<u>Film Property Enhancement utilizing Nano-particulates</u>
<u>In</u>
<u>Multilayer Blown Films composed of more than 25 layers</u>

Nano-particulate materials; specifically clay, when utilized in repeating/alternating multilayer film structures typically in excess of 25 layers will be examined for their impact on physical properties, optical properties, and permeability in polyethylene based and nylon based films.

<u>Background:</u>

Nanoclay raw material is montmorillonite, which is a 2 to 1 layered smectic clay mineral with a platey structure and when dispersed in a polymer matrix at levels of 5% can impact on Oxygen and CO_2 barrier, Water Vapor barrier, UV transmission, Thermal stability, Stiffness, Clarity, Anti-tack, and melt strength in the film. Aspect ratios of greater than 200 have been shown to reduce permeability by up to 50%.

Annular multilayer films in which repeating alternating layers are employed have demonstrated that when two different polymers are used in tandem, the resulting pair often exhibits both properties of the individual resin as opposed to a blended result which is an average at best of the property.

The objective of this work is to examine the use of nanocomposites in annular nanolayer/microlayer structures first in polyethylene based films and then in barrier based films.

The lab line consists of 4 extruders feeding a 29 layer die configured in the following manner:

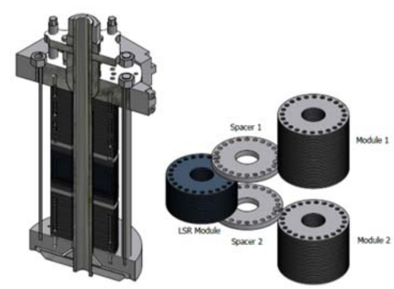
A/D/(B/C……C/B)/D/A

The pairing of B & C typically comprise 1/3rd of the cross section, so for example if the film is 24 microns in total thickness, the core will be 8 microns and each of the individual 25 layers will be 0.32 microns.

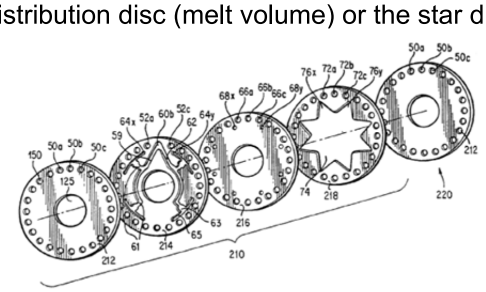
<u>Review of Annular Nanolayer Extrusion:</u>

Annular nanolayer extrusion is based on the use of a modular disc design.

- Can accept up to 12 melt feeds
- Practically can accommodate up to 200 layers
- Die construction is modular
- Layer configuration can be shuffled like a deck of cards
- Layers can be added/subtracted at any time
- Die lips readily changed to new size
- Discs are not material specific with the exception of PVDC & PVC
- Die body is same for wide range of sizes
    - 1X is small tubing to 220 mm
    - 2X is 200 mm to 660 mm
    - 4X is 500 mm to 1000 mm



Modular disc assembly is comprised of a cap disc, a distribution disc, a passage disc, a star disc, and a final cap disc. The assembly's throughput and cross section can be altered within a given range by changing the thickness of the distribution disc (melt volume) or the star disc (discrete layer constriction)



The layer sequence repeater is the extension of the single modular disc assembly in which two or three melt feeds are stacked in a combination of 25 or 50 discrete layers.

