EVA Specialties (Film application)

August 26, 2018

Hanwha TOTAL Petrochemical
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IV Film application

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I. HTC Introduction
HanwhaTotal Petrochemical

General information

Founded: 1988 (as Samsung General Chemicals)
Head Office: Daesan, Chungcheongnam-do
President & JRD: Kim Hee Cheul
EVP & JRD: Jean-Marc Otero del Val
Revenue: KRW 8.2 trillion (a/o 2016) 500 billion ruble
Employee Count: 1,590 (a/o 2016)

Base chemicals, Polymers and energy products from condensate and naphtha as main feed stocks

Feed Stocks
- Condensate
- Naphtha
- LPG

Main Products
- NCC
- Polymers (PE, PP etc.)
- Base chemicals (SM, PX etc.)
- Aromatics Plants
- Energy (jet fuel, diesel etc.)

Key Products
- Domestic No. 1 in packaging materials and film
- No. 1 in bottlecap production in Korea (76% market share) and China (50% market share)
- Domestic No. 1 in SM production (1.05 million tons)
- Nation’s 1st producer of jet fuel in Petrochemicals
- Gasoline, supplier to 30% of all cost-savings gasoline stations
- Global No. 1 in EVA for solar cell materials (35% market share)
Production Capabilities

Manufacturing performance

(Kilotons, a/o 2017)

- NCC
- Ethylene (1,090)
  - Propylene (932)
    - C4 (410)
    - Pygas (770)
  - HDPE (175)
  - LDPE / EVA (435)
  - LLDPE (125)
  - EO/EG (155)
  - PP (717) / PP Compound (130)
  - Butadiene (120)
  - Benzene (200)
  - SM (1,050)
- Benzene (1,015)
- PX (1,997)
- Jet Fuel/Kerosene (2,000)
  - Hi-sene (250)
- Mogas (120)
  - Diesel (1,030)
Polymer business

- EVA Solar Cell Sheet
- EVA Extrusion Coating
- LDPE Protection Film
- EVA/LD Wire & Cable

**EVA/LD**

- Film
- Blow
- Bottle Cap
- CPE (Chlorinated Polyethylene)

**HDPE**

- C4 film
- Wire & Cable
- Bottle Cap (HDPE)
- Roto

**LLDPE**

- HIPP (Homo & BCPP)
- Random, Terpolymer
- High MI BCPP
- ABS Replacement
- Battery Case

**PP**

- Flame Retardant
- Long Glass Fiber
- High Flow Comp. for Automotive

**PPC**

- Hanwha
- Total
II. EVA Overview
EVA (Ethylene vinyl acetate)

- **Ethylene-vinyl acetate random copolymer**
  - Copolymerization with ethylene and vinyl acetate monomer
  - Radical polymerization under high pressure

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{CH} \\
\text{O} & \\
\text{C} & \equiv \text{O} \\
\text{CH}_3 & \\
\text{H}_2\text{C} & \equiv \text{CH}_2 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2 & \\
\text{O} & \\
\text{C} & \\
\text{CH}_3 & \\
\text{X} = \text{acetate}
\end{align*}
\]

Vinyl acetate + Ethylene \[\rightarrow\] Ethylene vinyl acetate copolymer

Molar mass : \(86\text{ g/mol}\)  Molar mass : \(28\text{ g/mol}\)
**Effect of VA content**

*Increase of VA content gives:*

- More short chain branching
- Less crystalline (More amorphous)
- Lower melting temperature
- More elastic as solid
- Higher density
- Increased polarity

*Polymer properties*

- Better adhesion to polar substrate
- Increased tackiness
- Lower seal initiation temperature
- Greater flexibility
- Higher clarity & gloss
- Increased toughness

*Application properties*
Effect of Melt Index

- **Effect of Melt Index**

  **Decrease of MI gives:**

  - **Polymer properties**
    - Higher molecular weight
    - Higher viscosity
  
  - **Application properties**
    - Lower flowability
    - Higher melt strength
    - Increased impact resistance
    - Increased tensile strength
    - Higher abrasion resistance

  ![Decreasing MI diagram]

