



Tie Layer Resins for Multi-layered Plastic Medical Applications



Overview

- ❖ Introduction
- ❖ What are Multi-layered Plastic tubes & films?
- ❖ What are tie layer resins?
- ❖ What are Grafted PolyOlefins?
- ❖ How does Bonding Occur?
- ❖ What can Effect Bonding?
- ❖ Technical Selection Criteria
- ❖ Additional Criteria to Consider
- ❖ Current Tie Layer Resins



What's new out there?

Introduction

- ❖ Nathan Doyle
 - Sales & Marketing Manager for Compounding Solutions
 - 7 years
 - Since 2010 helped grow CS to triple the size.
- ❖ Prior to CS worked at Cyclics Corporation for 7 years.
 - Research & Development Engineer
- ❖ Bachelors & Master of Science degrees in Material Science & Engineering from RPI.



What are Multi-Layered Tubes & Films?



What are Multi-layered Tubes and Films?

- ❖ Is the extrusion of multiple layers of material simultaneously to produce multi-layered tubing, also referred to as co-extrusion.

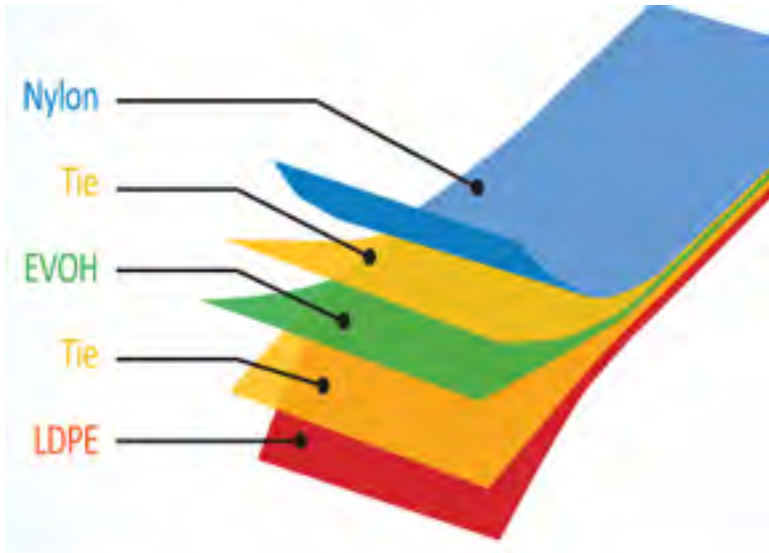


Figure 1 – Multi-layer Film

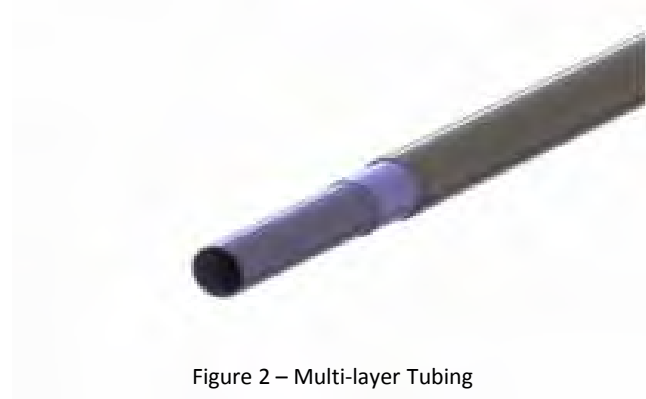


Figure 2 – Multi-layer Tubing

What are Multi-layered Tubes?

