2016 ASC HOT MELT SHORT COURSE

Amorphous Poly Alpha Olefin (APAO) Based Hot Melts

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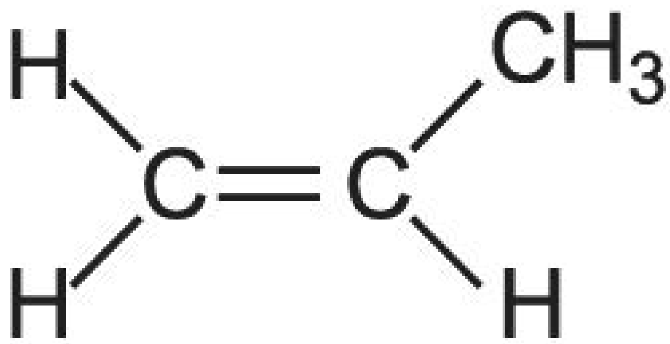
Outline

I. Brief historical description of the evolution of:
   Atactic polypropylene, APP; amorphous poly alpha olefins, APAO, or amorphous polyolefins, APO
II. Relevant properties that describe the physical and mechanical properties of APAO
III. Comparison between APAO and other polymer technologies.
IV. Industries/Markets
V. Addendum

I. Background, Historical Development

- Isotactic polypropylene (iPP) is synthesized from propylene monomer using the Ziegler-Natta (Z-N) catalyst system.
- Atactic polypropylene, APP, is a by-product of the synthesis of iPP and became available starting in the mid- to late-1950s

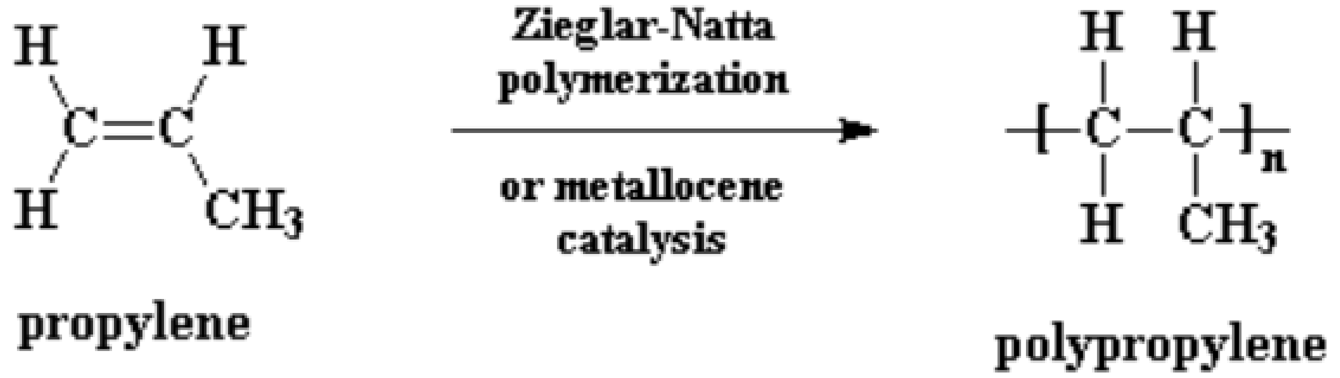
Propylene, the building block of polypropylene



Background, cont.

- First and early second generation Z-N catalysts, typically produced about 10-15 wt.% of APP.

Polymerization of propylene



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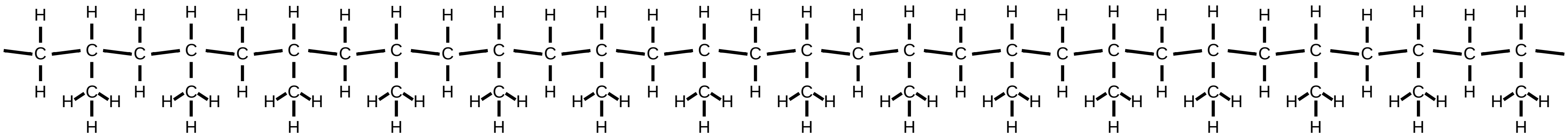
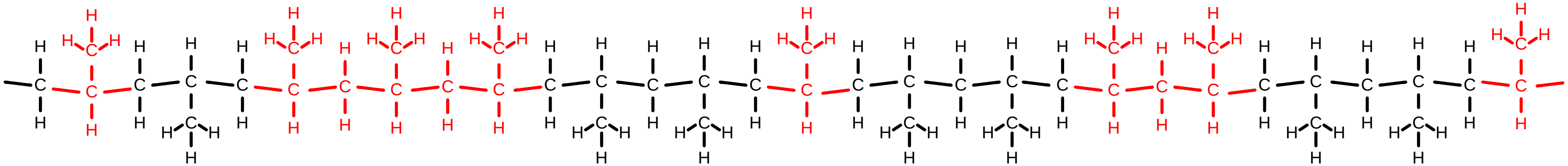
Linear Representations of: Isotactic Polypropylene



APP/APAO



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Background, cont.

- Manufacturing processes using those catalysts when carried out in solution simplified the elimination of the APP because of its solubility in the reaction medium,
- In other processes however, the APP had to be eliminated from the isotactic fraction by extracting with hydrocarbon solvents.