  From high MI to low MI.
## Reactor types

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Autoclave</th>
<th>Tubular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>Up to 22 %</td>
<td>Up to 36 %</td>
</tr>
<tr>
<td>Pressure</td>
<td>1100 ~ 2000 bar</td>
<td>2000 ~ 3500 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>130 ~ 280 °C</td>
<td>180 ~ 350 °C</td>
</tr>
<tr>
<td>Initiator</td>
<td>peroxide</td>
<td>oxygen, peroxide</td>
</tr>
<tr>
<td>Mixing</td>
<td>Stirred/Back Mixing</td>
<td>Plug flow</td>
</tr>
<tr>
<td>Residence time distribution</td>
<td>Broad</td>
<td>Narrow</td>
</tr>
<tr>
<td>VA content</td>
<td>Possible to produce EVA over 40 %</td>
<td>Max. 10 ~ 30 % (depending on the process)</td>
</tr>
</tbody>
</table>
## Characteristics of Tubular EVA

<table>
<thead>
<tr>
<th>MWD</th>
<th>Autoclave</th>
<th>Tubular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broad</td>
<td></td>
<td>Narrow</td>
</tr>
</tbody>
</table>

### LCB

- **Tubular**
- **Autoclave**

### Film surface roughness (AFM)

- **Tubular**
- **Autoclave**
Differences originated from Process

- Autoclave reactor EVA
  - Broad MWD, high MW tail, F/E (gel) level increase
- Tubular reactor EVA
  - Narrow MWD, high transparent
**Peeling Strength**

- Higher peeling strength compared to same MI competitor’s grade

---

**Peeling Strength**

<table>
<thead>
<tr>
<th>Extension (mm)</th>
<th>(kgf/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

- Glass/EVA/PET lamination
- Lamination Condition: 150 °C, Vacuum 6 min, Press (100Kpa) 11 min
**Lower Shrinkage**

- Less melt elasticity and memory effect of HTC EVA leads fast relaxation time
- Low residual stress in a sheet made from casting or calendering process
III. Hanwha Total's EVA
# Hanwha Total’s EVA Capacity

<table>
<thead>
<tr>
<th>Plant</th>
<th>Reactor</th>
<th>Licensor</th>
<th>Capacity (KT/Yr)</th>
<th>Start-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>Tubular</td>
<td>Mitsubishi</td>
<td>155</td>
<td>1991</td>
</tr>
<tr>
<td>No.2</td>
<td>Tubular</td>
<td>LyondellBasell</td>
<td>240</td>
<td>2014</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>395</td>
<td></td>
</tr>
</tbody>
</table>
HTC EVA consists of a range of vast array of industrial application such as photovoltaic encapsulant, footwear, food packaging, wire & cable and extrusion coating, agricultural greenhouse film, stretch hood
IV. Film application
## HTC’s EVA for Film

### Grade List

<table>
<thead>
<tr>
<th>Grade</th>
<th>MI (g/10min)</th>
<th>VA (wt%)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>E032A</td>
<td>0.5</td>
<td>3</td>
<td>Agricultural greenhouse film</td>
</tr>
<tr>
<td>E090A</td>
<td>0.8</td>
<td>9</td>
<td>Agricultural greenhouse film</td>
</tr>
<tr>
<td>E120A</td>
<td>1</td>
<td>12</td>
<td>Agricultural greenhouse film</td>
</tr>
<tr>
<td>E140A</td>
<td>4.5</td>
<td>14</td>
<td>Packaging film, Multi-layer film</td>
</tr>
<tr>
<td>E150A</td>
<td>1</td>
<td>15</td>
<td>Agricultural greenhouse film</td>
</tr>
<tr>
<td>E180A</td>
<td>0.8</td>
<td>18</td>
<td>Agricultural film, Stretch hood, Packaging film, Multi-layer film</td>
</tr>
</tbody>
</table>
Agricultural film E032A/E090A/E120A/E150A/E180A

- **Application:** Greenhouse film
- **Product characteristics**
  - Excellent light transmittance
  - Low Fish-eye and gel level
  - Excellent physical strength
  - Good dispersion of master batch

- **General film layer structure**
  - HTC EVA + master batch (UV, Anti-fogging agent, lagging material, etc)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>anti-aging layer (outer)</td>
<td>LDPE + mLLDPE</td>
</tr>
<tr>
<td>insulation layer (center)</td>
<td>EVA (3~18% VA) + LDPE</td>
</tr>
<tr>
<td>anti-droplet layer (inner)</td>
<td>EVA (3~18% VA) + LDPE</td>
</tr>
</tbody>
</table>