- ❖ The creation of tubing with different properties for the exterior and interior surfaces
- ❖ Materials with different properties to be combined to create unique tubing characteristics (increased functionality)
- ❖ Active materials to be located in their optimal location
- ❖ Bondable materials to be located inside or outside for ease of assembly of complex medical device
- ❖ Cost reduction

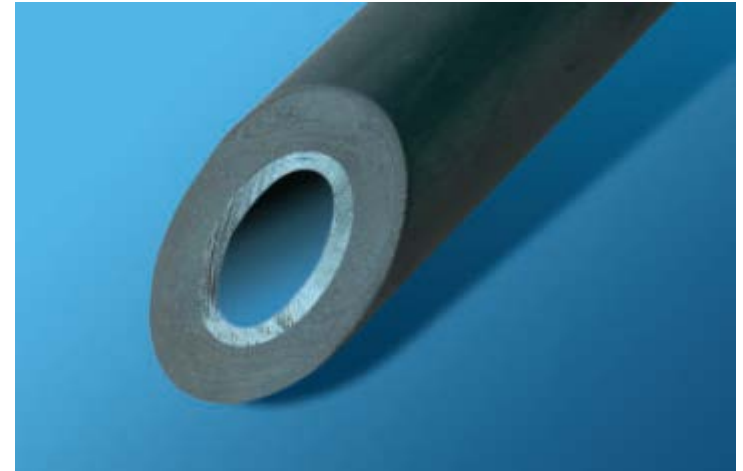


Figure 3 – Multi-layer Tubing



What are Multi-layered Tubes?

- ❖ Virtually all thermoplastic materials can be coextruded.
- ❖ Must take into account the material's processing temperature, flow characteristics and melt viscosity.
- ❖ Compatible materials will bond when extruded together.
- ❖ Dissimilar materials, a tie layer must be used, provides no additional mechanical functionalities and simply bonds the outer and inner layers



Figure 4 – Multi-layer Tubing

What are Multi-layered Tubes?

Multi-layer Component	Desired Primary Property on Inner Layer	Inner Layer Material	Desired Primary Property on Outer Layer	Outer Layer Material
PTA/PTCA Inner tubing	Lubricity	HDPE	Bondable to adjacent device components	Nylon 12
Infusion Tubing	Chemical Inertness	HDPE	Flexibility	PVC
Tungsten-Polymer Marker Band	Radiopacity	80% Tungsten filled PUR	Smoothness	PUR
Implantable Central Venous Catheter	Flexibility	PUR	Anti-microbial	Silver Ion-filled PUR
Coronary Implant Delivery System	Lubricity	HDPE	Bondable to adjacent device components	Pebax®

Table 1 – Multi-layer Tubing Device



What are Multi-layered Tubes and Films?



Figure 5 - Five Layer Extrusion Line

What are Tie Layer Resins?



What are Tie Layer Resins?

- ❖ Tie-layer resins are used as extrudable adhesives in coextrusion or coating operations to bond two dissimilar materials together that otherwise would have poor adhesion to each other. **
- ❖ Typically using in Tubing and Film packaging application.
- ❖ These tie-layer resins can be reactive or non-reactive.
- ❖ Non-reactive tie-layer resins achieve good adhesion through entanglement, polarity, or low level hydrogen bonding.
- ❖ With non-reactive tie-layer resins adhesion increases with increased temperature due to rate of diffusion of chain to entanglement.



What are Tie Layer Resins?

