Packaging & Industrial Polymers

Specialty Resins for Extrusion Coating & Films

Scott Marks

E. I. du Pont de Nemours & Company

TAPPI - “PLACE” Short Course

August 24 – 26, 2010

Charleston, SC

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?

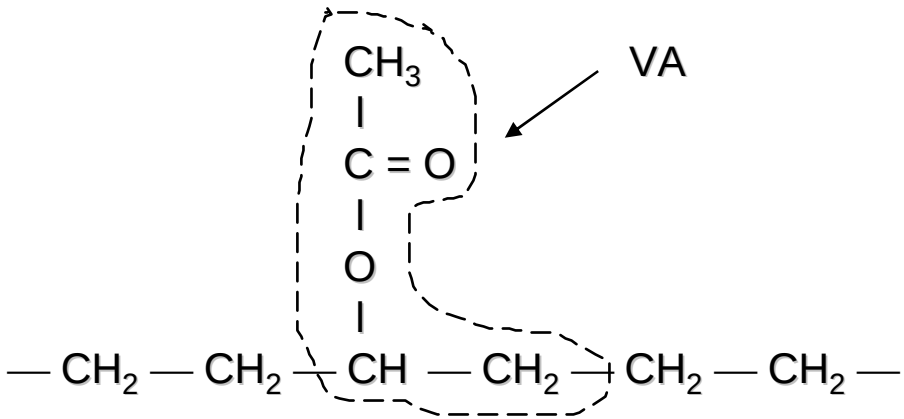
- Good end-use properties: --- for the Packager
  - **sealability** (through contaminants); **peelability** sometimes
  - long term **adhesion** to adjacent layers and substrates
  - contributes to machineability of structure on end user equipment (if it does not run at customer, processing in your shop 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

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, ExxonMobil, AT-Plastics, Equistar, Arkema, etc…...
- A resin will be **chosen <u>FIRST</u> 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)

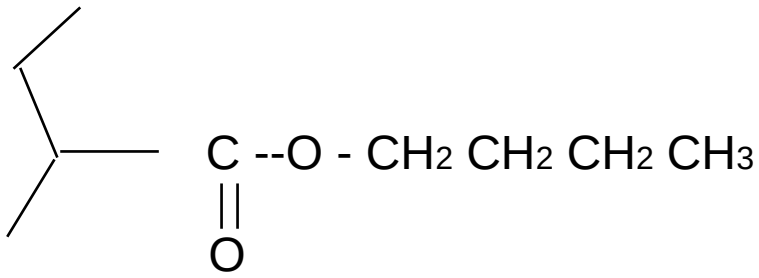
- Vacuum Skin Packaging films:
  - (ionomer - high% EVA)

Ethylene Acrylate Copolymers

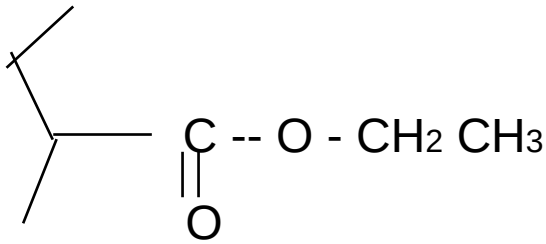
- Features:
  - similar to EVA, but with thermal stability up to 310C (590F).
  - Used more in **Industrial** versus **Packaging**.
  - will adhere to various materials in coextrusion
  - have “acrylate” smell (instead of “vinegar” smell of EVA)
- Suppliers:
  - **DuPont** EBA, EEA, EMA; **Mitsui-DuPont**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

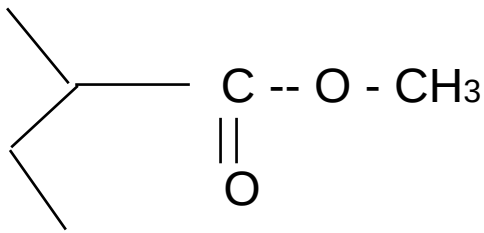
EBA (ethylene-butyl acrylate)



