Annular Nanolayer Film Extrusion Overview

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Outline

- Definition of a Nanolayer
- History and Function of the Modular Disc Die
- Explanation of the Observed Film Attributes
- Practical Application Example
- Ongoing Development
- Summary

What is a Nanolayer?

- A Nanolayer is an order of magnitude thinner than a microlayer
  - What is a microlayer
    - A microlayer is a thin layer typically not discernible by the human eye
      - What is a thin layer?
        - Something measured in parts of a millimeter, microns, nanometers

Continuum

The physical scale of a Nanolayer has a defined value, but as it applies to film properties that value varies according to the effect and interaction

Thin Layer | Microlayers | Nanolayers

Millimeter
m

Micrometer
µ

Nanometer
n

A Nanolayer may well be defined as:

"The thickness where unique physical characteristics to the polymeric film occurs imparting special properties not observed in that polymeric film as a thicker structure"

History & Design of the Modular Disc Die

- Modular Disc Co–extrusion Die was first patented on Nov 1999, based on an original filing from 1996, publish in 2002
- Layer Sequence Repeater Module for the Modular Disc Co–Extrusion Die published October 28th 2014
  - Patents awarded or pending USA, Canada, Europe, and China, patent on films pending

Modular Disc Die Construction

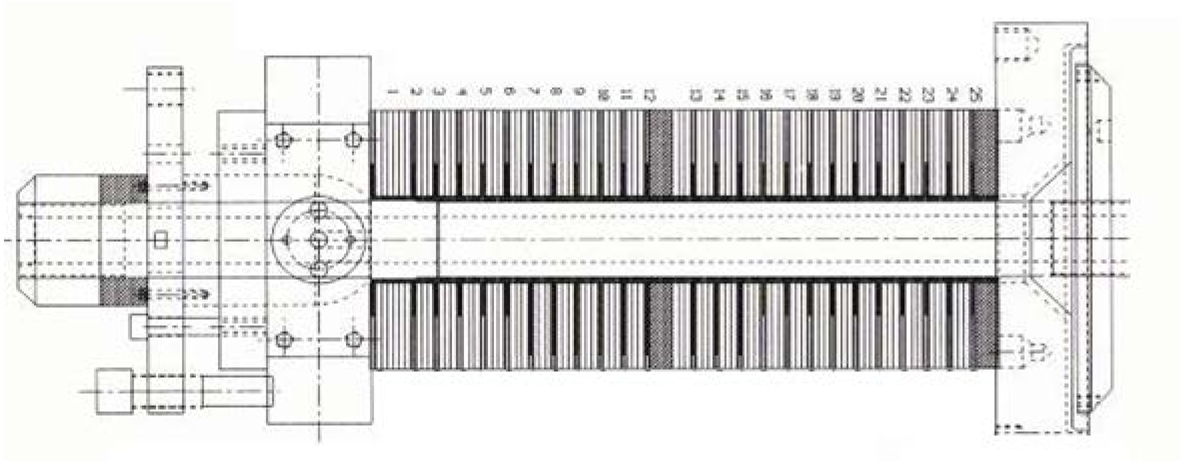
- Base
  - Melt entrance
- Adjustable inner mandrel
  - Pivot adjustment
- Melt Exit
  - Disc stack clamp & die lip assembly
- Modular Disc assemblies

Cross Section/Side View

Melt Exit Assembly

Base

Adjustable Inner Mandrel



Disc Stack Assemblies

Disc Stack Assembly

- 5 Discs per Assembly
  - Melt Introduction (Cap 1)
  - Melt Distribution
  - 8 point feed (Cap 2)
  - Layer disc (star)
  - Cap disc
    - Next stack bottom can be this disc