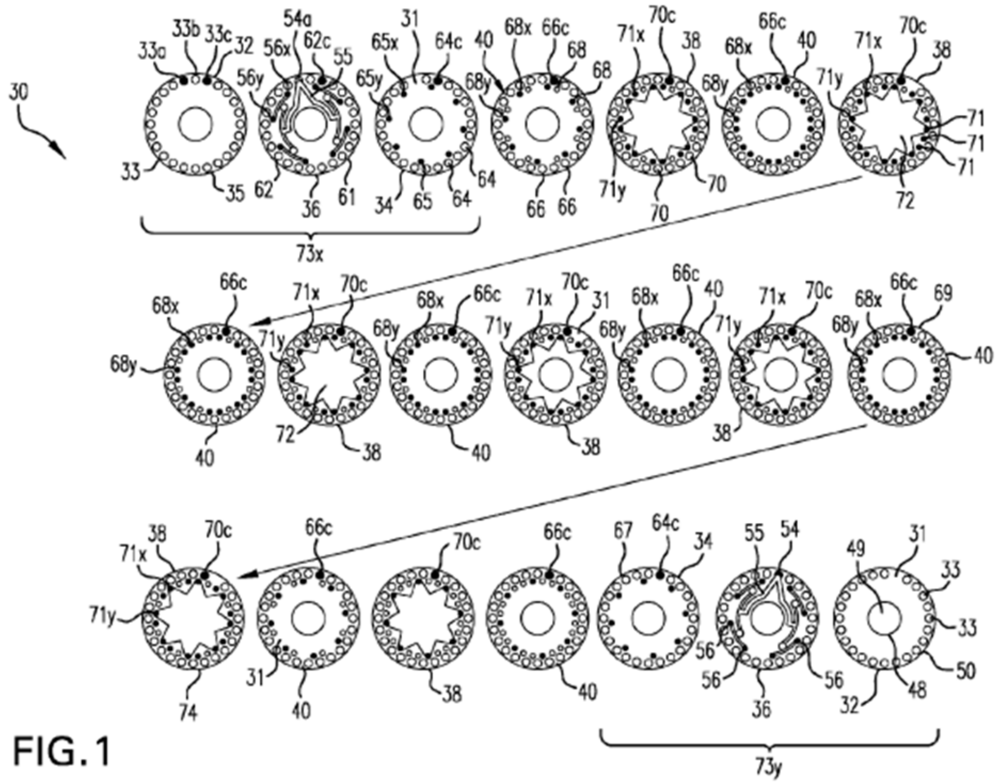


FIG. 1

In this you will note that the passage disc has two or three sets of holes that feed alternately aligned star discs. Proportional cross section can be modified as in the single layer by increasing supplied melt volume and decreasing the star disc thickness.

As this is an annular die, it can be employed to produce tubing, coating of wire and cable, film, pipe, and blow molding.

<u>Benefits of the Technology:</u>

This work is focused on film extrusion and the main benefits it provides to this process. These can be explained by following the resin path as it flows within the die, as it exits the die, and as it forms a finished film.

Within the die the key attributes are:
- Low pressure
- Short residence time
- Low shear

This results in lower than normal processing melt temperatures, a broad range of acceptable melt rheology, and adjacency of materials not typically allowed.

Exiting the die the key attributes are:
- Parallel melt flow
- Low exit pressure

As the melt exits the die in a relaxed state it demonstrates that it is highly extensible and as it exists at a low pressure the tendency to compete for layer proportion is lower yielding a lower circumferential variation. This demonstrates itself in that very thin film gauges can be achieved, that very high blow up ratios can be reached (BUR), and that items such as gels pass freely without comprising the film integrity.

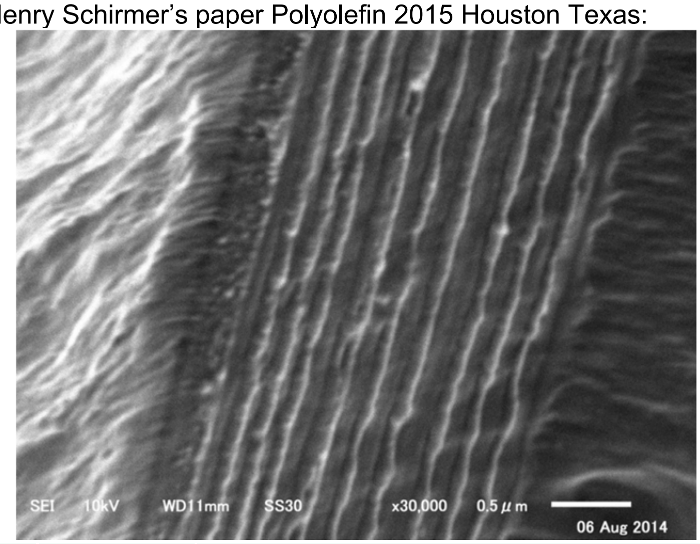
In film formation the key attributes are:

- “I” Beam effect
- Interlayer quenching
- Non-adulteration of layers
- Interlayer adhesion

This work has been covered in previous TAPPI Place papers and forms the basis for the examination of nanocomposites in their impact on extruded films.

<u>Prior Work on Barrier Films</u>

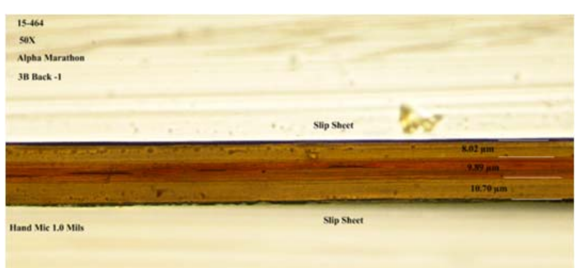
The key aspect in annular nanolayer barrier films is the ability to achieve a higher than normal BUR with typical structures. The consequence of this is the enhancement of OTR performance due to orientation of the polymer.
The following is from Henry Schirmer’s paper Polyolefin 2015 Houston Texas:



Sample ID	Nano-layers Total Thickness [um]	EVOH Thickness [um]	Calculated OTR [cc/m^2.day.atm]			Measured OTR [cc/m^2.day.atm][d]
			OTR$_{EVOH}$ [b]	OTR$_{a\text{-}Ny}$ [c]	OTR$_{Total}$	
22/16 (ET/a-Ny)	6.1	3.05	18.9	163.9	34	24
	5.9	2.45	23.6	204.1	51	25

In this example, one can see the orientated layers and the enhanced OTR performance.

In work conducted on the lab line, alternating layers of nylon and an adhesive resin at a BUR greater than 3.5 yielded similar results. The reasoning to alternate a tie material with the nylon was to reduce the nylon content and to increase the elastic properties of the film.



Nanocomposites in Polyethylene Films

Three sets of films were examined; the first being a pelletized scrap film sourced from printed white collation shrink film, the next two sets being LLDPE based films.

Pelletized Scrap
In all extruders, 100% repro was used with 8% let down ration of a nanocomposite masterbatch added to the material in extruder C. This would yield a net 1.3% additive content in the film.

100% Repro	MD Secant Modulus	TD Secant Modulus	MD Elongation	TD Elongation
Without Clay	27,185	29,581	387%	585%
With Clay	24,379	28,091	279%	592%

100% Repro	WVTR (gm/100 sq in day)	OTR (cc/100 sq in day)
Without Clay	1.09	295
With Clay	1.15	320

The results in this film set yield no enhancement of physical properties or barrier properties which given the high loading of exiting TiO_2, $CaC0_3$, and ink particles is not unsurprising.

100% LLDPE Film

In this sample the nanocomposite masterbatch is again added to one part of the LSR with no other materials, a single same resin in all other extruders.