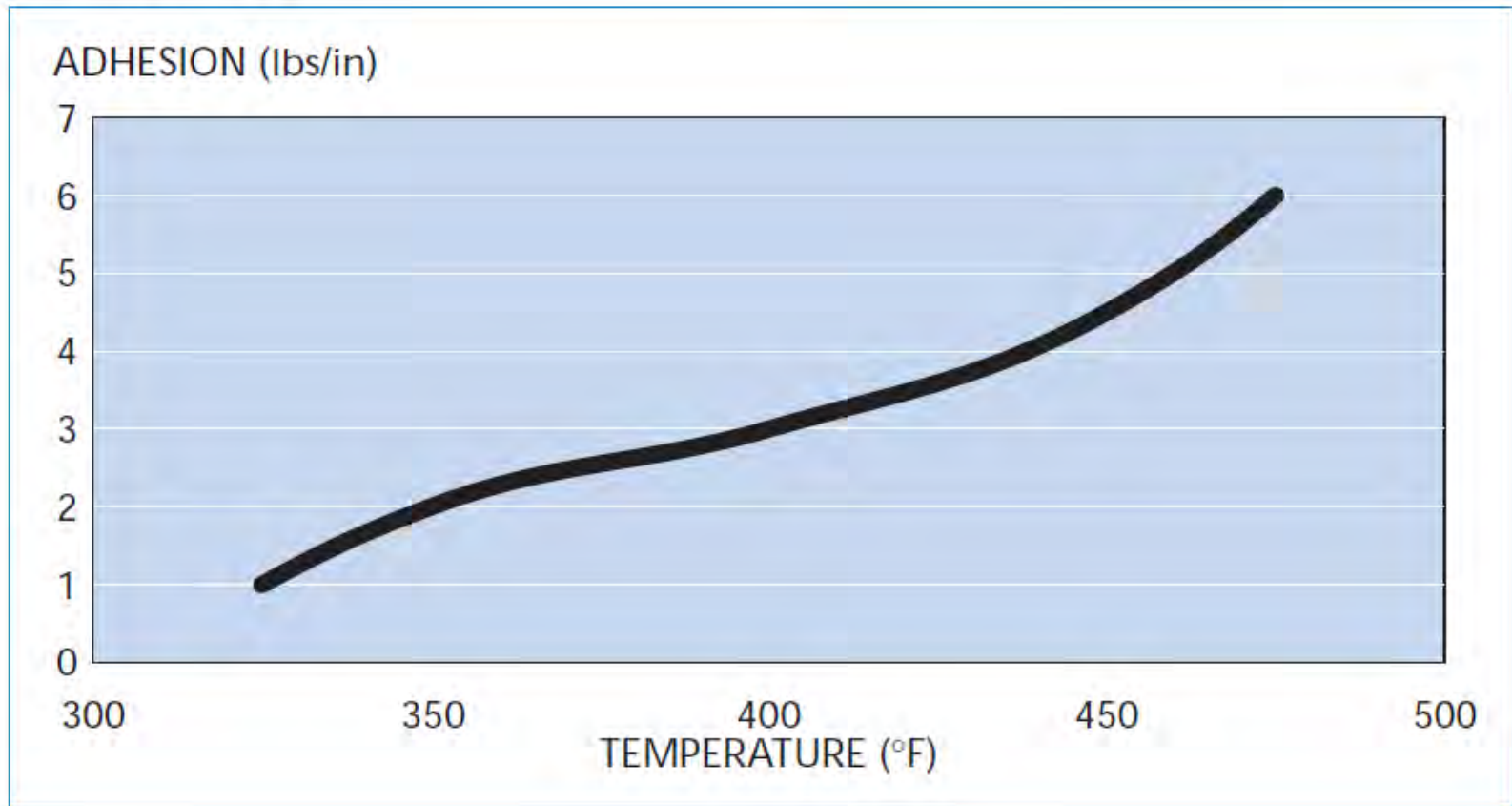


Figure 6 – Adhesion of an EVA Tie Layer

What are Grafted PolyOlefins?



What are Grafted PolyOlefins?

- ❖ Grafted PolyOlefin Tie layer resins are chemically modified with Maleic Anhydride (MAH). This can be done reactive extrusion with a modified twin screw extruder.