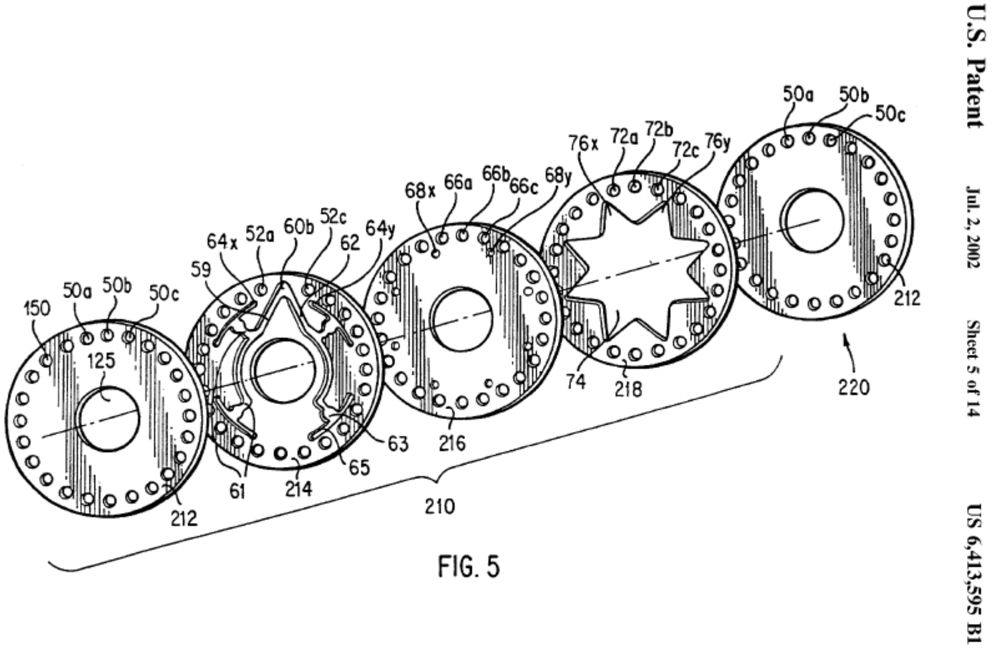
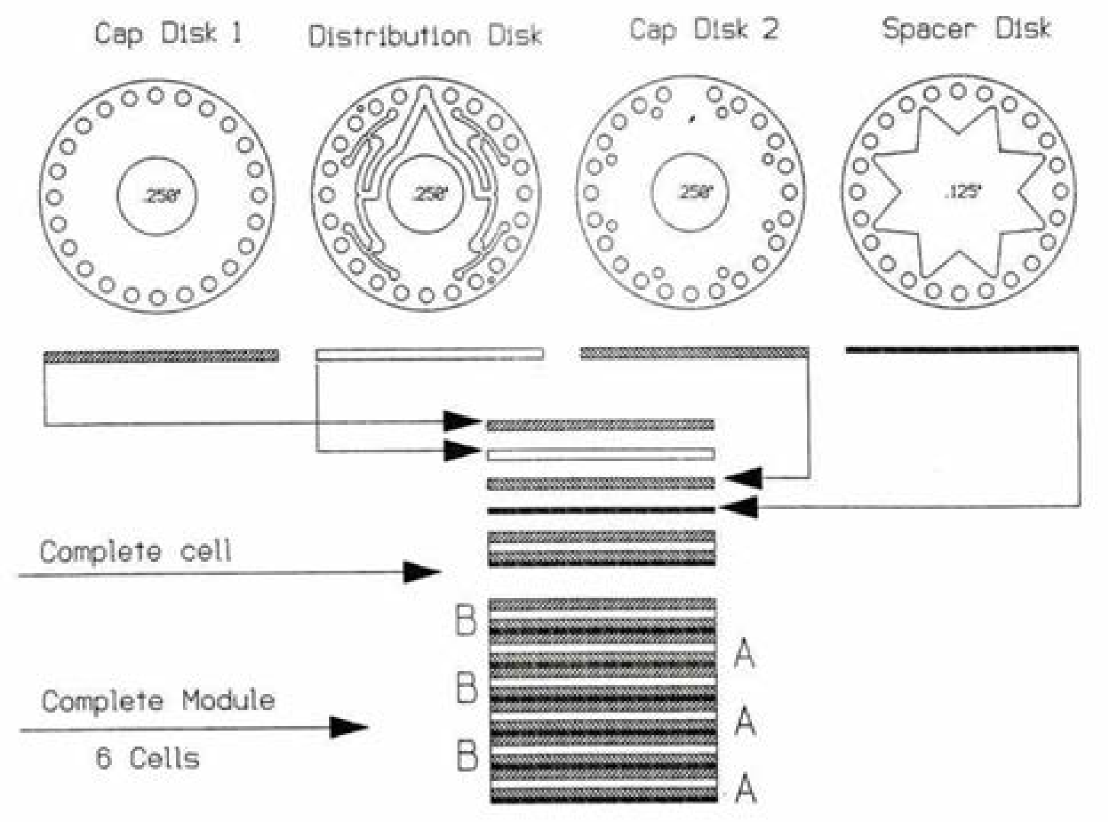