	WVTR (gms/100in2/day)	OTR (cc/100in2/day)
LLDPE in LSR	1.300	565
Clay in one part LSR	0.939	277

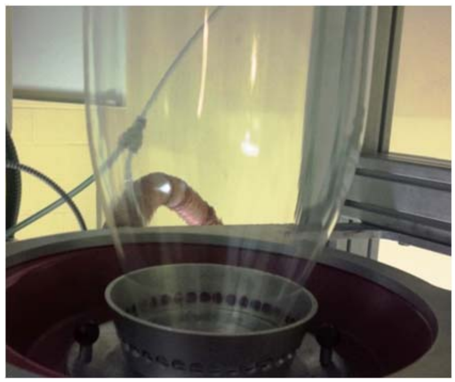
	Haze %	Gloss at 45 Degrees
LLDPE in LSR	12.1	51
Clay in one part LSR	11.5	70

	MD Secant Modulus MPA	TD Secant Modulus MPA	MD Elongation %	TD Elongation %
LLDPE in LSR	150.0	133.8	455	657
Clay in one part LSR	173.4	163.2	639	718

	MD Tear Gms/mil	TD Tear Gms/mil
LLDPE in LSR	229	331
Clay in one part LSR	456	464

In this sample besides the obvious improvement in general physical properties, particularly in tear properties. Also there is a subtle improvement in the exterior gloss of the film which is indicative that the thermal cooling characteristics have altered.

In a second set of polyethylene films the effect of HDPE in concert in the LSR with LLDPE is examined, knowing that interlayer quenching will be observed in the LL/HD pairing in the LSR. The nanocomposite masterbatch is added to the HDPE portion in the LSR. Results from the all LLDPE are included for reference.



	WVTR (gms/100in2/day)	OTR (cc/100in2/day)
LLDPE in LSR	1.300	565
19C in one part LSR	0.789	358
19C+Clay in one part LSR	0.735	350

	Haze %	Gloss at 45 Degrees
LLDPE in LSR	12.1	51
19C in one part LSR	7.0	80
19C+Clay in one part LSR	6.0	82

	MD Secant Modulus MPA	TD Secant Modulus MPA	MD Elongation %	TD Elongation %
LLDPE in LSR	150.0	133.8	455	657
19C in one part LSR	205.0	295.8	558	667
19C+Clay in one part LSR	264.8	350.6	607	673

	MD Tear Gms/mil	TD Tear Gms/mil
LLDPE in LSR	229	331
19C in one part LSR	244	423
19C+Clay in one part LSR	199	467

The impact of nanoclay is marginal when mixed with the HDPE in the LSR.

Nanocomposites in Nylon Barrier Film

Three films were extruded in which the LSR had in one part an adhesive resin and in the second part Pa6, Pa6 with clay, and MXD6 with clay.
The structures then are A being Nova FPs016-C, “D” being DuPont Bynel® 4157, “B” being DuPont Bynel® 4157, and “C” being BASF B40LN, PA6 with clay, and Imperm 103 in sequence. A reference sample produced on the same lab line is included in which both parts of the LSR are EVOH (EVAL® XEP-1321)

Sample	Tensile MD	Tensile TD	Elongation MD	Elongation TD
Nylon	3,611	2,812	378%	284%
Nylon + Clay	4,057	3,587	342%	384%
Imperm 103	4,603	4,583	284%	290%
EVOH	3,370	4,239	257%	270%

Sample	Haze %
Nylon	7.54
Nylon + Clay	16.37
Imperm 103	9.50
EVOH	6.20

Sample	OTR cc-mil/m2-day @ 50% Rh	WVTR gm mil/m2-day	Thickness of barrier per mil in microns
Nylon	177.95	24.85	6.8
Nylon + Clay	65.75	20.45	6
Imperm 103	10.25	22.9	6.4
EVOH	1.73	19.85	11.8