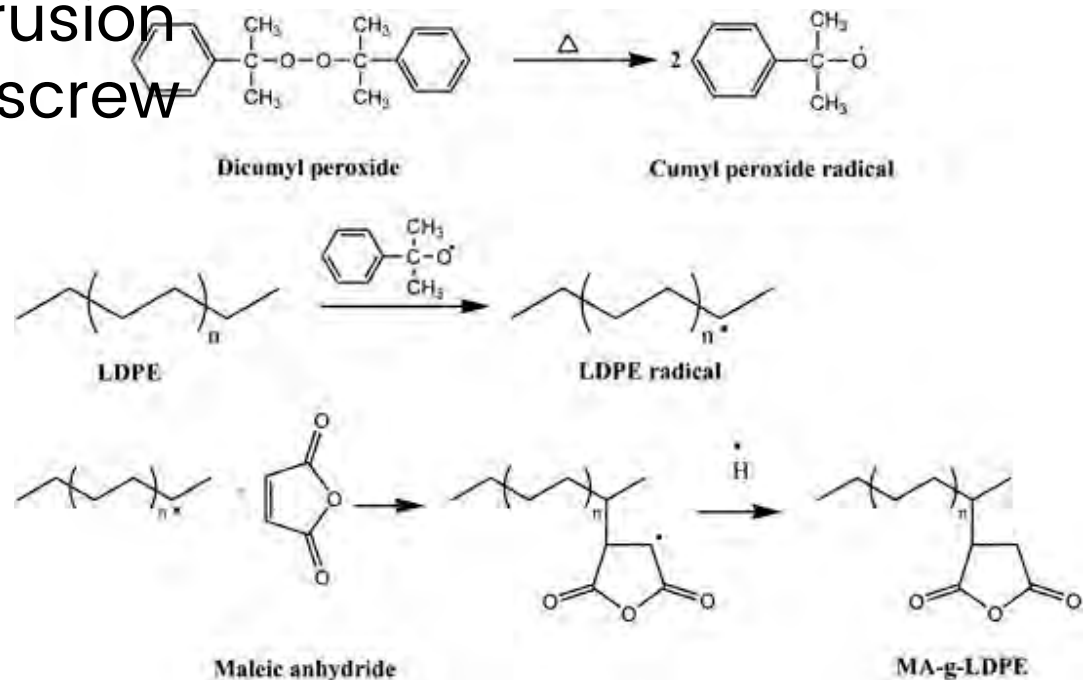


Figure 7 – Grafting Process of MAH to LDPE

What are Grafted PolyOlefins?