Background, cont.

- The development of newer highly active and stereospecific supported Z-N catalysts meant that the proportion of atactic polymer in the crystalline isotactic polypropylene was substantially reduced, to typically less than 2 to 3 wt.%.
- Therefore, the polypropylene product generally did not require any additional purification steps to remove the atactic or low crystalline fraction.
- This meant that the traditional APP supply from polypropylene plants using standard first- and early second-generation Z-N catalysts decreased as new and existing commercial plants used the high activity catalysts.

Background, cont.

- In other words, very little by-product APP was produced with the use of these new catalysts in PP manufacture.
- Because APP is a by-product, it frequently has a broad range of product properties such as melt viscosity, needle penetration and ring & ball softening point.
- It would be highly desirable, particularly for hot melt adhesive users and formulators, to have an APP-like polymer produced to tight product specifications,
- This type of polyolefin is called an on-purpose APAO, just APAO, or APO.

Background, cont.

- The synthesis and manufacture of APAO has been accomplished by properly designing the process of manufacturing the amorphous polyolefin, using a special catalyst system based on a Ziegler-Natta supported catalyst and an alkyl aluminum co-catalyst (e.g., TEA), and by the use of co-monomers.
- This on-purpose process results in products which have a controllable range of melt viscosity, softening point, needle penetration and open time – narrow standard deviation values.

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Background, cont.

- There are four distinctive product types of on-purpose APAO:
  - homopolymers of propylene
  - copolymers of propylene and ethylene (up to 20% ethylene and the balance in propylene)
  - copolymers of propylene and 1-butene (up to 65% 1-butene) or other higher α-olefins (e.g., 1-pentene, 1-hexene, 1-octene, etc.)
  - Terpolymers of ethylene, propylene and 1-butene

II. Product Characterization

- **Key properties determined for APAO:**
  - Melt Viscosity, MV, indicates processability and substrate wettability, and is typically determined at 375°F (190°C). Ranges from about 200 up to 150,000+ cps
  - Needle Penetration, NP, indicates resistance to deformation, hardness. Ranges from less than 10 up to 75 dmm,
  - Ring and Ball Softening Point, RBSP, indicates resistance to heat and ranges between about 80°C and 162°C (175°-324°F)
  - Open Time, OT, indicates how long it takes for a film of adhesive to set to a destructive bond. Ranges from less than 5 seconds, up to ~ 30 minutes.

Product Characterization, cont.

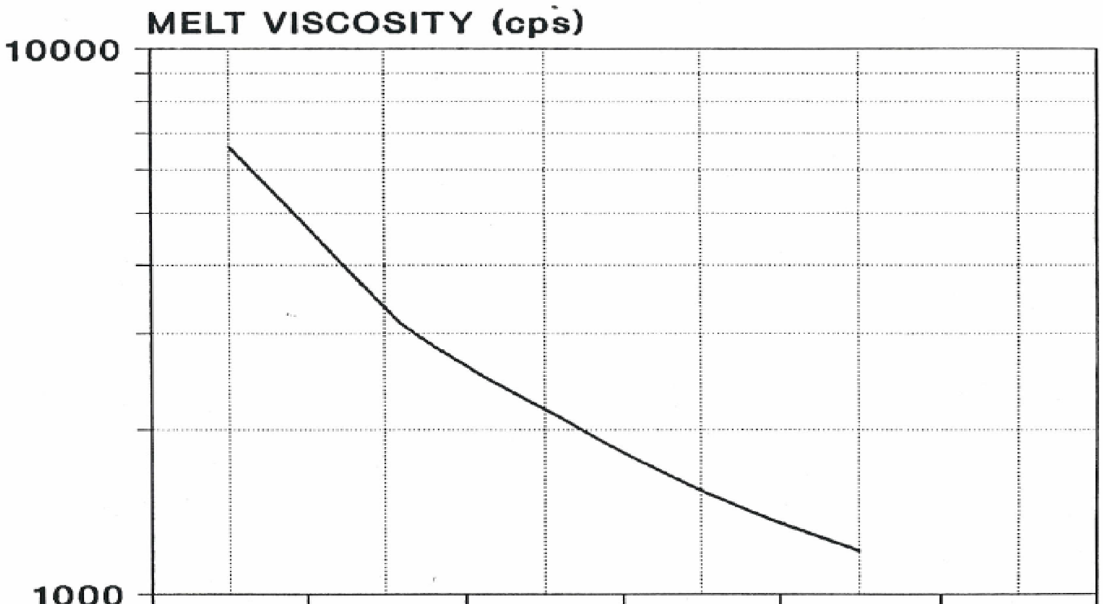
- Other tests carried out to determine product properties:
  - Rheology – flow characteristics. Measured with a rheometer
  - Tensile strength - measures mechanical properties. Measured using a tensile tester
  - Molecular weight – determined by polymer chain length. Determined by Gel Permeation Chromatography, GPC - used to obtain the weight average, number average and molecular weight distribution MWD.
  - Shear Adhesion Failure Temperature (SAFT) and Peel Adhesion Failure Temperature (PAFT) – heat resistance of laminates bonded with APAO.
  - Differential Scanning Calorimetry (DSC) – used to determine heats of fusion, from which the degree of crystallinity can be calculated. Also used to obtain the glass transition temperature or Tg.
  - FT infrared spectroscopy (FTIR) - Composition of APAO

Melt Viscosity, MV

- Most distinctive APAO property
- Determines the degree of wetting or penetration of the substrate by the adhesive
- Gives an indication of the processability of the adhesive
- Determined by molecular weight (MW) which is controlled in-process by the precise addition of hydrogen as a MW modifier
  - The higher the hydrogen concentration in the reactor, the lower the MW, and therefore the lower the melt viscosity of the polymer.
- Use of hydrogen allows the manufacture of products with a wide range of melt viscosities.

