* was developed. This new HDPE resin shows 15–30% higher MD tear and 15–20% higher dart drop than other *Equistar Chemicals* products used as the bulk material in these structures and also maintains a similar level of stiffness and WVTR compared to these same HDPE resins. The haze of *M5410* is significantly improved and extremely low for HDPE, which could be an added advantage for film structures requiring contact clarity. Finally, by having a similar melt index as *M6210*, *L5885* and *L5485*, *M5410* can provide sufficient bubble stability that allows it to be a greater part of the film structure.

Table 3 compares mono-layer film properties of *M5410* with *M6210*, *L5885* and *L5485*. Film properties obtained from testing 64 micron mono-layer blown films except WVTR measured on 32 micron mono-layer blown films.

Developmental product in moisture barrier

While all of the commercial *Equistar Chemicals* barrier products show excellent film appearance, some HDPE resins in the industry face trade-offs between providing lower WVTR and maintaining acceptable melt fracture. Through further resin design improvements and in combination with nucleation, *Alathon M6010X03* was developed with an even lower WVTR compared to *M6020* and *M6010SB* while maintaining good film surface appearance.

The nucleated *M6010X03* provides more than 40% improvement in WVTR compared to *M6010SB*. While nucleated *M6010X03* has a melt index of 2.7 g/10 min, its resin architecture provides melt strength similar to typical HDPE resins with a melt index of 2.0. The combination of the melt strength and good film aesthetics allows the nucleated *M6010X03* to be used in any layer of the film structure including the skin layer. The ability to use this new product in any layer of the film structure is important because it allows such properties as WVTR to be fully optimised as required by the target application.

Table 4 compares mono-layer film properties of *M6010SB* with nucleated *M6010X03*. Film properties obtained from testing 64 micron mono-layer blown films except WVTR measured on 32 micron mono-layer blown films.

Test		Method	M6010SB	Nuc. M6010X03
Melt index (190C, 2160 g)	[g/10 min]	ASTM D1238	1.15	2.7
Density	[g/cc]	ASTM D2839	0.960	0.962
Haze	[%]	ASTM D1003	35	40
Dart Drop at 26 inches	[g]	ASTM D1709	66	51
1% MD Secant modulus	[psi]	ASTM E111	134,000	161,000
MD Elmendorf tear	[g]	ASTM D1922	46	32
TD Elmendorf tear	[g]	ASTM D1922	280	103
WVTR	[g-mil/100 si/day]	ASTM F1249	0.25	0.14

Table 4: Comparison of mono-layer film properties of M6010SB with nucleated M6010X03. Film properties obtained from testing 64 micron (2.5 mil) mono-layer blown films except WVTR measured on 32 micron (1.25 mil) mono-layer blown films.

Use of new products in WVTR film applications

Blown film producers with multi-layer capability may be able to take advantage of these new HDPE products to create optimised film structures to service barrier sensitive applications such as cereals, cookies and crackers. For example, positioning the *M6010SB* or nucleated *M6010X03* in the proper layer of the film structure to take advantage of the improved barrier properties should result in a film with better WVTR or allow for a reduction in the premium priced barrier layer resulting in improved cost. In addition, the use of *M5410* in the bulk layer may improve the film's toughness sufficiently to allow film down-gauging while maintaining the same overall MD tear strength. By using both types of materials in the same structure, it may be possible to maintain the same level of WVTR and toughness, but at a thinner gauge.

Another example, the *M5410* could be used as the majority film component to allow film down-gauging due to improved toughness, but the barrier layer with *M6010SB* or nucleated *M6010X03* could remain at its current thickness. This would likely provide a film with an improved barrier, which may allow longer shelflife. This can also allow a HDPE-based film to be used for a product that requires better barrier than historic films could provide.

These are just two potential ways to utilise these new products, but there are numerous other routes to maximise their benefits throughout the supply chain.

Conclusions

The *Equistar Chemicals* HDPE products used historically in the moisture barrier market continue to meet their end-use product requirements. However, as the number of co-extruded layers continues to increase (3 to 5 to 7 to 9) and as new packaging needs (down-gauging, improved optics, improved tear, improved puncture resistance, etc) emerge, *Equistar Chemicals* continues to broaden its HDPE product line to meet the ever increasing demands of the industry. Various combinations of current and new products position the converter to achieve their goals to improve film structure performance and optimise costs to maintain existing markets while potentially opening the door to new markets that currently do not use HDPE for barrier performance.

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