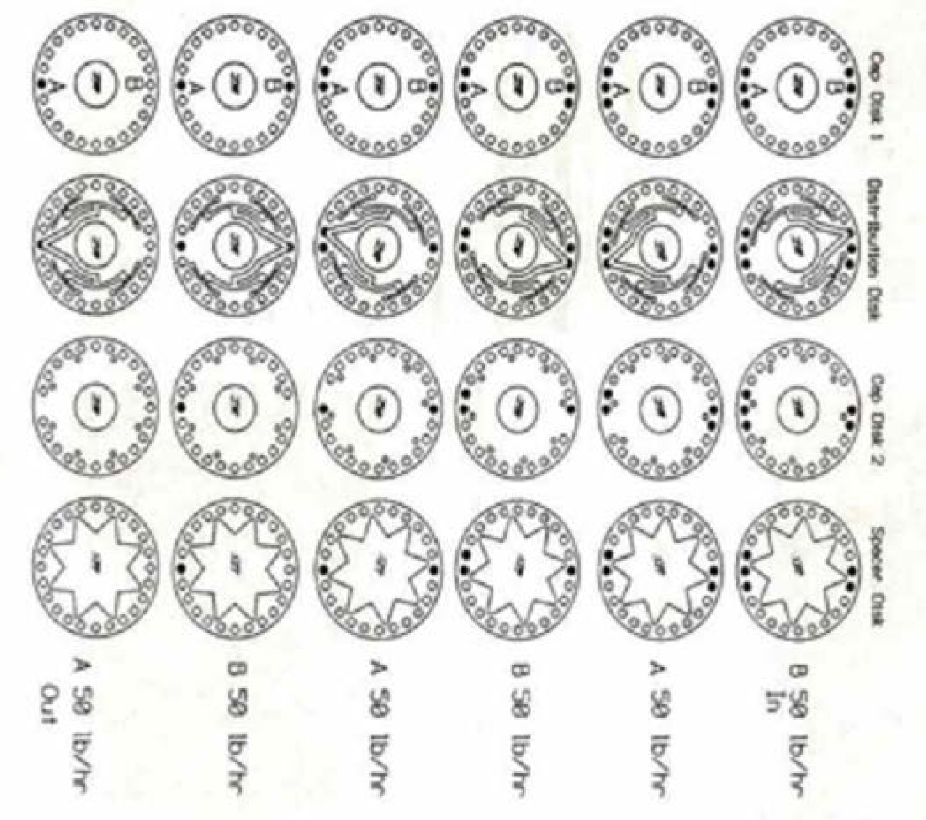
FIG. 5

General Assembly



Sequenced Assembly

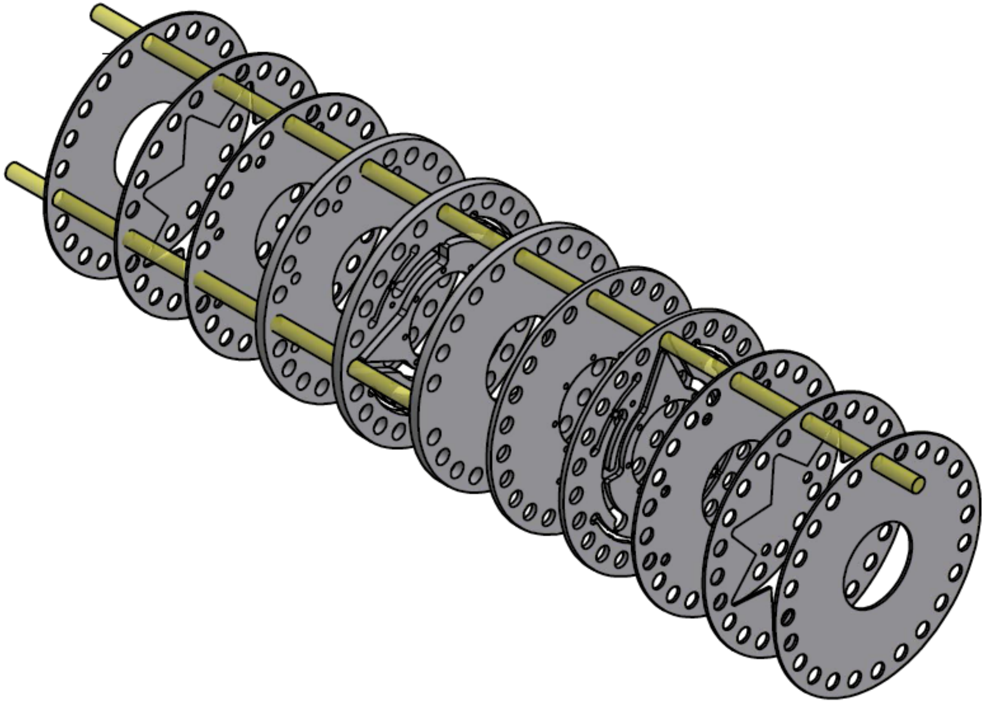
From left to right
1st feed A1 side
2nd feed B1 side
3rd feed A2 side
4th feed B2 side
5th feed A3 side
6th feed B3 side