Melt Viscosity, cont.

- In addition, the melt viscosity of the product depends on the temperature.
- Conventionally, the MV for APAO is measured at 375°F.
- MV values increase as temperature decreases, as seen below.



	300	325	350	375	400	425
15 ——	6600	3075	2200	1500	1200	

TEMPERATURE (F)

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Needle Penetration, NP

- With thermoplastics and elastomers, hardness is often used as a simple measure of stiffness.
- Needle penetration indicates the resistance to deformation (or hardness) of the polymer
  - It is an indication of how soft, or how hard, the APAO is at the testing temperature of either 23°C or 25°C.
- Hardness is determined by the degree of crystallinity - which is a function of the catalyst system and of the copolymer composition - and, to a lesser degree, by the MW.

R & B Softening Point, RBSP

- APAO, like most polymers, does not have a well defined, sharp melting point
- Instead, as the temperature increases, APAO becomes softer and softer, changing from a solid to a high viscosity fluid over a wide temperature range.
- A high RBSP means that the polymer softens at a high temperature
- A low RBSP means that the polymer softens at a lower temperature.

R & B Softening Point, RBSP, cont.

- The softening point of a polymer is important in that it has a major influence on the heat resistance and application temperature of the APAO or HMA.

- As is the case for the needle penetration, the softening point is primarily determined by the copolymer composition and, to a lesser extent, by the MW.

- In particular for the ethylene copolymers, increasing the co-monomer concentration decreases the softening point but increases the NP, as shown in the following slide.

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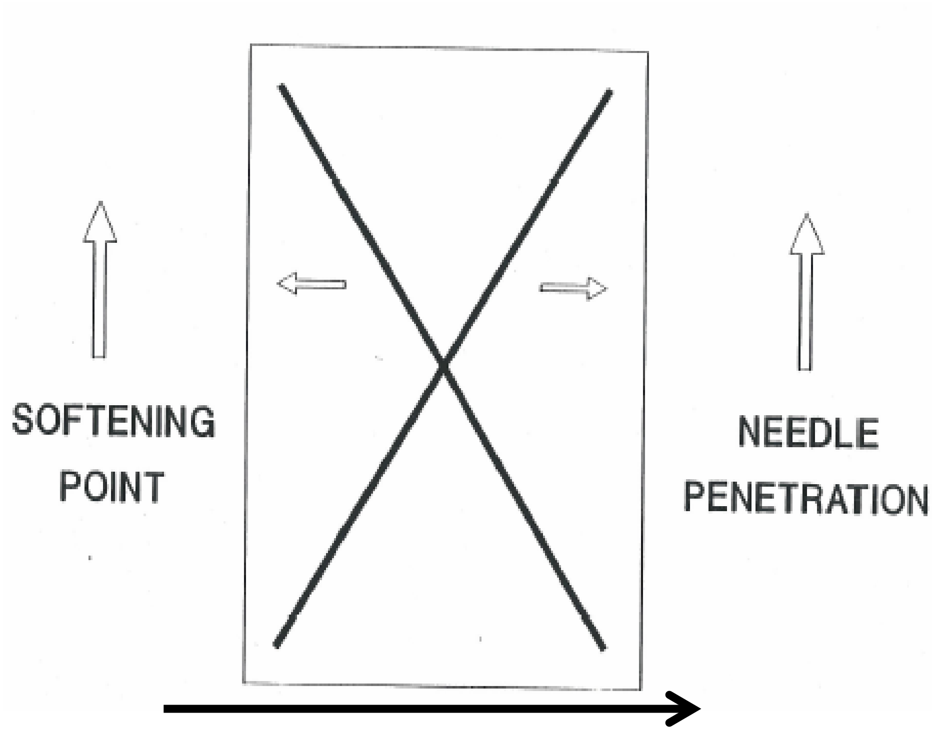
Effect of co-monomer concentration on NP and RBSP



Increasing co-monomer concentration

Effect of Co-monomer

- Homopolymer APAO
  - High R&B Softening Point (305°-324°F) – higher heat resistance.
  - Low Needle Penetration (hard) (< 10 dmm)
- Co-monomer addition (Ethylene or 1-Butene)
  - Lowers the R&B Softening Point
  - Raises the needle penetration (softer)
  - Extends the open time
  - Lowers the tensile strength

Open Time

- Open time - defined as the time elapsed between applying (drawing down) a hot melt adhesive as a film and the time just prior to the hot melt's losing its wetting ability because of solidification.