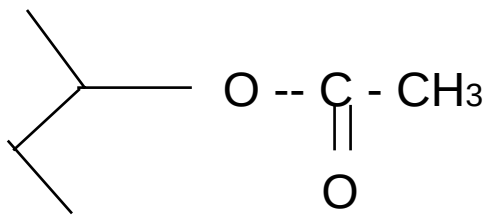
EEA (ethylene-ethyl acrylate)



EMA (ethylene-methyl acrylate)



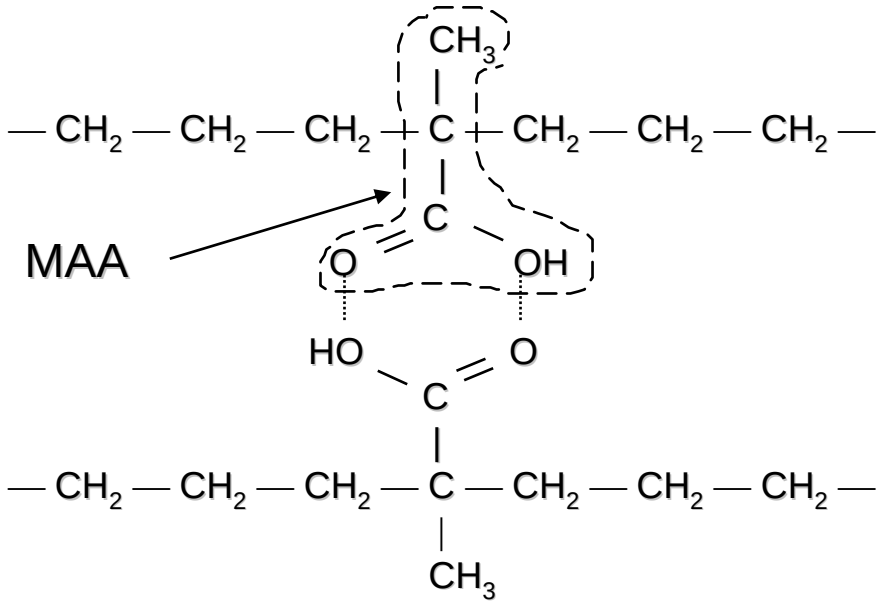
EVA (ethylene- vinyl acetate)



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, ExxonMobil, Sumitomo

ACID COPOLYMER CHEMISTRY



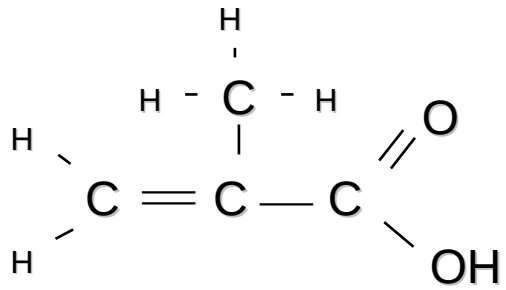
Adding MAA (or AA) to the polymer gives:

- lower crystallinity
- strong polarity
- attraction between the polymer chains

Types of Acid

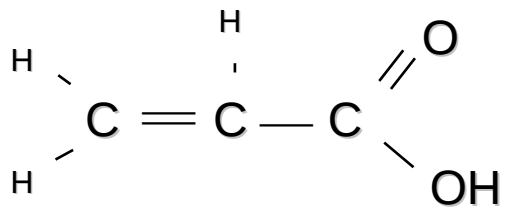
Methacrylic acid:

(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 ExxonMobil

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.