3-D Depiction of Melt Feed

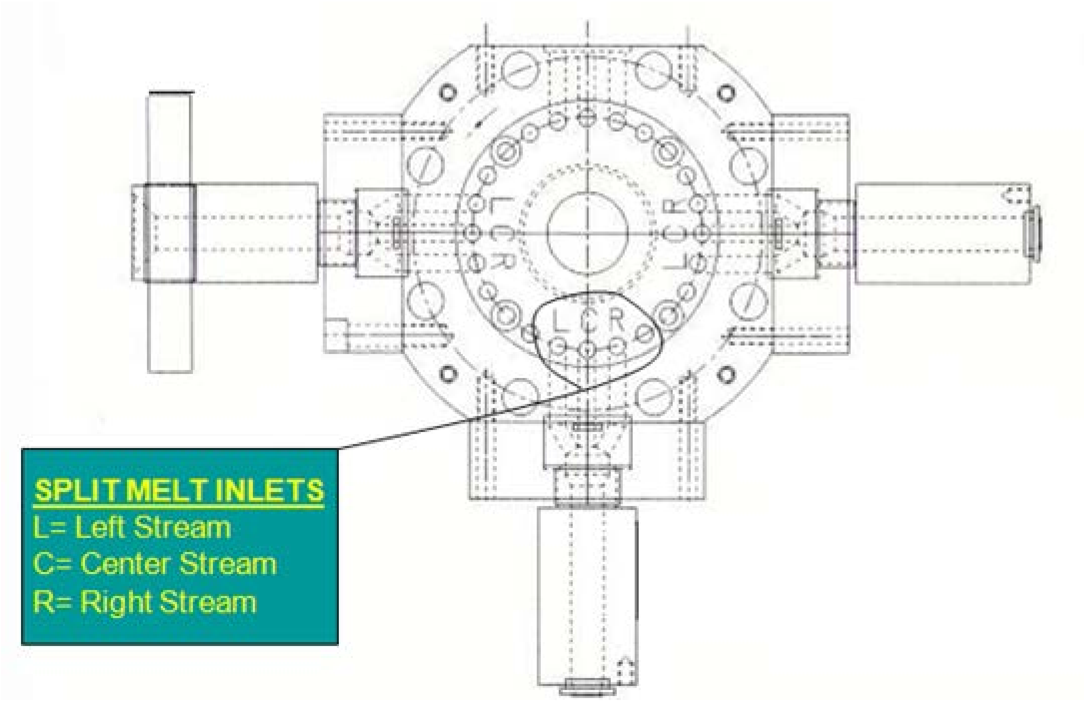
Melt Feed Left to Right

- In this case there are two melt feeds with one disc assembly being inverted
- One feed continues to another module



Base

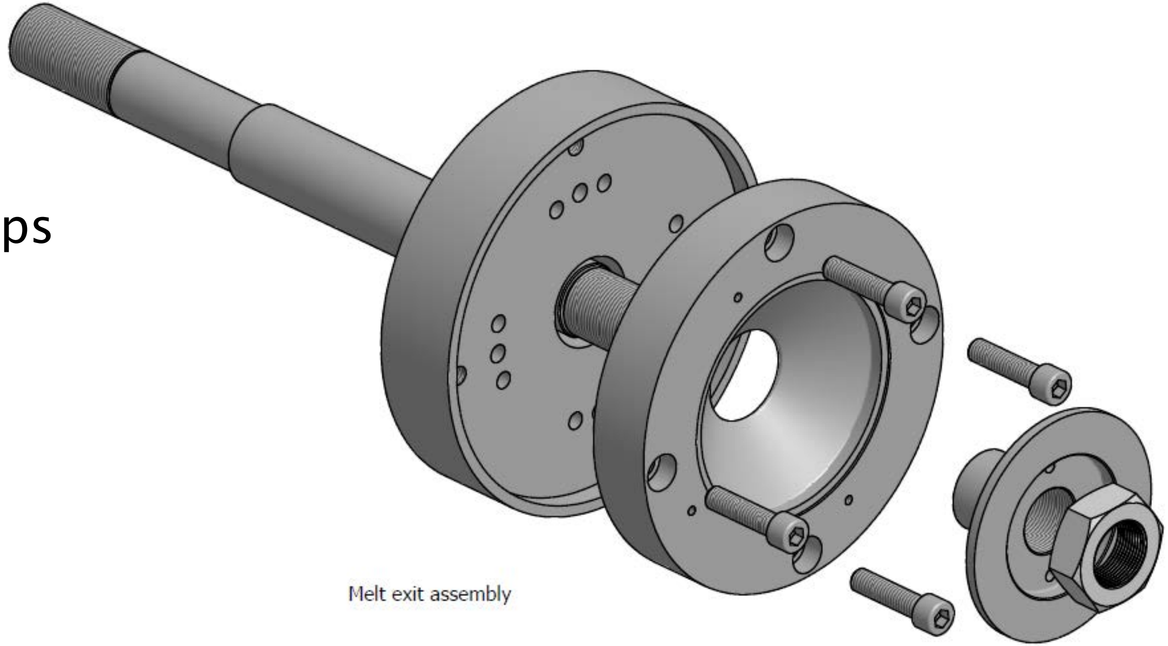
Every base is configured for up to 12 melt feeds