- An APAO with a short open time sets up quickly

- An APAO with a long open time takes longer to set or solidify.
  - A longer open time gives more time to the user to bond two substrates one to the other.

- As is the case for the NP and RBSP, the open time of an APAO is typically determined by the co-monomer content.
  - Homopolymer has a very short OT (typically less than 20 seconds)
  - High ethylene and α-olefin copolymers have longer OTs (as long as 30 minutes)

Shear Adhesion Failure Temperature, SAFT

- SAFT - defined as the temperature at which specimens bonded with APAO or HMA fail in a shear mode.
  - Strips of Kraft paper or Mylar, delaminate under a static load in shear mode.

- The failure might be a cohesive or an adhesive bond failure.

- The SAFT is mainly determined by polymer composition and somewhat by molecular weight.

Tensile Strength

- The tensile strength, TS, of a polymer plays an important role in the cohesive strength of an adhesive.

- In the absence of hydrogen bonds or polar-to-polar interactions, the TS in an APAO tends to increase with molecular weight and with crystallinity.

- In general, with increasing molecular weight, the chain entanglements, as well as the intra-chain interactions, increase, resulting in higher TS values.

Tensile Strength, cont.

- TS in APAO is also determined by the APAO's composition
  - Homopolymers show high values, up to about 350 psi (2.4 MPa),
  - As the ethylene or α-olefin content in the copolymers increases, the TS tends to decrease.
    - For example, for a high ethylene APAO, it can be as low as 50 psi (0.24 MPa) or less.
    - However some high 1-butene grades made with an added external additive, can have TS values as high as 1100 psi (7.6 MPa)

Molecular Weight

- Molecular weights of APAO are typically measured using gel permeation chromatography (GPC)
  - One of the most powerful and versatile analytical techniques available for understanding and predicting polymer properties and performance.
- GPC is the only proven technique for easily characterizing the complete molecular weight distribution, MWD, of a polymer.
- Outputs of a GPC
  - Number average molecular weights (MWn)
  - Weight average molecular weights (MWw)
  - Z-average molecular weights (MWz)

Molecular Weight, cont.

- The molecular weight distribution, MWD, is calculated from the MWw/MWn ratio,
- For APAO/APO, the MWn typically varies from a low of about 3,000 g/mol to as high as 25,000 g/mol,
- MWw varies from about 10,000 g/mol - 120,000 g/mol,
- MWDs are typically broad - ranging from about 4 to 8.

Features and Benefits of APAO

Features	Benefits
• Propylene Based Polymer	• Ample Availability of Feedstock • Chemical and UV Resistance • Excellent Thermal Stability
• Low Molecular Weight	• Ease of Processing • Polymer-rich Formulations
• Low Density (~0.85-0.88 grams/cc)	• Improved Mileage

More Benefits of Using APAO

- Excellent adhesion and hot tack properties,
- Bonding to various substrates
- Good cohesion
- Good moisture and gas barrier behavior

Excellent Adhesion to Substrates:

- Polyethylene (corona or plasma treated)
- Polypropylene (corona or plasma treated)
- Polyurethane foam
- Paper
- Fiber
- Nonwovens (Personal hygiene)
- Corrugated cardboard (lightly formulated)

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Limitations of APAO

– Poor adhesion to low surface energy and to smooth surface substrates,
– Galvanized metal (APAO cannot be used neat, but can be used with an adhesion enhancer/promoter),
– Bond strength is limited to ~50°F below RBSP,
– Tensile strength below 1,200 psi,
– Limited chemical resistance to some organic solvents,
– Limited miscibility/compatibility with polar chemicals.

Application Methods:

- APAOs have melt viscosities below about 150,000 cps at 190°C,
- Therefore, they can easily be applied by:
  - Spraying
  - Pumping
  - Roll coating
  - Slot coating
  - Extrusion, etc.

APAO Compatibility Table

APAO is compatible/miscible with:	APAO is incompatible/immiscible with:
Hydrogenated Styrene Block Copolymers (SBCs) such as SEBS	Mildly to quite incompatible with SBS and SIS, particularly those with high styrene content
Hydrogenated tackifiers such as DCPD, hydrogenated and partially hydrogenated C5s.	C5/C9s, polar, aromatic and unsaturated resins such as phenolics, terpene phenolics, styrenics, rosin esters, indene-coumarone resins.
Low density metallocene PE and PP (mPE, mPP) of similar molecular weight and crystallinity	High MW, crystalline iPPs, HDPEs, LDPEs
Saturated PE and PP, FT, microcrystalline and paraffinic waxes. Can be blended with low MW iPPs, LLDPEs.	Due to vast differences in MWs and saturation, not compatible with EPRs, butyl rubbers, EPDMs.
EVAs of high MFI and low (< 12 %) VA content	EVAs of medium to low MFI and VA content of higher than 12 %
Naphthenic, paraffinic and mineral oils.	Condensation polymers such as polyamides, polyesters

Formulating Adhesives with APAO

- APAO can be blended with any of the aforementioned compatible chemicals:
  - In a batch process using low or high shear mixers such as double planetary and sigma-blade mixers,
  - Static mixers,
  - Extruders – Single and double screw
  - In solution at high temperatures, in a hydrocarbon solvent. Solvent evaporation can become an issue.