Greenhouse film (3 layers)
- **Optical property**
  - Excellent light transmittance
  - Lower haze

### Light Transmittance (%)

![Graph showing light transmittance](image)

### Haze (%)

<table>
<thead>
<tr>
<th></th>
<th>E180A</th>
<th>EVA-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haze</td>
<td>10.2</td>
<td>17.5</td>
</tr>
</tbody>
</table>

*Processing conditions: PLACO 50mmΦ Blown film M/C (Die Gap 2.5mm)*

Temperature 180 °C, Screw rpm 50, Film thickness 50 μm
### Surface property

- Better clarity due to uniform surface

<table>
<thead>
<tr>
<th></th>
<th>E180A</th>
<th>EVA-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness (nm)</td>
<td>98</td>
<td>246</td>
</tr>
<tr>
<td>Haze (%)</td>
<td>10.2</td>
<td>17.5</td>
</tr>
</tbody>
</table>

**3D Image**

![3D Image](image_url)
■ Physical property

- Excellent impact strength, puncture strength, etc

**Impact strength (g)**

- E180A: 600
- EVA-A: 500

**Puncture resistance (N)**

- E180A: 80
- EVA-A: 70
# Agricultural film

<table>
<thead>
<tr>
<th>Resin type</th>
<th>LDPE</th>
<th>LLDPE</th>
<th>HDPE</th>
<th>EVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade</td>
<td>310A</td>
<td>4220U</td>
<td>F120U</td>
<td>E032A</td>
</tr>
<tr>
<td>MI (g/10min)</td>
<td>0.8</td>
<td>1.0</td>
<td>0.044</td>
<td>0.5</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.922</td>
<td>0.921</td>
<td>0.956</td>
<td>0.923</td>
</tr>
<tr>
<td>VA (wt%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

## Additives
- Anti-oxidant agent
  - LDPE: ●
  - LLDPE: ●
  - HDPE: ●
  - EVA: ●
- Anti-block agent
  - LDPE: ●
  - LLDPE: ●
  - HDPE: ●
  - EVA: ●
- Slip agent
  - LDPE: ●
  - LLDPE: ●
  - HDPE: ●
  - EVA: ●
- UV agent
  - LDPE: ●
  - LLDPE: ●
  - HDPE: ●
  - EVA: ●

## Applications
- Greenhouse
  - LDPE: ●
  - LLDPE: ●
  - HDPE: ●
  - EVA: ●
- Mulching
  - LDPE: ●
  - LLDPE: ●
V. Fisheye
What is Fisheye / gel

■ Fisheye / gel
  - Film imperfections or defects developed during forming due to disturbances in the polymer flow
    - size: tens of micro meters to few millimeters
    - foreign materials, oxidized or crosslinked polymers
    - Insufficiently melted/dispersed polymer due to high molecular weight of polymer

■ Source of fisheye
  - Resin production stage
    - high molecular weight polymer
    - oxidation, degradation
    - inorganic additives, impurities
  - Transport, storage, processing, handling stage
    - contamination from environment
    - sluggish region, dead space in extruder (screw / die)
Inspection and analysis

■ Visual inspection
  o Count all kind/size of fisheye within defined area
  o Count only specified fisheye (large fisheye, black spot, scratch, etc.)

■ Automatic fisheye counter (AFC)
  o Advantage
    – cover large area
    – analysis fisheye trend, size distribution
  o Disadvantage
    – limitation on distinguishing fisheye type
    – resolution limited by measuring area
  o Type : online measure, offline measure

■ Identification of fisheye
  o Visual inspection
  o Microscope & hot stage melting test
  o Instrumental analysis : material & element analysis
Analysis with AFC

- Time trend, position & frequency, shape of fisheye

![Graph showing time trend and position distribution with AFC analysis.](image-url)
Identification of fisheye

Visual inspection

DSC & FT-IR

OM & Hot stage

SEM / EDS

Inorganic microtoming

Organic cross-sectioning

EDS

SEM
Classification of fisheye

- **Degradation, crosslinking, oxidation of polymer**
  - During polymerization and extrusion
  - Crosslinked gel, oxidized gel