Melt Exit Assembly

Assembly consists of

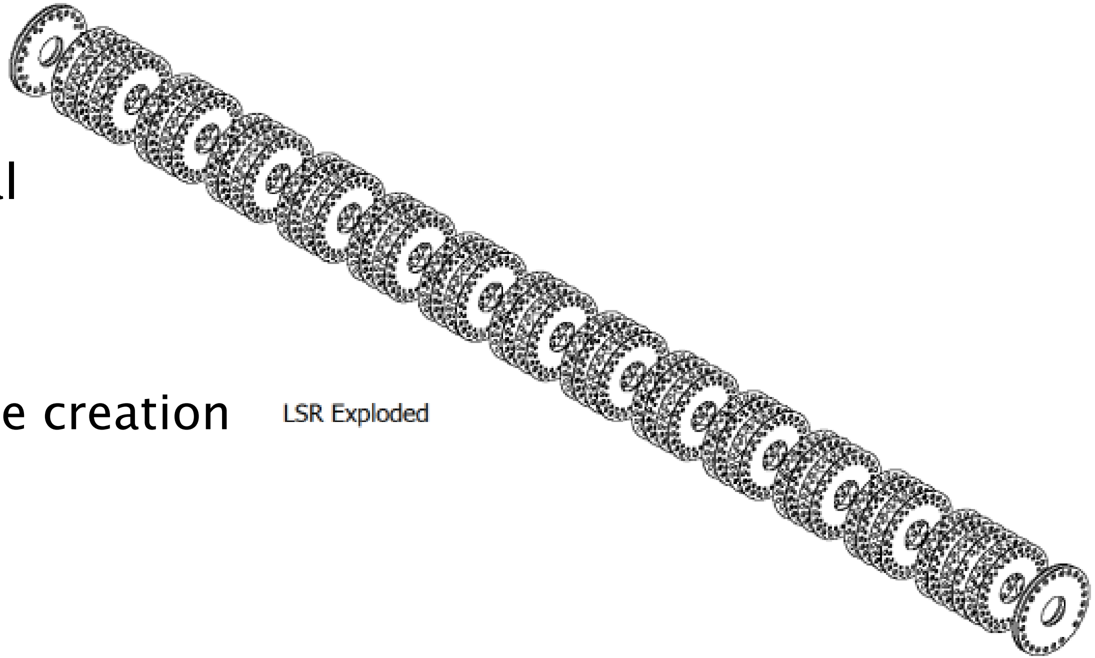
1) Top clamp stack unit
2) Inner and outer die lips



Melt exit assembly

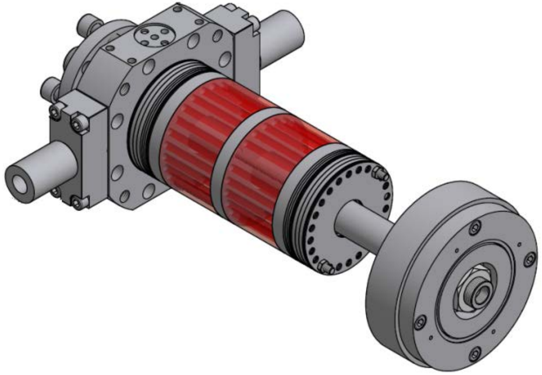
LSR Module Exploded View

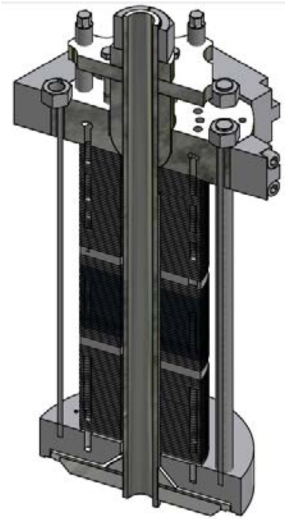
Assembly sequence critical
A/B/A....B/A
A/B/C/B/A/B/C/B/...A
A/B/C/A/B/C/...A
Set of 25 or 50 ensures the creation of a eight pattern repeat