III. Comparison between APAO and other Polymer Technologies in Adhesives.

APAO vs. SBS/SIS/SEBS

	APAO	SBS/SIS/SEBS
Thermal Stability	Excellent	Average to excellent
Cost	Low Cost / lb	Medium/High Cost / lb
Formulated	None/lightly	Heavily
Heat resistance	Good	Poor to good
Polarity	Non-polar	Polar, none to some unsaturation
Density	< 0.9 g/cc	0.9 < d < 1.05 g/cc

APAO vs. Metallocene- or single site catalyst-made PE/PP

	APAO	Metallocene/SSC – PE/PP
Thermal Stability	Excellent	Excellent
Cost	Low Cost / lb	Medium/High Cost / lb
Formulated	None/lightly	Heavily
Heat resistance	Good	Excellent
UV Stability	Excellent	Excellent
Density	< 0.9 g/cc	< 0.9 g/cc
MWD	Broad, a plus for processability	Narrow

APAO vs. EVA

	APAO	EVA
Thermal Stability	Excellent	Poor
Heat resistance	High	Poor
Open Time	Very wide range	Short
Processing	Excellent due to low viscosity	Limited
Applications	Broad	Primarily packaging
Formulated	None/lightly	Heavily
Density	< 0.9 g/cc	> 1 g/cc

APAO vs. Polyamide

	APAO	Polyamide
Chemical Resistance	Ok	Excellent
Thermal Stability	Excellent	Poor
Ease of Process	Excellent	Ok
Resistant to Salt Water	Excellent	Poor
Temperature Required	275°F-375°F	375°F-420°F
Cost	Low Cost / lb	High Cost / lb

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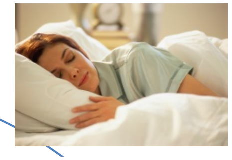
APAO vs. Water-Based Adhesive

	APAO	Water-Based
Mixing Requirement	None	Yes
Clean Up Waste	None	Yes
Coverage	100% solid	< 60% solid
Processing	Fast line speeds	Slower line speeds
Productivity	High	Low

IV. Industry Applications/Markets.

APAO

Mattress



Woodworking

Book Binding

Packaging

Nonwoven

Automotive

Wire and Cable

Hygienic Nonwoven

- Applications:
  - Feminine Hygiene
  - Baby Diapers
  - Adult Incontinence
  - Gowns & Drapes
  - Mattress Protector Pads
  - Dental Bibs
  - Meat Pads
  - Pet Training Pads

Hygienic Nonwoven

- Why APAO?
  - Quality, low cost adhesive technology
  - Proven thermal stability
  - High initial and aged peel values
  - Low in odor and VOCs
  - Application temperatures: ~275°F-375°F
  - Due to low density (< 0.9 gr/cc), higher mileage than other polymer technologies.

Transportation

- Applications:
  - Vibration/Sound Dampening
  - Battery Assembly
  - Load Floor/Package Tray
  - Cabin and Air Filter Assembly
  - Headliner Component
  - Pillar Trim and Carpet Bonding
  - Door and Instrument Panels

Transportation

- Why APAO?
  - Inherent moisture resistance
  - Good UV stability
  - Functionality over wide range of temperatures
  - Flexible open time
  - Excellent thermal stability
  - Allows for rework
  - Amorphous vs. other crystalline alternatives
  - Low MV leads to great substrate penetrability and wetting

Furniture

- Applications:
  - Mattress
    - Pocket coil assembly
    - Upholstery layer/pillow top attachment
    - Mattress ticking
    - Foam lamination
  - Woodworking
    - Case back
    - Drawer liners
    - Nonstructural assembly
    - Foam binding/upholstery
  - Office Furniture
    - Panel lamination
    - Foam bonding
    - Edge lamination

Furniture

- Why APAO?
  - Low cost, high initial tack, excellent cohesion
  - Flexible open time
  - High productivity
  - Good green strength
  - Low MV leads to great substrate penetrability and wetting

Product Assembly

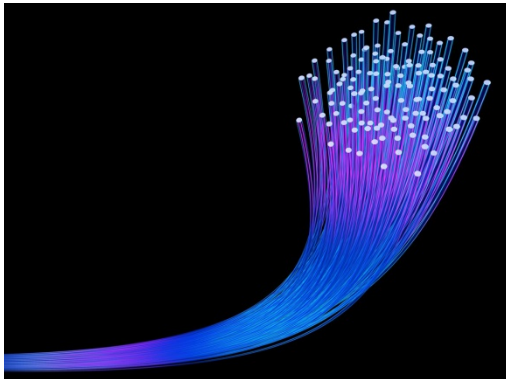
- Applications:
  - Electronics
    - Low Pressure Molding Systems
  - Laminates
  - Appliances
  - Filtration
    - Heating, Ventilation and Air Conditioning (HVAC)
    - Transportation Cabin Filter
    - Water & Fluid
    - Power Generator

