EVA Specialties (Film application)

August 26, 2018

Hanwha TOTAL Petrochemical

Contents

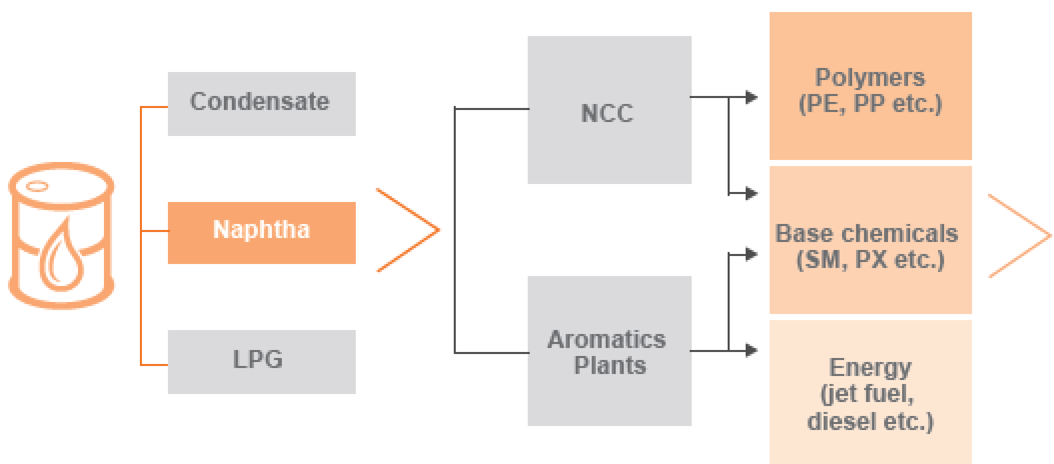
I. HTC Introduction

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) 500billion ruble
Employee Count	1,590 (a/o 2016)