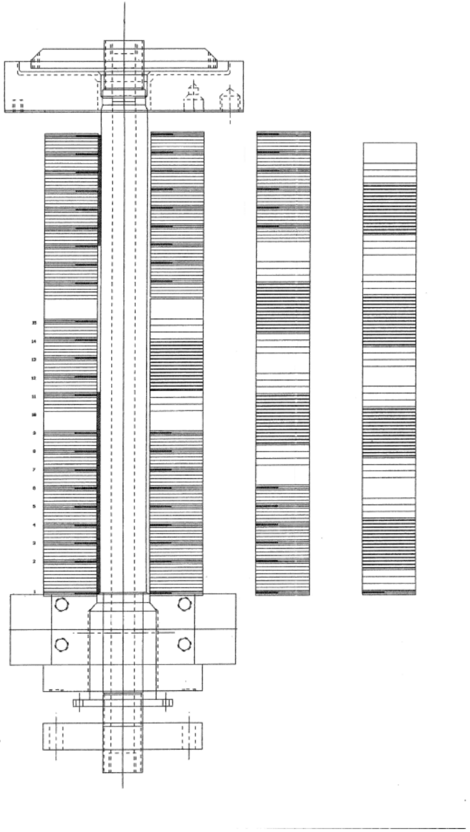


LSR Exploded

Die Assembly Configurations







Virtually limitless in possibilities

Resultant Film Attributes

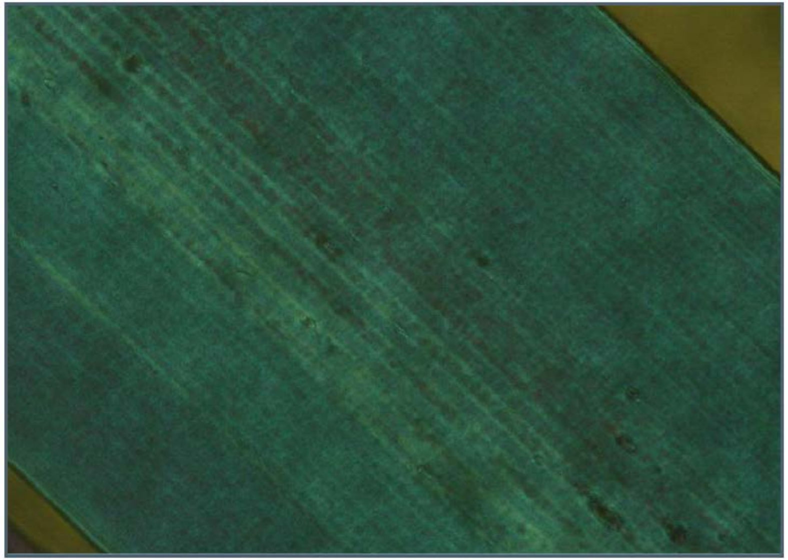
- Benefits can be categorized in 3 zones as it is related to the polymer flow
  1) Within the die
     1) Low pressure, low temperature, low residence time, and a parallel melt flow
  2) As it exits the die
     1) Parallel melt flow, apparent melt strength
  3) As the film forms
     1) Extensibility of the film, interlayer quenching, “I” beam affect

Melt Flow Within The Die

- The analogy of melt flow volume of an MDD die is that of a screen pack, the large cross section of the screen promotes back pressure but allows a large particle size to flow though the screen
- Liquids prefer to flow in a straight line and once they are layered onto the mandrel they progress along its length with no/little interface interaction to the adjacent material
- This results in a broad acceptance of MFI both in a base resin and when compared to the adjacent material (delta MFI)
- As the flow is low shear, the melt can be conducted at temperatures above the melting point and below traditional processing temperatures
- The flow path is short, very low residence time

Melt Flow Exiting the Die

- The parallel melt flow yields two attributes
  - 1st is that as a low pressure exiting material it does not "compete" for die gap yielding a reasonable gauge uniformity in a standard alignment on inner/outer mandrels
  - 2nd is that the polymer layers exiting have the maximum alignment for extensibility



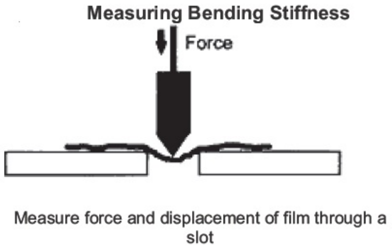
77 layer film X-section

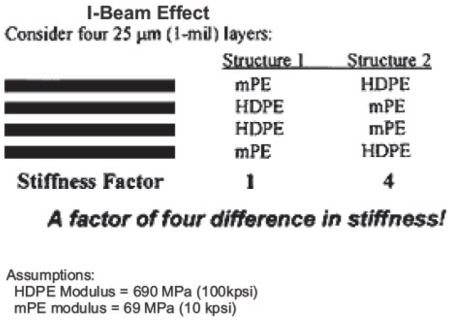
Film Formation

- Due to high apparent melt strength BUR's on materials have a greater range
  - Nylon films for example can be made at a 5 BUR in a standard blown film condition
- Due to the extensibility of the film, orientation limits are extended
  - Double bubble films can be run at 7.5 by 7.5 orientation, versus typical 4.5 by 4.5
- When repeating very thin materials with differential melting points are air cooled, the higher melting point material is rapidly quenched by the transfer of heat to the lower melting point material
  - Has been observed with as delta as low as 5 degrees Celsius
  - This presents the opportunity to orientate layers above their glass transition temperature

Final Film Attributes

- The major attribute in the finished film is the potential to create an “I” beam effect.
- The repeated layering of two materials with a different property can create a new film that can exceed the average or the maximum value of the individual layers.
- Normally “I” beam effect is applied to the tensile strength characteristics, but in this case it can be observed in a broad gamut of physical properties such as tear, puncture, elongation, recovery, secant modulus





Attribute Summary Benefit Table (Within the die)

Characteristic	Benefit	Commercial Value
High effective melt volume	Tolerant of "unmelts"	Reprocessed material Low occurrence of bubble failure
Low disturbance melt flow	Broad application of varying MFI	Purchase resin based on its end properties not processing potential
Lower melt temperature	Less degradation, less net energy to process	Broader selection of materials, lower energy costs, lower organoleptic
Low residence time	Less degradation	Lower organoleptic, greater shelf life of finished product