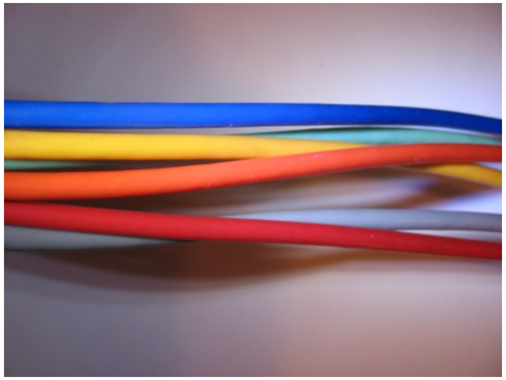
Product Assembly

- Why APAO?
  - Breadth of viscosity and temperature offerings
  - Outstanding adhesion to a variety of substrates
  - Water resistant
  - Flexible open time
  - Low cost
  - Excellent thermal stability

Wire and Cable

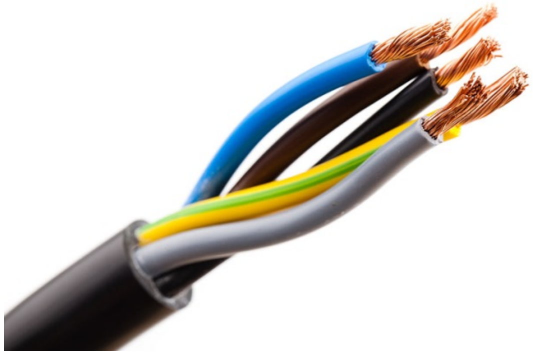
- Applications:
  - Filling
  - Flooding Compound
  - Fiber Optics





Wire and Cable

- Why APAO?
  - Inherent moisture resistance prevents water-penetration into the inner insulation
  - Protects core of the cable
  - Inhibits corrosion
  - Can sustain wide range of temperatures
  - Acts as a cushion and lubricant to protect cables from damage due to mechanical handling
  - Prevents telescoping
  - Provides cohesive bonding between external and metal jackets

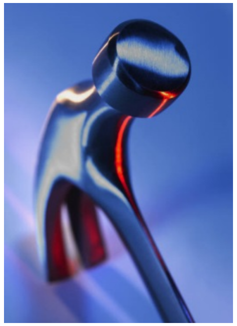


Building & Construction

- Applications:
  - Window Sealant*
  - Garage Door Sealing
    - Panel lamination for hollow/insulated garage doors
  - Pipe Wrap
  - Carpet Seaming Tape
  - Peel & Stick Flooring
  - Shower Sealing
  - Modified Bitumen Roofing
  - Pavement Modification

*must be formulated

Building & Construction



- Why APAO?
  - Broad environmental range of use
    - Offering both high heat resistance and cold temp flexibility
  - Inherent moisture resistance
  - Resistant to acids, alkalis, and other chemicals

Packaging

- Applications:
  - Pallet Stabilization
  - Case & Carton Sealing
  - Litho-laminating
    - Large graphics on corrugated box
  - Glued lap
    - Manufacturer's joint on corrugated box
  - Tyvek envelope (FedEx) side and center seam

Packaging

- Why APAO?
  - Lightly formulated to adjust the set time and fiber tear strength,
  - Broad temperature range,
  - Adheres to many cellulose-based substrates.
  - May also adhere to corona-treated P.O. substrates used in packaging boxes

APAO Manufacturers

Manufacturer	Trade Name
EASTMAN www.eastman.com	Eastoflex
EVONIK INDUSTRIES www.evonik.com	Vestoplast
REXtac LLC APAO Polymers (www.rextac.com)	Rextac

Addendum

Product Characterization

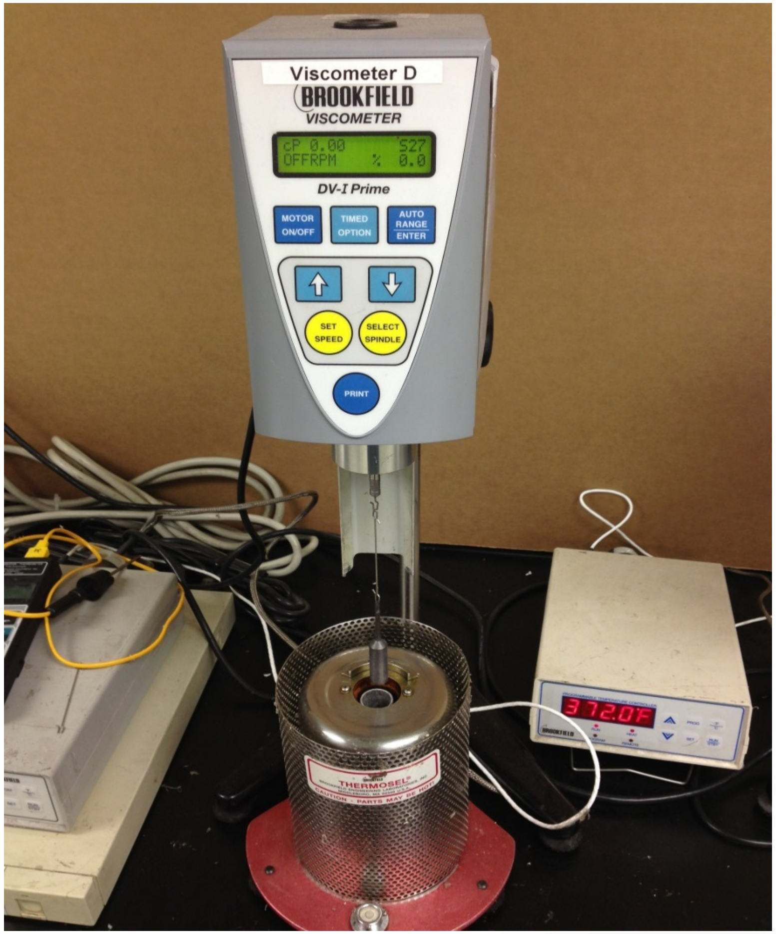
Typical properties determined for APAO and their test methods:

- Melt Viscosity (MV) - typically determined at 375°F (190°C), as per the ASTM D-3236 or DIN 53019 test methods.
- Needle Penetration (NP) - typically determined as per ASTM D-1321, ASTM D5 or DIN EN 1426 test methods.
- Ring and Ball Softening Point (RBSP) - typically determined as per ASTM E-28 or DIN EN 1427 test methods.
- Open Time (OT) - typically determined as per ASTM D-4497.
- Tensile Strength (TS) of APAO is typically measured following the testing protocols described in ASTM D-638, D-412 or DIN EN ISO 527-3 test methods.
- SAFT - Measured following either TMHM-32 or a modified WPS 68 test method.

Product Characterization

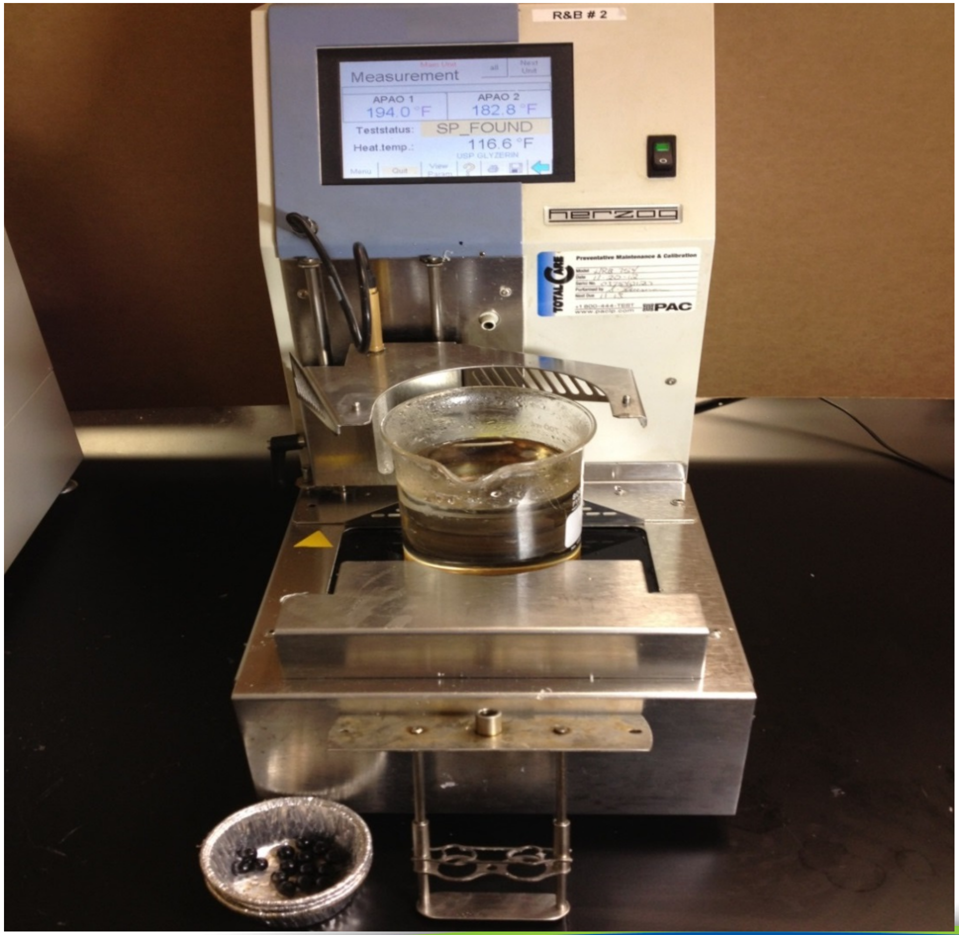
- The MWs and MWDs are typically determined using test methods ASTM D-3593 or DIN 55 672. Molecular weight determinations are typically carried out using a Waters 150-C GPC, or similar instrument equipped with a µ-Styragel column, on 0.1 wt.% solutions of the polymers in trichlorobenzene at 140°C.
- The column is calibrated using narrow molecular weight polystyrene or polyethylene standards.