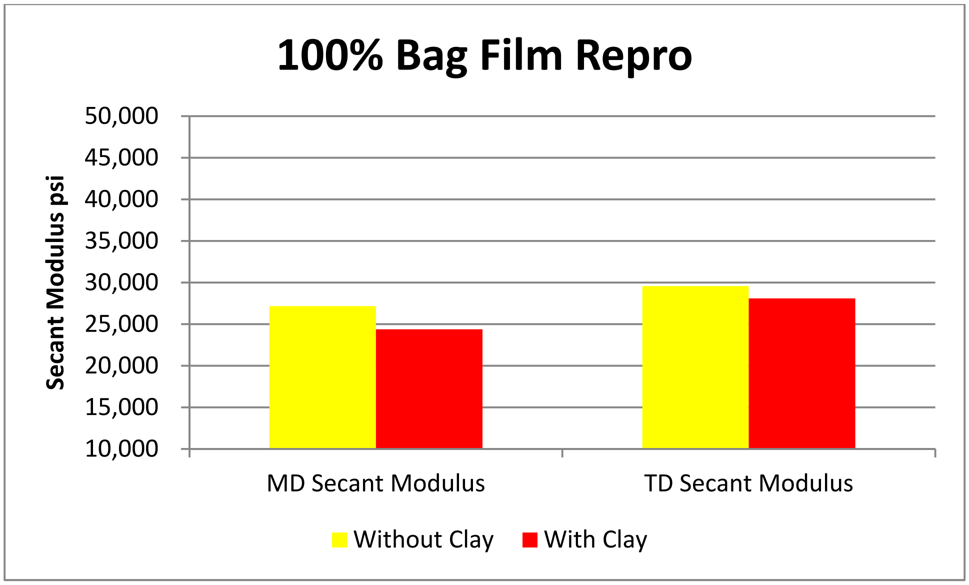
If we first look at only comparing Pa6 to Pa6 with clay, there are apparent physical properties which improve, but the most significant aspect is a reduction of OTR by 2/3rds.

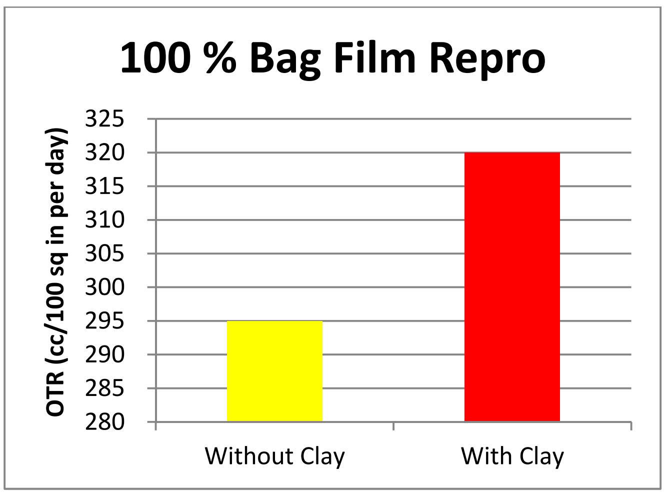
It is important to note that the targeted BUR of 3.5 for all films was not obtained in the Pa6 and Pa6 with clay samples as the stability of the bubble was lacking and an alternative adhesive material was required. These films were run at a BUR of 2.5; the remainder of the films were at 3.5 BUR. The Imperm 103 was extremely stable.