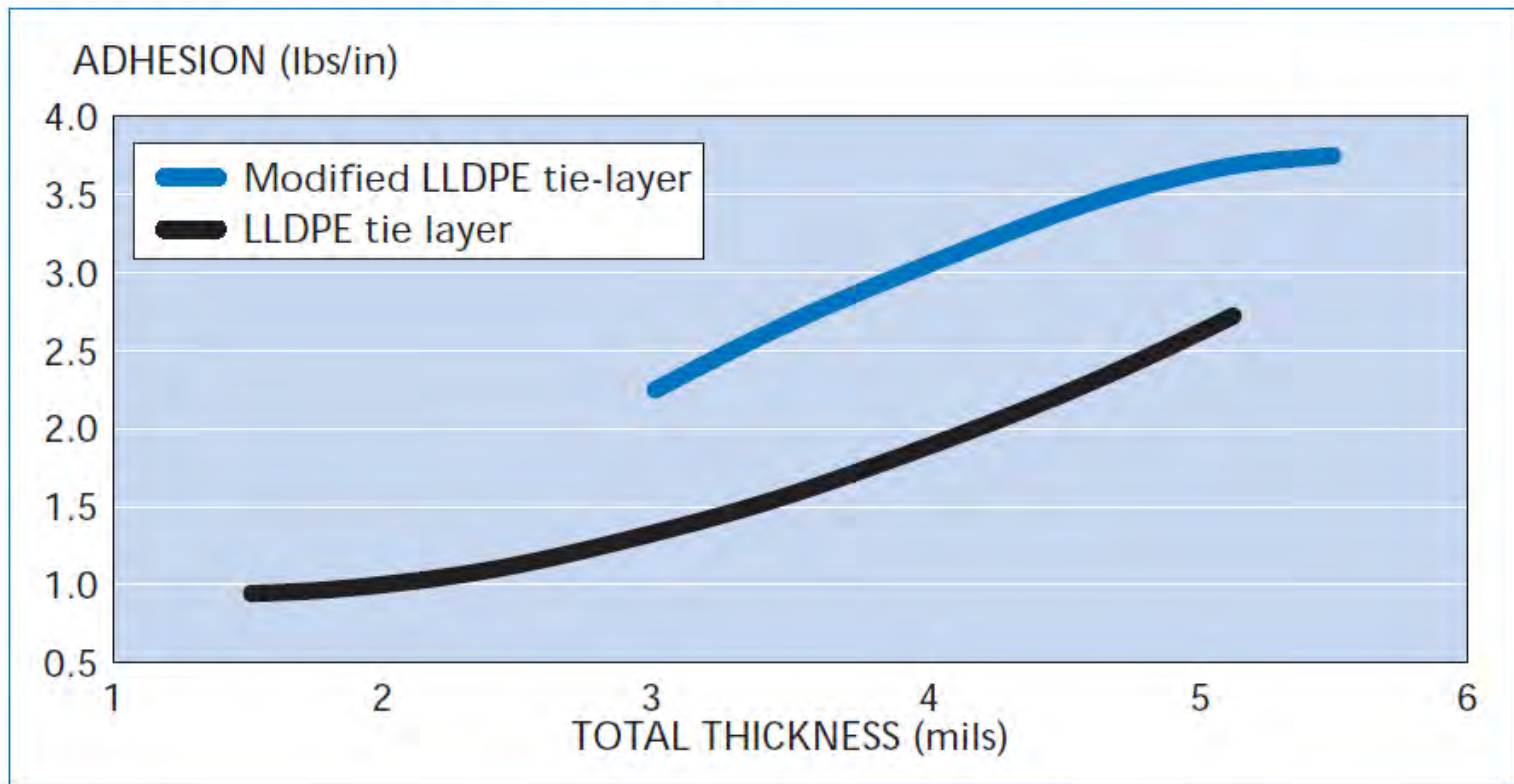


Figure 8 – Adhesion vs Thickness of a LLDPE Tie Layer

How does Bonding Occur?



How does Bonding Occur?

- ❖ Reactive tie-layer resins create covalent bonds by the reaction of two chemical groups and typically result in the highest adhesion.
- ❖ Covalent bonds can result from the reaction that occurs between the functional group in the tie-layer and the bonding substrate. Anhydrides will react with the groups that contain labile hydrogen, such as hydroxyls and amines.



How does Bonding Occur?

