2013 ASC HOT MELT SHORT COURSE

Amorphous Poly Alpha Olefin Based Hot Melts

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I. Brief historical description of the evolution
   I. Atactic polypropylene, APP, amorphous polyalphaolefins, APAO, amorphous polyolefins, or APO

II. Relevant properties that describe the physical and mechanical properties of APAO,

III. Intra-APAO blends and different APAO-based compositions that can be used in hot melt adhesive, HMA, applications,

IV. Markets and applications
I. Background, Historical Development

- Starting in the mid- to late-1950s, atactic polypropylene was a by-product of the synthesis of isotactic polypropylene (iPP).

- First and early second generation Ziegler-Natta (Z-N) catalysts, typically produced 10-15 wt% of APP.

- Most of the processes using those catalysts were carried out in slurry or in solution, simplifying the elimination of the APP.

- In other processes, the APP had to be eliminated from the isotactic fraction by washing/extracting with hydrocarbon solvents.
The development of new highly active and stereospecific supported Z-N catalysts meant that the proportion of atactic polymer to crystalline isotactic polypropylene in the polymers produced was substantially reduced, to typically less than 2 or 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 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.
Therefore, 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 broad product specifications for such properties as melt viscosity, needle penetration and ring & ball softening point.

It would be highly desirable, particularly to 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.
The synthesis and manufacture of APAO has been accomplished by properly designing the process of synthesizing the amorphous polyolefin, specifically, by the proper choice of the catalyst system and the use of co-monomers.

This on-purpose process results in products which have well defined properties, such as:
- Melt viscosity
- Softening point
- Needle penetration
- Open time
The amorphous polyalphaolefins are synthesized by a specially designed catalyst system based on a Ziegler-Natta supported catalyst and an alkyl aluminum co-catalyst.

The polymerization process produces a mostly amorphous polymer with low crystallinity.

Crystallinity depends not only on the catalyst system but also on the use of co-monomers.
There are four distinctive product types of on-purpose APAO:
- homopolymers of propylene
- copolymers of propylene and ethylene
- copolymers of propylene and 1-butene or other higher α-olefins
- terpolymers of ethylene, propylene and 1-butene

The composition of the APAO is typically determined by using infrared spectroscopy, specifically, FTIR.
Three of the structural conformations for polypropylene made with the Z-N catalyst (I) isotactic, (II) syndiotactic, and (III) atactic.
II. Product Characterization

Typical properties determined for APAO:

- **Melt Viscosity (MV)** - indicates processability and is typically determined at 375°F (190°C), as per the ASTM D-3236 or DIN 53019 test methods.

- **Needle Penetration (NP)** - indicates resistance to deformation and hardness, and is typically determined as per ASTM D-1321, ASTM D5 or DIN EN 1426 test methods.

- **Ring and Ball Softening Point (RBSP)** - indicates resistance to heat, and is typically determined as per ASTM E-28 or DIN EN 1427 test methods.
• **Open Time (OT)** - indicates how long it takes for a film of adhesive to set to a destructive bond. Typically determined as per ASTM D-4497.

• Other tests carried out to determine product properties:
  - **Rheology** - measured with a rheometer
  - **Tensile strength** - measures mechanical properties
    - **Tensile Modulus** - measured using a tensile tester
  - **Molecular weight** - used to obtain the molecular weight distribution, MWD, determined by Gel Permeation Chromatography, GPC
  - **Shear Adhesion Failure Temperature (SAFT)**
    - **Peel Adhesion Failure Temperature (PAFT)**
Melt Viscosity, MV

- Most distinctive 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
  - 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 obtainment of products with a wide range of melt viscosities.
In addition, the melt viscosity of the final product depends on the temperature. Conventionally, the MV for APAO is measured at 375°F. MV values increase as temperature decreases, as seen below.
Melt Viscometer used to determine MV
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.
Needle Penetrometer
R & B Softening Point, RBSP

- APAO, like most polymers, does not have a well defined, sharp melting point

- Instead, as the temperature is increased, 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.
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.
RBSP Apparatus
Effect of co-monomer concentration on NP and RBSP

Increasing co-monomer concentration
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 5 to 10 minutes)
Shear Adhesion Failure Temperature, SAFT

- **SAFT** - defined as the temperature at which specimens bonded with APAO or HMA
  - 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.
  - Measured following either TMHM-32 or a modified WPS 68 test method.
The tensile strength, TS, of a polymer is an important factor 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.