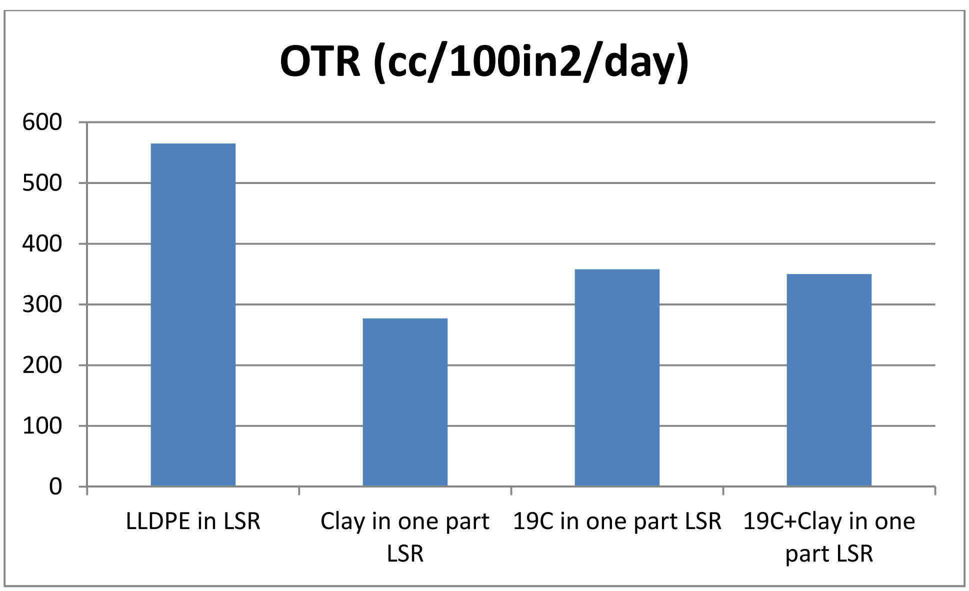
General Observations Polyethylene

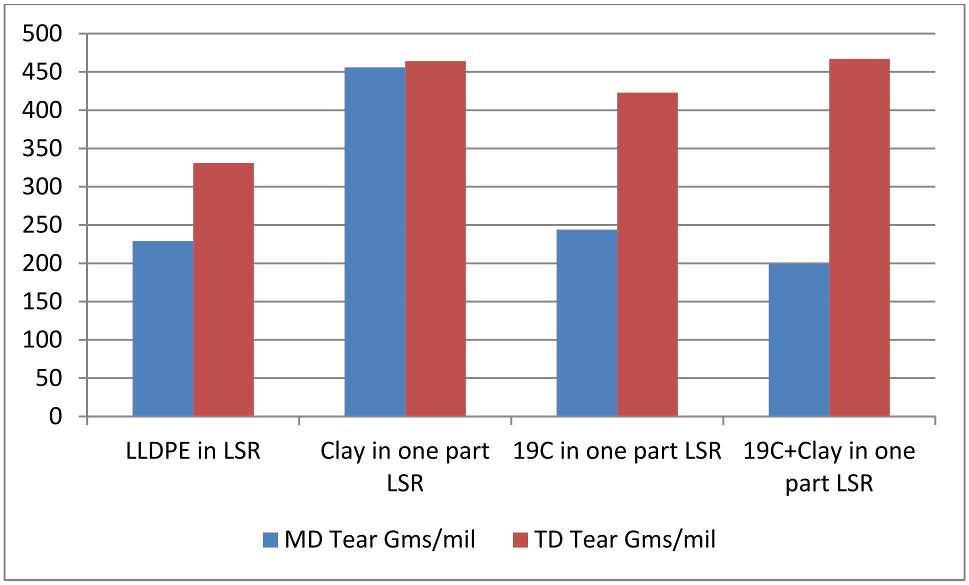
It is important to note that the net additive amount is 1.3% or 8% of 15% of the film structure.

1) Effectiveness of nanocomposite materials in filled blends not observed.
2) Enhancement in OTR performance greater than 40%
3) Enhancement of secant modulus and elongation which is a unique set of properties, stiffer and more elastic
4) Enhancement of tear properties.
5) Alteration of thermal cooling characteristics creating a smoother skin


100% Bag Film Repro
Secant Modulus psi
50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
MD Secant Modulus
TD Secant Modulus
Without Clay
With Clay


100 % Bag Film Repro
OTR (cc/100 sq in per day)
325
320
315
310
305
300
295
290
285
280
Without Clay
With Clay