Attribute Summary Benefit Table
(Existing the die)

Characteristic	Benefit	Commercial Value
Parallel melt flow exits at low pressure from the die lips	"Non-compete" for die lip concentricity compared to traditional dies	Base gauge variation is equivalent or better to exiting high quality spiral dies
Parallel melt flow exits relaxed and aligned	The polymer chain condition is as it exits configured for maximum extensibility	BUR's obtainable at 5 for most materials in single blown film and almost 70% greater for double bubble In a single bubble process, shrink values close to 50% have been obtained
Parallel melt flow is in a low shear condition	Yields an apparent high melt strength	Materials with poor melt strength can be processed thinner and at higher BUR's and higher throughputs

Attribute Summary Benefit Table
(Film Formation)

Characteristic	Benefit	Commercial Value
High Melt Strength	Higher Throughput Thinner Film	Limit on output is effective cooling Film as thin as 2.5 microns has been achieved
Interlayer Quenching	Higher clarity Orientation above glass transition	Use of materials such as PP, HD with haze values close to 20 have yielded less than 5 Unique combinations can create new films, shrink film made from 85% LL and 15% PP
"I" Beam effect	Improved physicals	Utilizing unadulterated repeating layers create stronger, tougher films
Interlayer Adhesion	As thickness decreases, energy for adhesion decreases	Materials not normally compatible are, adhesives can be diluted

Practical Example

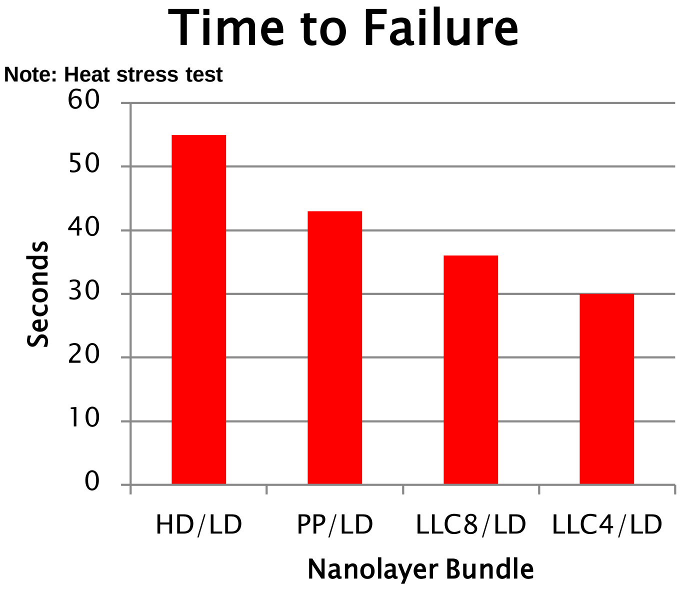
Critical Requirements
- Film web handling stiffness*
  - Secondary printing operation
  - High speed shrink wrapper
- Shrink Tunnel Heat resistance
- Puncture/Tear Characteristics
- Cost
- Shrink Properties

Nanolayer Approach

Sample	Skins	Encapsulating	Nanolayer Combination
A	LL	LL	HDPE/LDPE
B	LL	LL	PP/LDPE
C	LL	LL	LL (C4)/LDPE
D	LL	LL	LL (C8)/LDPE

Sample Results

Nanolayer Combinatio n	1% Secant Modulus MD/TD	Haze %	Tear MD/TD (gms) & Puncture (lbf)
HDPE/LDPE	38,813/48,480	7.7	305/554 & 2
PP/LDPE	36,319/41,854	8.8	289/604 &1.6
LL (C4)/LDPE	33,301/32,697	11.1	251/428 &1.7
LL (C8)/LDPE	26,730/30,429	10.6	251/657 &1.5



Example Summary & Benefit

- Potential to use commodity homopolymer polypropylene or high density in the formulation
- Potential to reduce gauge by a nominal 25%
- Potential to increase run speed on press as well as shrink tunnels
- Throughput increase due to increased bubble strength

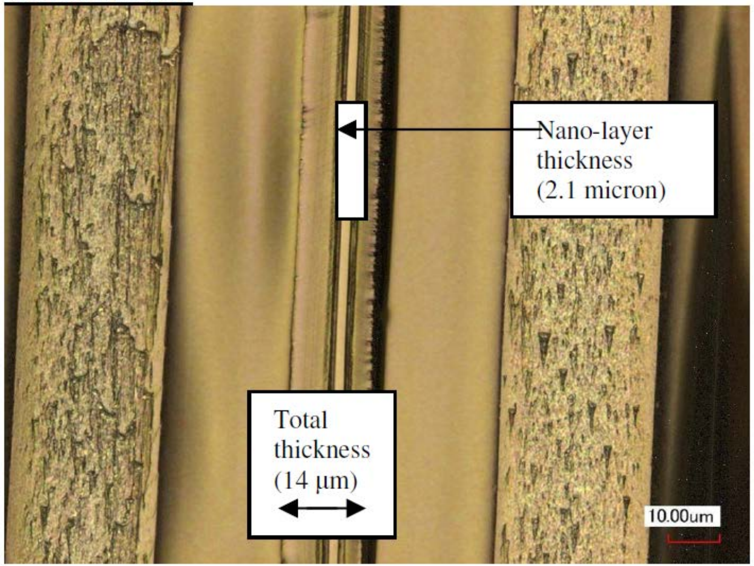
Ongoing Development

- LSR Proportion
- Barrier materials
- All nanolayer structures
- Nanoparticle additives
- Broadened scope of materials
- Temperature sensitive materials

