Specialty Resins for Blown & Cast Films, and Extrusion Coatings

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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 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

Adding VA to the polymer gives:

**VA**

\[
\text{CH}_3 \quad \text{C} = \text{O} \\
\text{O} \\
\text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\
\]
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 235°C (455°F)**
  - “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 235°C or before a shutdown.
EVA Resins
Selection Factors

- Resins typically available for extrusion coating:
  - 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, AT-Plastics, Equistar, Arkema, 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 Extrusion Coating

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

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

- **Condom package sealant**
  - OPET-ink / adhesive // foil / PE / EVA
  - Cello-ink / primer / PE / foil / PE / EVA
EVA application examples in Film Extrusions

- Cereal Box liner sealant:
  - (HDPE - HDPE - 18% EVA with additives)

- Vacuum Skin Packaging films:
  - (ionomer - high% 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; **Eastman** EBA, EMA;
- **Dow** EEA; **Arkema** 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
ACID COPOLYMER

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.
ACID COPOLYMER end-use Extrusion Coating examples

- Flavored edible oil sachet sealant
  - OPET or BONy - ink / primer / ACR

- Shampoo sachet foil adhesion/sealant
  - OPET-ink / primer / PE / foil / ACR

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

- Toothpaste tube tie layer
  - PE film / white ACR / foil / ACR / PE film
ACID COPOLYMER end-use
Film Extrusion examples

- Edible oil standup pouch sealant
  - OPET or BONY / ink / adhesive // (PE - ACR)

- Shampoo sachet sealant
  - OPET-ink / adhesive // vmPET / adhesive // (PE - ACR)

- Cable Shielding thermal laminating film
  - Black PE / (PE - ACR) //TL// 200u alu foil //TL// (ACR - PE) // cable bundle
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
- Very good metal (aluminum) adhesion
- Low sealing temperature
- Very broad sealing temperature range
Film Stiffness

Stiffness increases w/neutralization

- SSC mPE's
- CGCT mPE's
- Z-N LPE's
- EVA resins
- Ionomers
- E/MAA

Weight Percent Comonomer

% Secant Modulus (kpsi)
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
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

Suppliers:

- DuPont and Exxon
IONOMER end-use examples

- Processed meat sealant
- Canister inner liner
- Snack food sealants
- Cookie/Biscuit sealants
- Condom Package sealants
- Skin Packaging films
- Powdered Products
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, Hiroyde, etc……
Coextrudable Adhesive Resins
(“Tie” Resins)

- Used to bond together resins in a “coextrusion”
- Some resins will bond to others to various degrees of strength
  - e.g.-- EVA bonds to many things if the VA level is high enough, but perhaps not sufficiently.
- Thus, “tie” resins are formulated with additions of grafted materials, or other compounded modifiers to enhance adhesion
- Proper choice of the correct “tie” resin is based on many variables. Processing parameters, enduse parameters, etc…
- Consult your “tie” resin supplier.
Coextrudable Adhesive Resins
(“Tie” Resins)

- **Base Resins:**
  - LDPE, LLDPE, HDPE
  - EVA, PP
  - Acrylate copolymers
  - Acid copolymers

- **Modifiers:**
  - maleic anhydride
  - olefinic tougheners
  - tackifiers
  - rubbers

**Suppliers:**
- DuPont
- Equistar
- Rohm & Haas
- Mitsui
- Mitsubishi
- DSM
- Arkema
- ...and several others.
Coextrudable Adhesive Resins
(“Tie” Resins)

Extrusion Issues:

- get help to choose correct resin
- watch for temp limits on EVA based tie resins
- must match “rheology” with adjacent materials
  - layer uniformity, no “interfacial instability”
- there is a minimum temp needed for generating adhesion with some materials
- coextrusion feedblock and die design are also influential factors for adhesion
- extrusion “process time” is also an important factor. Time of “cooling / drawing” of resins varies.
Selecting a resin for Ext/Ctg as a Sealant:

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<th>Some Sealing Properties</th>
<th>Some Processing Properties</th>
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<td>Hot Tack Peak Str</td>
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<td>mLLDPE</td>
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<td>EVA</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.