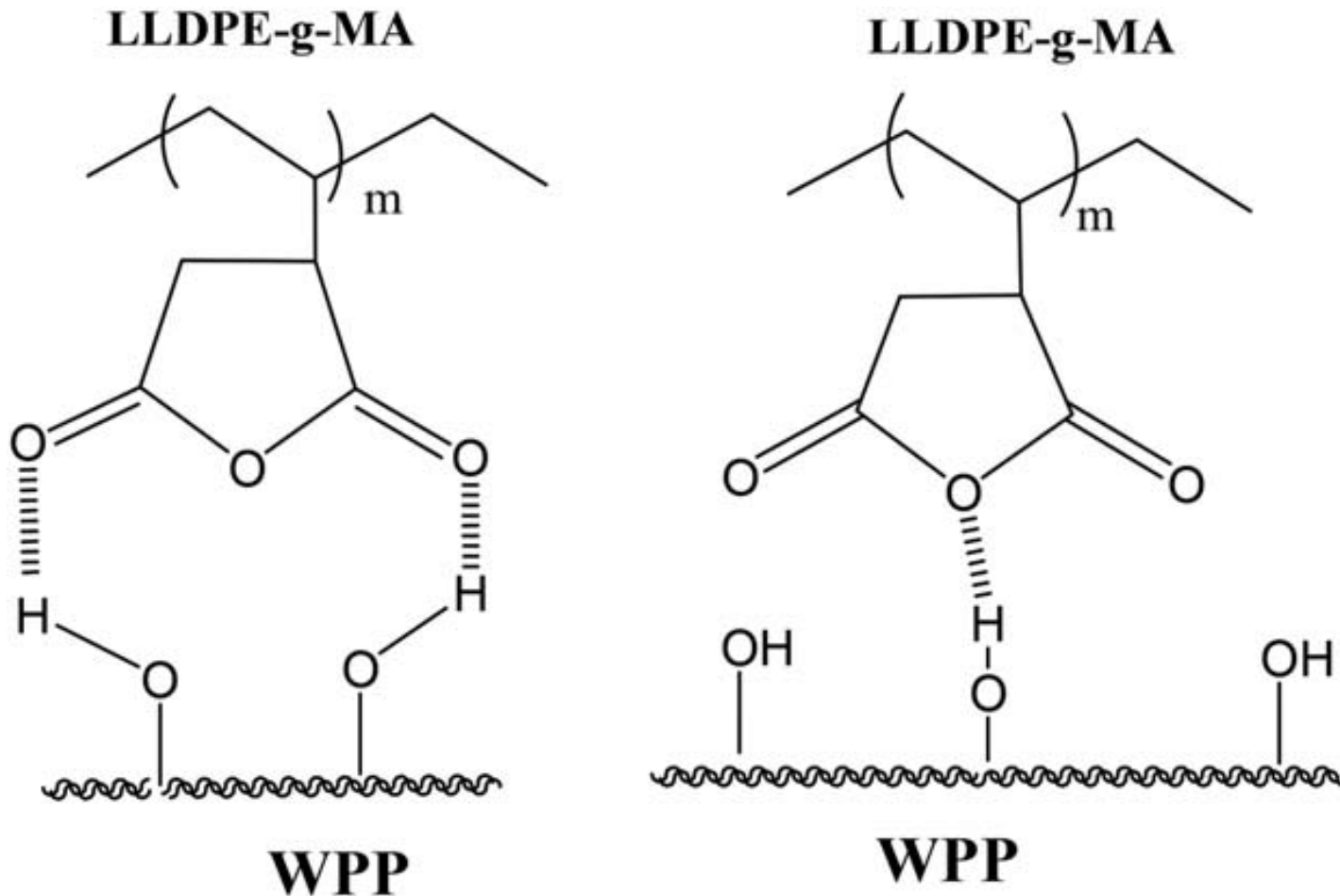


Figure 9 – Mechanism of MAH bonding to Substrate

What can Effect Bonding?



What can Effect Bonding?

Adhesion **increases**
with an increase in:

Adhesion **decreases**
with an increase in:






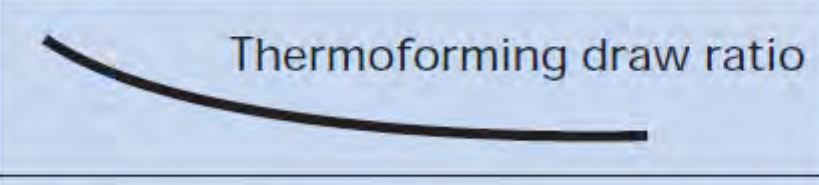
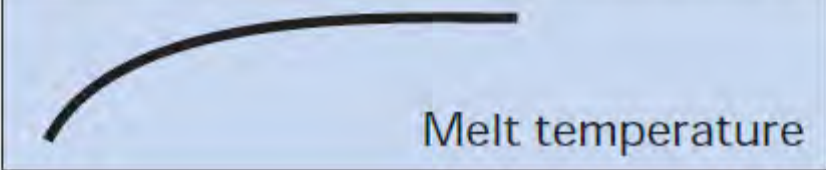
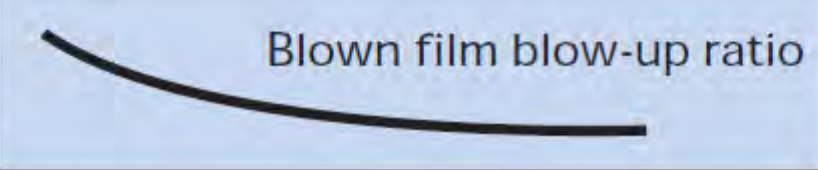
 <p>Tie-layer thickness</p>	 <p>Orientation</p>
 <p>Contact time</p>	 <p>Line speed</p>
 <p>Functionality</p>	 <p>Thermoforming draw ratio</p>
 <p>Melt temperature</p>	 <p>Blown film blow-up ratio</p>