In general, with increasing molecular weight, the chain entanglements, as well as the intra-chain interactions, increase, resulting in higher TS values.
• TS in APAO is also determined by the APAO’s composition
  o Homopolymers showing the highest values
  o As the ethylene or α-olefin content in the copolymers increase, the TS tends to decrease.
    ▪ For example, the TS for a homopolymer can be about 350 psi or higher, while for a high ethylene APAO, it can be as low as 50 psi or less.

• 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.
Instron Tensile Tester
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.

Molecular weight determinations are typically carried out using a Waters 150-C GPC, or similar instrument, on 0.1 wt% solutions of the polymers in trichlorobenzene at 140°C.

The μ-Styragel column is calibrated using narrow molecular weight polystyrene or polyethylene standards.
• Outputs of a GPC
  ○ Number average molecular weights (MWn)
  ○ Weight average molecular weights (MWw)
  ○ Z-average molecular weights (MWz)

• The molecular weight distribution is calculated from the MWw/MWn ratio. The MWs are typically determined using test methods ASTM D-3593 or DIN 55 672.

• For APAO/APO, the MWn typically varies from a low of about 3000 da to a high of 25,000 da or more

• MWw varies from about 10,000 da - 120,000 da.

• MWDs are typically broad - ranging from about 4 to 8.
III. Intra-APAO blends

- Due to the limited number of APAO product types that are produced, an HMA formulator might be in need of a particular product that has some specific properties of melt viscosity, needle penetration, or softening point not available as a neat product.

- Most commonly used method for establishing miscibility in polymer-polymer blends is through the determination of the glass transition temperatures of the blends
  - Can be done using dynamic mechanical analysis, DMA, and the comparison of the values with those of the pure, unblended components.

- Based on the DMA results, APAO are miscible in all proportions with one another
Intra-APAO blends, cont.

- Composition vs. glass transition temperature profile for a blend of a high ethylene and a medium ethylene APAO.
Benefits of Using APAO

- Excellent adhesion and hot tack properties,
- Bonding to various substrates
- Good cohesion and high thermal stability
- Good moisture and gas barrier behavior
- Good hydrolytic and UV stability
Industry Applications

- Mattress
- Wire and Cable
- Woodworking
- Automotive
- Book Binding
- Nonwoven
- Packaging
- APAO
Industry Applications

- Personal hygiene
  - Baby diapers
  - Adult incontinence
  - Feminine hygiene

- Paper and packaging
  - Paper lamination
  - Cardboard and case sealing
  - Labels

- Bookbinding

- Woodworking
  - Edge banding
Industry Applications, cont.

- Product assembly
  - Mattresses
  - Bonding to metals
  - Automotive
  - Footwear

- Windows, as component in insulation

- As a component in modified bitumen roofing, MBR, membranes and in asphalt modification

- Cable filling and cable flooding

- Polymer modifier and as an additive, particularly if it has been modified by grafting maleic anhydride or silane grafting
### APAO in Some Example HMA Formulations

#### Adhesive for Packaging

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Percent by Weight</th>
<th>Physical Constants</th>
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<tbody>
<tr>
<td>RT 2780</td>
<td>40</td>
<td>Melt Viscosity (mPa.s)</td>
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<tr>
<td>RT 2180</td>
<td>10</td>
<td>Needle Penetration (dmm)</td>
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<tr>
<td>Escorez 1102</td>
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<td>Softening Point °C (°F)</td>
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<td>B-Square wax</td>
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<td>Cloud Point (°C)</td>
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#### Laminating Adhesive for Higher Requirements, Medium Open Time

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<tr>
<th>RT 2280</th>
<th>80</th>
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<tr>
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<td></td>
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<tr>
<td></td>
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<td>S.A.F.T. °C (°F)</td>
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#### Additional Information

- Open Time (sec.)
- R.T. 190°C
### Adhesive for Multi-Line Application for Diapers

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<th>Adhesive Type</th>
<th>RT 2760</th>
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<th>AMOCO H1500</th>
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<td>Open Time</td>
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<td>S.A.F.T. °C</td>
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### Adhesive for Assembly of Diapers

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### APAO Manufacturers

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<tr>
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<td>Evonik (<a href="http://www.evonik.com">www.evonik.com</a>)</td>
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<tr>
<td>REXtac, LLC (<a href="http://www.rextac.com">www.rextac.com</a>)</td>
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