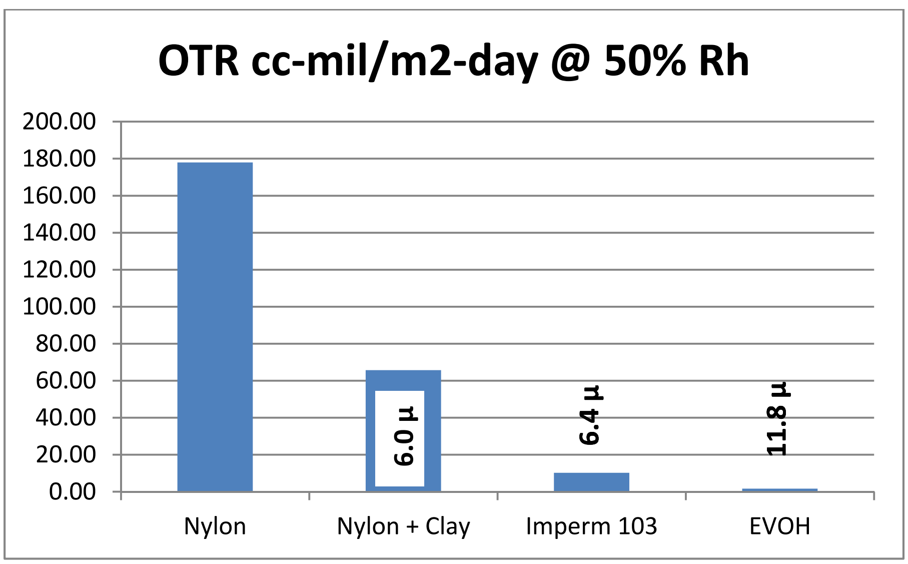

OTR (cc/100in2/day)
600
500
400
300
200
100
0
LLDPE in LSR
Clay in one part LSR
19C in one part LSR
19C+Clay in one part LSR