- **Contamination**
  - Fiber: gloves, clothes, dust
  - Inorganic material: additives
  - Metal
  - Foreign resin
Microscope & Hot stage

- Fisheye analysis using microscope
  - shape, size
  - melting or unmelting
  - measuring Tm
Examples: Oxidized fish-eye

- Observed fish-eye seed after melting. Fish-eye is not melted in high temp.
- $\text{C=O}$ peak is observed in FT-IR.
Examples: other resin contamination

- Shape of fisheye: round, oval shape
- Hot stage melting
  - matrix is melted at 75~85°C
  - seed of fisheye melted at 110~115°C => contamination of LDPE dust

30°C  80°C  110°C  115°C
Examples: Fiber

- Fiber can be classified by shape, and identified with FT-IR analysis
  - Cotton, polyester, nylon, etc.

![Cotton Image](image1)

![Polyester Image](image2)

FT-IR: Cotton, Cellulose
Examples: inorganic material

- Inorganic material can be identified with elemental analysis

=> identified as anti-blocking agent
Examples : metal

- Metal
  - no melting and same shape under hot stage
  - black shadow under transmission microscope, but bright color under reflection microscope (depends on material)
  - material can be identified with SEM/EDS elemental analysis
Formation of crosslinked fish-eye during process

- PE/EVA can be crosslinked under excessive heat and shear.
- Crosslinked molecule grows and become visible fish-eye during extrusion process
- Growth rate increases when the temperature is higher and the residence time is longer

Ref: Henk Lourens
Degradation of EVA

- **Thermal stability of olefin copolymer**
  - (stable) HDPE > LDPE > LLDPE > EVA (unstable)

- **Degradation by thermal radical**
  - Degradation rate increases,
    - at excessive high temperature
    - by oxygen contact
    - by impurities such as acid, oxides, metal ion
  - High VA EVA degrades faster

  ![Degradation of EVA, releasing acetic acid](attachment:image.png)

  EVA in Air, 180°C

  FT-IR: oxidation peak
Aging inside the die

- After finishing film extrusion, machine stopped and the EVA (VA 18%) had exposed to excessive high temperature 240 °C for 5 hours
  - showed severe die line
  - oxygen had diffused into die, make EVA severe degradation

☞ Proper shutdown procedure is required to maintain low gel condition

Inside the die; after 5 hours aging at 240°C
**Processing temperature and antioxidant**

- Crosslinking reaction becomes faster at higher temperature
  - Crosslinked/oxidized gel increases as processing temperature increases
- Adding antioxidants can help suppressing crosslinking reaction
  - Blocking radical generation cycle involving oxygen

![Graphs showing the effect of temperature on fisheye formation with and without antioxidants.](image_url)
## Countermeasure

<table>
<thead>
<tr>
<th>Fisheye type</th>
<th>Possible cause and countermeasure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting type</strong></td>
<td>- resin contamination</td>
</tr>
<tr>
<td></td>
<td>- incomplete melting in extruder, insufficient mixing</td>
</tr>
<tr>
<td></td>
<td>→ increase melting efficiency of extruder.</td>
</tr>
<tr>
<td></td>
<td>→ raise processing temperature, use fine mesh</td>
</tr>
<tr>
<td><strong>Fiber</strong></td>
<td>- contamination</td>
</tr>
<tr>
<td></td>
<td>→ do not use cotton gloves</td>
</tr>
<tr>
<td></td>
<td>→ clean air filter, transport line</td>
</tr>
<tr>
<td><strong>Metal, inorganic, Black particle</strong></td>
<td>- contamination</td>
</tr>
<tr>
<td></td>
<td>→ use fine mesh</td>
</tr>
<tr>
<td><strong>Crosslinked Gel</strong></td>
<td>- decomposition, oxidation, crosslinking reaction</td>
</tr>
<tr>
<td><strong>Oxidized Gel</strong></td>
<td>→ reduce exposure to oxygen during processing</td>
</tr>
<tr>
<td></td>
<td>→ reduce processing temperature and shear</td>
</tr>
<tr>
<td></td>
<td>→ increase stabilizer content</td>
</tr>
<tr>
<td></td>
<td>→ review start-up &amp; shut down procedure, minimize exposure to high temperature</td>
</tr>
</tbody>
</table>
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