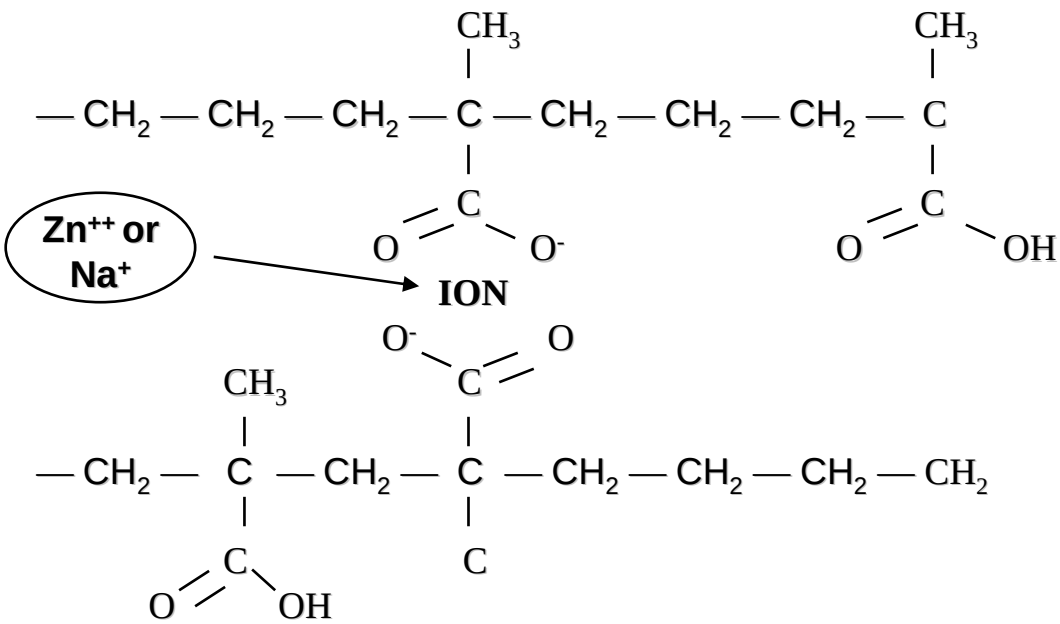
ACID COPOLYMER end-use Extrusion Coating examples

- 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 PE- ACR) / foil / (ACR – PE)/ 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

