CoPolymers in Extrusion Coating
What, Why, Where?

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Δ DuPont Packaging & Industrial Polymers
Selecting a Specialty Resin

What do you have to consider?

➤ Processability
➤ Coextrudability
➤ Physical Properties
➤ Barrier Properties
➤ End use requirements
➤ Economics
What Does A Specialty Resin Have To Exhibit?

➤ Good Processability:
   ➤ --- for the **Extrusion Coating** converter
      ➤ good melt quality
      ➤ good drawability
      ➤ good “green” adhesion to substrates
      ➤ good adhesion to coextruded layers
      ➤ runs on conventional equipment
      ➤ does not require excessive horsepower
      ➤ not too difficult to purge from extrusion system
      ➤ etc…..
What Does A Specialty Resin Have To Exhibit?

➤ Good end-use properties: --- for the Packager
  ➤ *sealability* (through contaminants); *peelability* sometimes
  ➤ long term *adhesion* to adjacent layers and substrates
  ➤ contributes to machineability of structure on end user equipment (if it does not run at customer, processing in your shop does not mean a thing)
    ➤ proper COF, stiffness, durability, static, etc…
  ➤ *durability* of seals / adhesions / barrier, when exposed to;
    ➤ aggressive “chemicals” (oils, surfactants, spices,…)
    ➤ modified atmosphere gas pressures
    ➤ vacuum packaging
    ➤ etc…..
Selecting a Specialty Resin: The “Choices”

- **POLYETHYLENE FAMILY**
  - LDPE
  - LLDPE
  - HDPE
  - mPE

- **POLYPROPYLENE**
  - CoPP extr/ctg
  - CPP film

- **SPECIALTY RESINS**
  - E / VA
  - E / acrylates
  - E / terpolymers
  - Acid Copolymer
  - Ionomer
  - PET
  - Nylon, EVOH, ...
EVA (ethylene vinyl acetate)

CHEMISTRY

Adding VA to the polymer gives:

1) lower crystallinity
2) slight polarity
EVA
Characteristics

**Increasing the percent Vinyl Acetate:**
- increases adhesion to many things
- increases toughness
- increases flexibility
- increases optics
- lowers seal initiation temperature
- increases tackiness
- increases “vinegar” odor
- increases “chill roll sticking”
EVA
Characteristics

➤ **EXTRUSION ISSUES:**

➤ not moisture sensitive

➤ limited to processing temp **max of 235C (455F)**

➤ “Vinegar” (acetic acid) type odor

➤ Tackiness: with increasing VA content

➤ in coextrusion, EVA will bond with:
  ➤ PP, PE, PS, PVC, PVdC, and other resins to various degrees

➤ you must **purge it out well** before raising extruder temps back above 235C or before a shutdown.
EVA Resins
Selection Factors

- Resins typically available for extrusion coating and films:
  - 2.0% - 50% VA / 0.35 - 43.0 MI (dg/min)
- Additive grades available containing slip, anti-block, chill roll release
- Suppliers: many worldwide in low VA levels (up to 15%); several worldwide in high VA level (15 - 50%)
  - DuPont, Exxon, Arkema,
  - Celanese (formerly AT-Plastics), LyondellBasell (formerly Equistar)
  - etc......
- A resin will be chosen FIRST based upon the end use performance characteristics needed, and the processability for extrusion coating, blown film, or cast film production.
EVA application examples in Flexible Barrier Pkgg, via Extr/Ctg

- **Block Cheese package sealant**
  - OPP-PVdC / ink / primer / 18% EVA with slip

- **Cookie / biscuit package sealant**
  - OPP-ink / adhesive // met-OPET / primer / PE / EVA

- **Condom package sealant**
  - OPET-ink / adhesive // Alu foil / PE / EVA
  - Cello-ink / primer / PE / Alu foil / PE / EVA
Ethylene Acrylate Copolymers

Features:
- similar to EVA, but with **thermal stability up to 310°C** (590°F).
- Used more in **Industrial** versus **Packaging**.
- will adhere to various materials in coextrusion
- have “acrylate” smell (instead of “vinegar” smell of EVA)

Suppliers:
- **DuPont** EBA, EEA, EMA;  **Mitsui-DuPont** EEA;
- **Exxon** EnBA, EMA;  **Arkema** EBA, EMA;
- **Dow** EEA;  **Westlake** EBA, EMA
- **Mitsubishi** EMA, EEA

MA=methyl acrylate, EA=ethyl acrylate, BA=butyl acrylate, nBA=normal butyl acrylate, iBA=isobutyl acrylate
Molecular structures

EBA  (ethylene-butyl acrylate)

EEA  (ethylene-ethyl acrylate)

EMA  (ethylene-methyl acrylate)

EVA  (ethylene-vinyl acetate)
Ethylene based Terpolymers

- Polymers produced by polymerization of three feed streams, of which one is ethylene to create the major components of the molecular chains. These are “functionalized” resins.
- The 2nd and 3rd monomers can come from a variety of options;
  - various acrylate types, maleic acid/anhydride, acrylic or methacrylic acids, carbon monoxide, vinyl acetate, etc…
- Suppliers:
  - DuPont and Mitsui-DuPont
  - Arkema, Exxon, Sumitomo
Adding MAA (or AA) to the polymer gives:

- lower crystallinity
- strong polarity
- attraction between the polymer chains
Types of Acid

Methacrylic acid:
(E/MAA)

Acrylic acid:
(E/AA)
ACID COPOLYMER
CHARACTERISTICS

Excellent metal (aluminum) adhesion
Low sealing temperature
Very good hot tack strength (melt strength)
Broad sealing temperature range
Good Toughness
Good paper adhesion
Extrusion Issues:
- runs basically like LDPE
- not moisture sensitive
- can be used as tie layer for some resins
- requires corrosion protected equipment
- needs to be “purged” after use, and not left in the equipment at shutdown
- some degree of tackiness
- can cross-link at high extruder temperature or residence time.
ACID COPOLYMER RESINS

E/MAA (ethylene methacrylic acid):
  ➢ DuPont

E/AA (ethylene acrylic acid):
  ➢ Dow, DuPont, and Exxon

3% - 12% acid content common available commercially, but higher weight percent grades are also available.

For extrusion: 0.8 - 20 MI (dg/min)

Additive grades available containing slip, antiblock, and / or chill-roll release.
ACR application examples in Flexible Barrier Pkgg

- Edible oil stand up pouches and flavored oil sachets sealant
  - OPET or BONy - ink / primer / ACR
  - OPET or BONy / ink / adhesive // (PE - ACR)

- Shampoo sachet foil adhesion/sealant
  - OPET-ink / primer / PE / Alu Foil / ACR
  - OPET-ink / adhesive // vmPET / adhesive // (PE - ACR)

- Condiment foil adhesion/sealant
  - OPET-ink / primer / PE / Alu Foil / ACR
  - OPET-ink / primer / white ACR / Alu Foil / LLDPE

- Toothpaste tube tie layer
  - PE film / (white PE- ACR) / Alu Foil / (ACR – PE )/ PE film
IONOMER CHEMISTRY

Partially neutralizing the acid:

- gives outstanding melt strength
- retains adhesion properties
Ionomer Clusters

“Thermally reversible crosslinks”
IONOMER CHARACTERISTICS

- Excellent hot tack strength
- Excellent optics
- Excellent oil/grease resistance
- Excellent formability
- Excellent seal through contamination
  - especially meat fats
- Very good metal (aluminum) adhesion
- Low sealing temperature
- Very broad sealing temperature range
IONOMER

- **Extrusion Issues:**
  - runs basically like LDPE, but with slightly more torque needed
  - *moisture sensitive*
  - some degree of tackiness
  - needs to be “purged” after use, and not left in the equipment at shutdown
  - can cross-link at high extruder temperature or residence time
  - can be used as tie layer for some resins
  - *requires corrosion protected equipment*
IONOMER RESINS

Grades can be modified by:

- base acid content
- neutralization ion type and neutralization level
- viscosity (molecular weight) of the base resin
- viscosity of the final product (0.7 - 14 MI)
- Additive grades available containing slip, antiblock, and/or chill-roll release

Traditional & Newer Suppliers:

- DuPont (very long history of supply)
- Exxon (medium history of supply)
  - Dow, Schulman (new entrants to market)
IONOMER end-use examples

Processed meat sealant
Canister inner liner
Snack food sealants
Cookie/Biscuit sealants
Condom Package sealants
Skin Packaging films
Powdered Products
Ionomer application examples in Flexible Barrier Pkgg

➤ Flavored Cereal Box liner sealant:
  ➤ (HDPE – tie – EVOH – tie – Ionomer)
    ➤ Made via coex film
  ➤ OPP / adhesive // metallized PET / (PE – ionomer)
    ➤ Made via lamination and coating

➤ Barrier Lidding:  via lamination and coating
  ➤ Paper/adh// Alu foil / Ionomer
  ➤ OPET-PVdC/ink/primer/PE/ Alu foil / Ionomer
Peel Seal Resins

Typically these are *formulated* resins.

They commonly use base resins of:

- LDPE, EVA, Acrylate copolymers, Acid copolymers, …
- they may contain one or more of the following modifiers:
  - “tackifiers” --- modified phenols for example
  - “rubberizers” --- EPR or mVLDPE for example
  - “controlled contaminants” --- PB for example
  - fillers and other materials……

Suppliers:  - resin manufacturers;  - converter’s own formulae  
  - ‘ready to use’ resins from suppliers such as  
    - DuPont, Toyo Petrolite, Showa-Denko, Hiroydyne, etc……
面霸120
Selecting a resin for Ext/Ctg as a Sealant:

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Some Sealing Properties</th>
<th>Some Processing Properties</th>
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<td>Hot Tack Temp Range</td>
<td>Low Seal Temp</td>
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x=fair performance  xxxx=high performance
Selecting a resin for Film as a Sealant:

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What’s on the Horizon?

New polymers…
New additives…
Improved polymers…
Improved additives…
New treatments…
… etc.
Thank You

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         DuPont Packaging & Industrial Polymers

Please remember to turn in your evaluation sheet...