Melt Viscometer, used to determine MV



Needle Penetrometer

RBSP Apparatus



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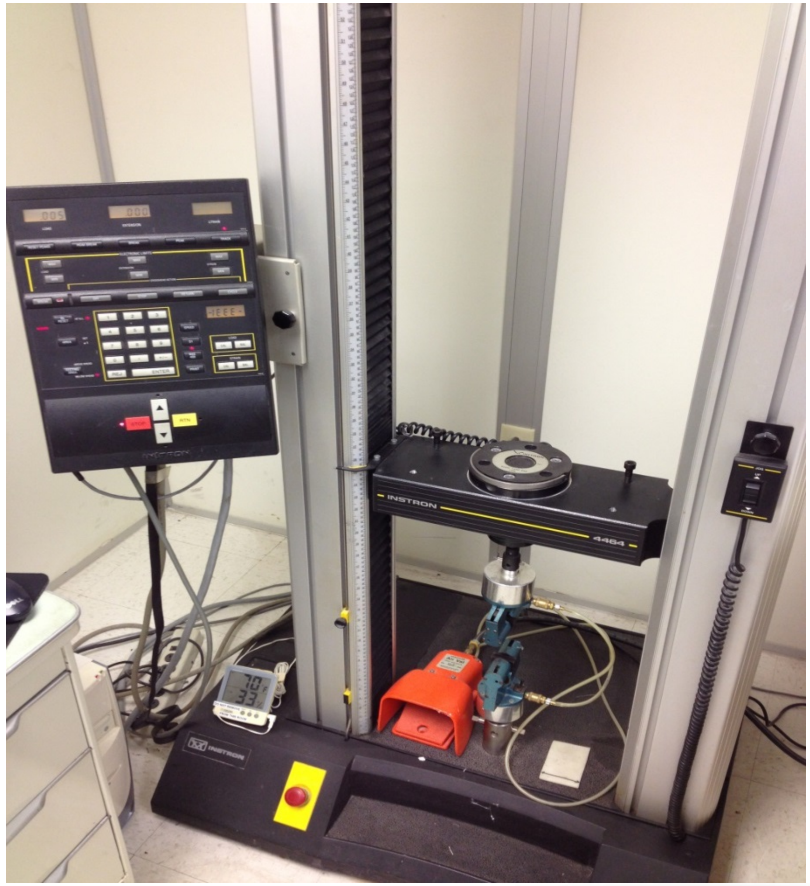
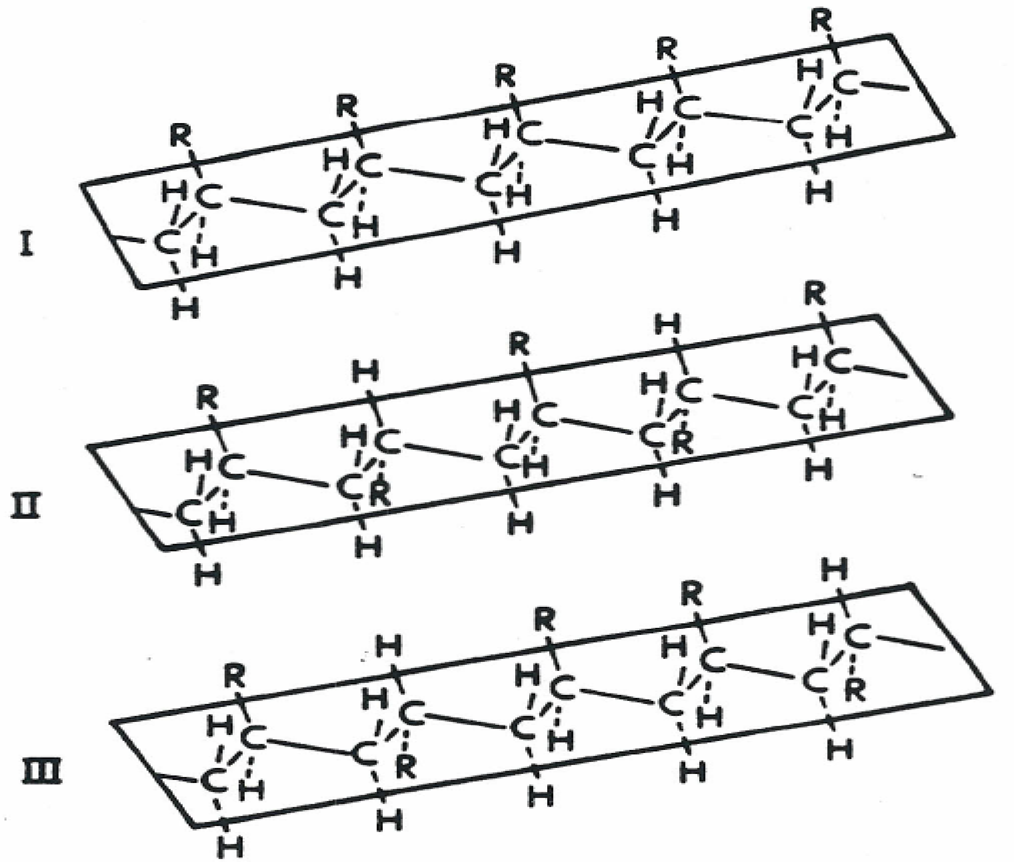
Instron Tensile Tester



Three of the structural conformations for polypropylene made with a Z-N catalyst: (I) isotactic, (II) syndiotactic, and (III) atactic



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