IONOMER CHEMISTRY

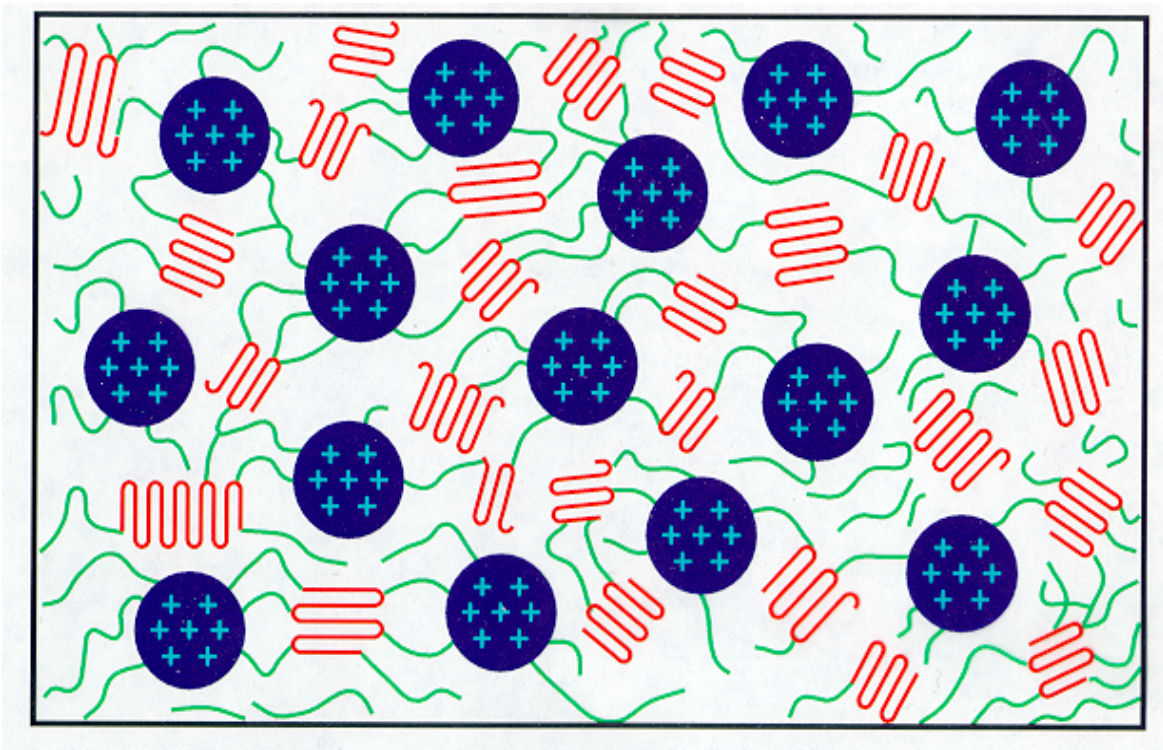


Partially neutralizing the acid:

- 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

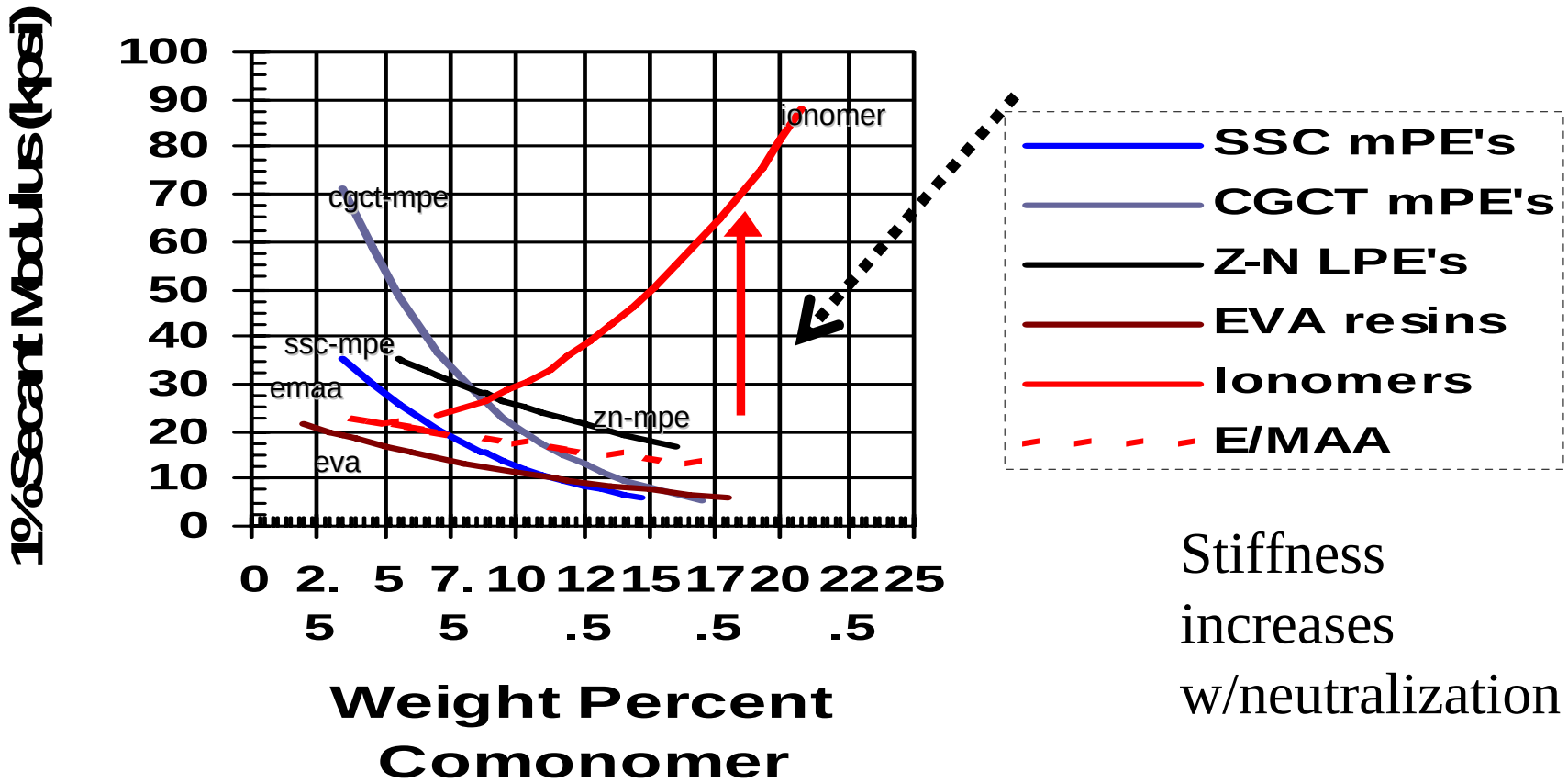
Excellent seal through contamination

Very good metal (aluminum) adhesion

Low sealing temperature

Very broad sealing temperature range

Film Stiffness



Stiffness increases w/neutralization

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

Suppliers:

- DuPont (very long history of supply)
- ExxonMobil (medium history of supply)
- Dow, Schulman (newer 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

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, Hirodyne, etc…...

Selecting a resin for Ext/Ctg as a Sealant:

Resin Type	Some Sealing Properties				Some Processing Properties			
	Hot Tack Peak Str	Hot Tack Temp Range	Low Seal Temp	Seal Thru Contam	Foil Adh	Draw-ability	Low Ext Torque	Low Neck-in
LDPE	x	x	xx	x	X	XX	XXXX	XX
mLLDPE	xx	x	x	xx	X	X	X	X
EVA	xx	xx	xxxx	xx	NIL	XX	XX	XX
EMA	xx	xx	xxxx	xx	X	XX	XXX	XX
mVLDPE	xxxx	x	xxxx	xxx	X	X	X	X
Acid Copolymer	xxx	xxx	xxxx	xxx	XXXX	XXX	XXX	XXX
Ionomer	xxxx	xxxx	xxxx	xxxx	XXX	XXXX	XXX	XXXX

x=fair performance xxxx=high performance

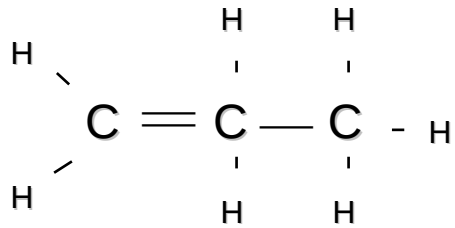
Selecting a resin for Film as a Sealant:

Resin Type	Some Sealing Properties				Some Processing Properties			
	Hot Tack Peak Str	Hot Tack Temp Range	Low Seal Temp	Seal Thru Contam	Tackiness	Draw	Low Ext Torque	Bubble Strength
LDPE	x	x	xx	x	X	X	XXXX	XX
mLLDPE	xx	x	x	xx	X	XXX	X	X TO XX
EVA	xx	xx	xxxx	xx	X TO XXXX	XX	XXX	X TO XX
EMA	xx	xx	xxxx	xx	X TO XXX	XX	XXX	X
mVLDPE	xxxx	x	xxxx	xxx	X TO XXX	XXXX	X	X TO XX
Acid Copolymer	xxx	xxx	xxxx	xxx	XX	XXX	XXX	XXX
Ionomer	xxxx	xxxx	xxxx	xxxx	XX	XXXX	XXX	XXXX