LSR Proportion

- In the past year, work has been conducted that has resulted in the LSR proportion being as little at 10% and as much as 75%

Cross Section

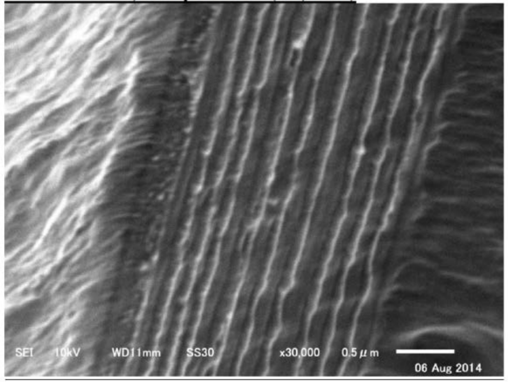


by Laser Digital Microscope(x2,000)

Barrier Materials

- Extensive work has been conducted on Nylon, EVOH, G21
- In this example evidence of cold stretch exits supported by increased barrier properties

Cross Section, Sample 22/16 (30,000x)



Calculated OTR vs. Measured OTR

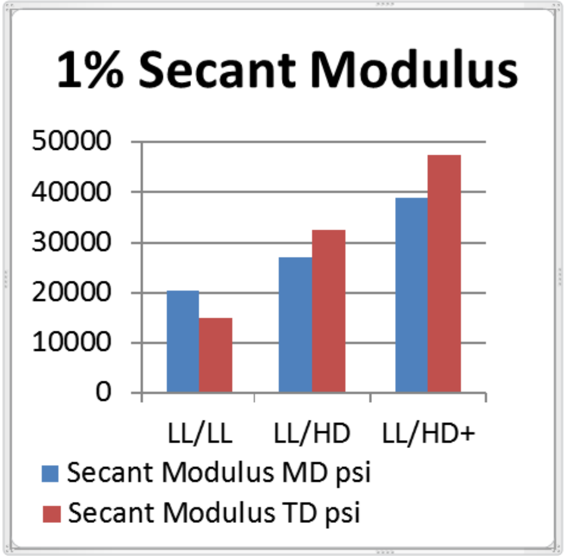
Sample ID	Nano-layers Total Thickness [um]	EVOH Thickness [a] [um]	Calculated OTR [cc/m^2.day.atm]			Measured OTR [cc/m^2.day.atm][d]
			OTR_{EVOH} [b]	$OTR_{a\text{-}Ny}$ [c]	OTR_{Total}	
22/16 (ET/a-Ny)	6.1	3.05	18.9	163.9	34	24
	5.9	2.45	23.6	204.1	51	25

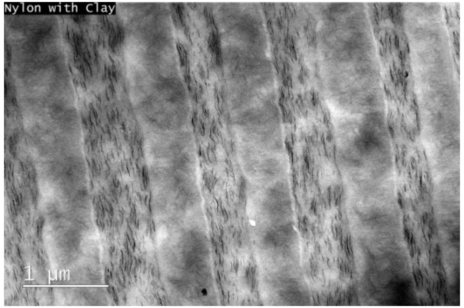
All Nanolayer Structures

- Empirical data is being evaluated on films made using the same material at 77 layers yielding significant improvement in properties compared to the single version of the same material
  - Not previously observed on less than 77 layers and on low BUR's

Additives

- The employment of nano/fine particle additives in nanolayer films yields substantial increase in properties while maintaining cost





Magnified cross section showing
Nanoclay platelets aligned
improving OTR performance
by 300% in alternating layers
Of nylon and tie material

Broadened Scope of Materials

- Films have been made utilizing
  - Polyester, polycarbonate, polyolefins, nylon, EVOH, adhesives, polystyrene, PVDC, Kraton, COC
    - If a resin is not on this list, it is most likely we have not been asked to test it to date

Summary

- Declarative Statements*
  - No loss in throughput, potential for highest throughput as compared to any existing technology
  - Potential to utilize more commodity raw materials
  - Potential to reduce overall gauge maintaining current properties
  - Potential to have properties not existing with any materials or process
  - Potential to produce more products on existing/new equipment
  - Potential to expand capabilities with incremental upgrades
- There is typically a minimum of 25% cost benefit available in this approach*

* Dependent on film formulation and application

Thank You

Questions