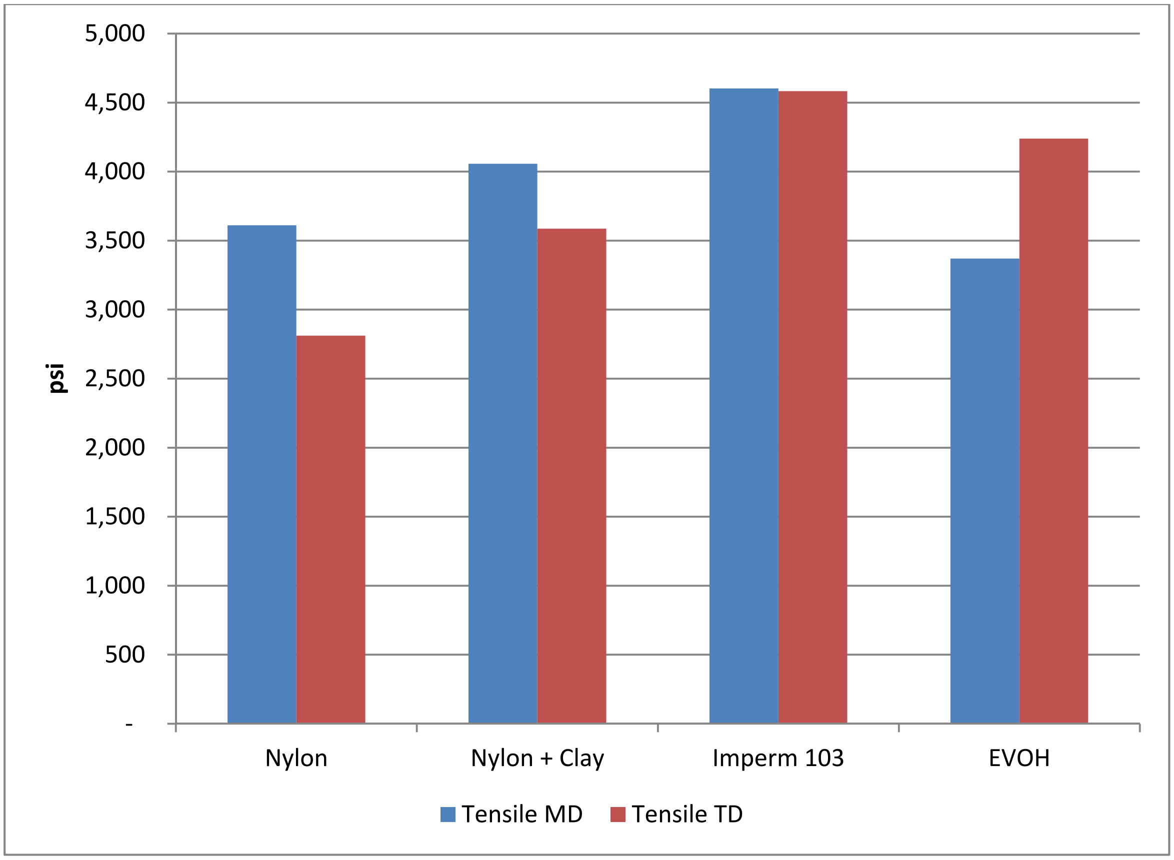


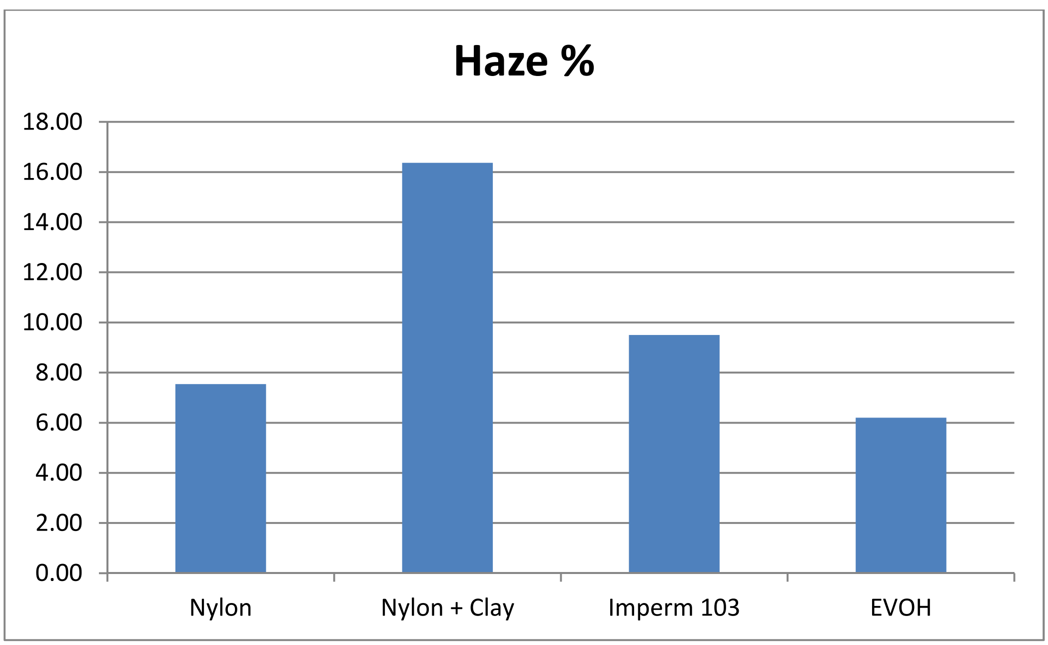
General Observations Barrier

It is important to note that the total typical cross section target of actual nylon was 6 microns and the results indicated are to the total film thickness of 25 microns.

1) Enhancement in OTR performance greater than 65% of Pa6 to Pa6 with clay
2) Tensile properties and elongation similar
3) Haze in the nylon and Imperm reflect interlayer quenching, not so with the Pa6 and clay. (probably due to the lower Bur and bubble instability)
4) The MXDS Nylon with clay achieves barrier results very close to that of an EVOH.







Closing Points:

This preliminary work has demonstrated that nanocomposites in both polyethylene and nylon barrier structures can yield significant enhancement in physical and barrier performance when combined in thin repeating layers in an annular microlayer extrusion format.

Further work is required to quantify the commercial benefits, but from a barrier perspective it is reasonable to project a 50% reduction in the use of a barrier material to achieve similar performance.

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