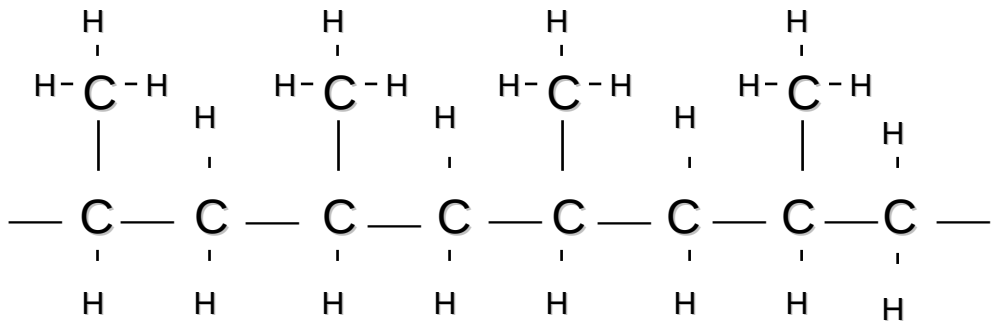
x=fair performance xxxx=high performance

POLYPROPYLENE

Made from propylene:



Polypropylene:



Film is often oriented (“OPP”) to improve strength, optics, and barrier properties

PROPERTIES OF POLYPROPYLENE

Good clarity

Relatively low cost

Good moisture barrier

Good seal strength

No oxidation needed

POLYPROPYLENE AS A SEALANT

"Copolymer" - propylene / ethylene

"Terpolymer" - propylene / ethylene / butene or others...

- ➢ reduced crystallinity
  - ➢ lower sealing temperature (but still high vs. PE)

Snack package:

- ➢ OPP-ink /primer/LDPE/metal-OPP/CoPP extr.ctg.
- ➢ OPP-ink/CoPP extr.ctg.
- ➢ OPP-ink/adhesive//vmCPP cast film

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
Mitsui
Equistar
Mitsubishi
Arkema
Dow (Rohm & Haas)
DSM
…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 importanat factor. Time of "cooling / drawing" of resins varies.

Nylon

- Types:
  - Nylon 11 and 12: MP= 180C (360F)
  - Nylon copolymers: MP= 210C (410C)
  - Nylon 6: MP= 220C (430F)
  - Nylon 66: MP= 250C (480F)
  - Amorphous Nylon
- Nylon screws are generally a different design than screws for PE and ethylene copolymers
- Suppliers:
  - Honeywell, BASF, Bayer, DuPont, EMS,
  - Mitsubishi, Ube, etc…

Nylon

- Features:
  - Good gas barrier
  - Good thermoformability
  - Good toughness, abrasion resistance, tensiles...
  - Good optics
  - Good oil resistance

Nylon

- Extrusion Issues:
  - **crystalline melt point**
  - flow properties change rapidly from solid to melt and back to solid. SAFETY!
  - moisture sensitive
  - various types, so need to choose extrusion temperature profiles carefully
  - “high” extrusion temperature needed
  - almost always processed in coextrusion

POLYESTER

Many types of polyester:

- ➢ most important type for films / sheet is PET (polyethylene terephthalate)

PET is typically oriented to provide strength, clarity, and barrier properties.

PET for extrusion coating is more challenging than olefins, and requires special equipment. Use of coextrusion makes it easier for running, but you still need dryers and proper screw designs for the PET.

Suppliers of extrusion coating grades in the USA would be: Eastman, DuPont, M&G (formerly Shell), ...

EVOH
Ethylene Vinyl Alcohol

- good oxygen barrier when dry
- almost always run in coextrusion
  - needs tie layers (except to Nylon)
- moisture sensitive
- thermal sensitivity
  - **needs short, smooth flow paths**
- good optical properties
- high stiffness
- flex crack sensitivity
- Suppliers:
  - Evalca, Kuraray, Nippon-Gohsei

What’s on the Horizon?