Table 2 – Effects on Adhesion Strength

Technical Selection Criteria



Technical Selection Criteria

- ❖ Adhesion Strength
- ❖ Substrates to be bonded
- ❖ Physical requirements
- ❖ End-use requirements
- ❖ Optical Requirements
- ❖ Conversion methods
- ❖ Regulatory Requirements
- ❖ Processing Temperature

EVA	Clarity	Polarity For Adhesion
LDPE-g	Processability	Clarity
LLDPE-g	Elongation	Tensile Strength
HDPE-g	Moisture Barrier	Stiffness

Table 3 – Tie Layer Materials Selection Criteria



Additional Criteria to Consider



Additional Criteria to Consider

- ❖ Melt Index
 - ❖ The melt index of the tie layer should be selected so that the layers in contact have similar viscosities; otherwise, flow instabilities can lead to waviness or poor layer distributions.
- ❖ Storage Conditions
 - ❖ MAH grafted resins should be stored at room temperature, in a low humidity area.
 - ❖ The resin should be in a seal bag if to re-stored and reused.
- ❖ Drying
 - ❖ Moisture will react with the MAH to create diacids, resulting in low adhesion.
- ❖ Clean out Procedures
 - ❖ If shutdown improperly, MAH-g-PolyOlefins will degrade within 30min, creating gels and char. Use a fractional melt PE to purge.



Current Tie Layer Resins



Current Tie-Layer Resins Used in Medical Applications

❖ EVA

- ❖ Elvax
- ❖ Ateva

❖ PolyOlefin-g-MAH

- ❖ Plexar
- ❖ Orevac
- ❖ Lotader
- ❖ Bynel
- ❖ Amplify
- ❖ Polybond

❖ Current Issues

- ❖ Availability
 - ❖ Long lead times
 - ❖ Non-stocked items
- ❖ High Minimums
 - ❖ 1500lbs or more
- ❖ Overall pullback from the medical industry.
- ❖ Animal-Derived Components
- ❖ No Biocompatibility testing complete
- ❖ Resistance to no change agreements
 - ❖ Risk to supply chain
 - ❖ Discontinuation



What's New out there?



What's new out there?



Figure 10 – Black hole

At the moment there is no Anhydride-Modified Polyolefin product that meet the following medical requirements.



What's the Medical Market Needs?

- ❖ Availability
 - ❖ 3 day lead times
 - ❖ Always in stock
- ❖ Low Minimum Order Quantities
 - ❖ 10lbs
- ❖ ISO10993-05 Cytotoxicity Testing
- ❖ No Animal-Derived Components
- ❖ No change agreements
 - ❖ 12 months would be favored
 - ❖ Last time buy options
- ❖ Offset to current product offering
- ❖ Good for Tri-layer tubing and multi-layer film packaging for the medical/Pharma industry



ReZilok Rx 101

Test	Units	Admer AT1414	Orevac 18360	Plexar 3080	ReZilok Rx 101
Density	g/cc	0.92	0.91	0.91	92
MFI	g/10min	1.9	2	1.8	2
Hardness	ShA	100	95	95	95
FTIR	vs. Rezilok	90%	90%	95%	-

Bonding to Substrates:
ReZilok = Plexar > Orevac > Admer



Questions



Acknowledgements

- ❖ Shawn Champagne, R&D Manager, Compounding Solutions
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 - ❖ Figure 10



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- ❖ Figure 1



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