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

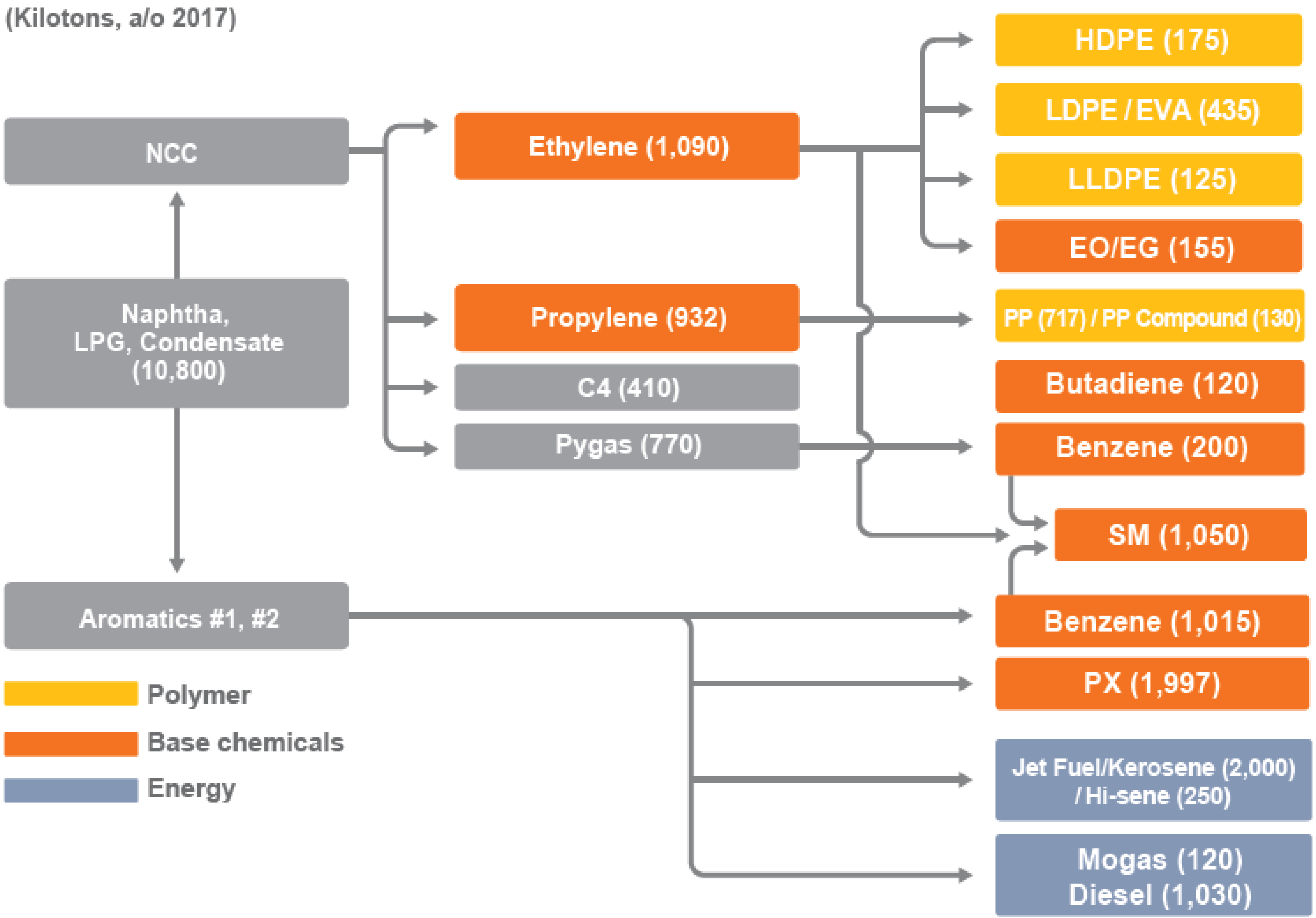


Key Products

- 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



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Polymer business

EVA/LD

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

HDPE

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

LLDPE

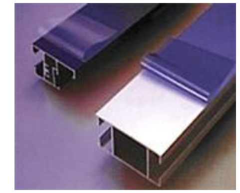
- C4 film
- Wire & Cable
- Bottle Cap (HDPE)
- Roto

PP

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

PPC

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











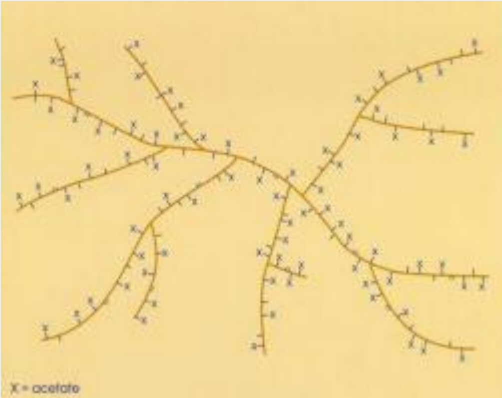


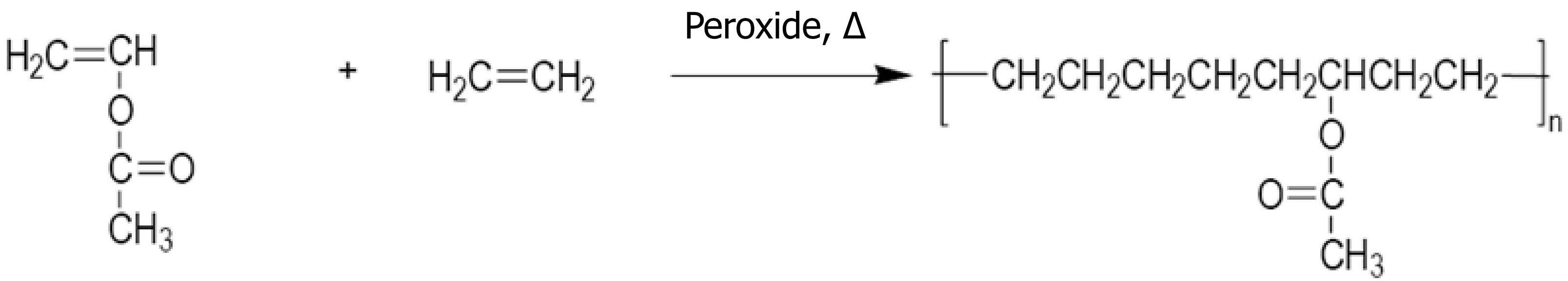
II. EVA Overview

EVA (Ethylene vinyl acetate)

■ Ethylene-vinyl acetate random copolymer

- Copolymerization with ethylene and vinyl acetate monomer
- Radical polymerization under high pressure





Vinyl acetate

Ethylene

Ethylene vinyl acetate copolymer

Molar mass : 86g/mol

Molar mass : 28g/mol

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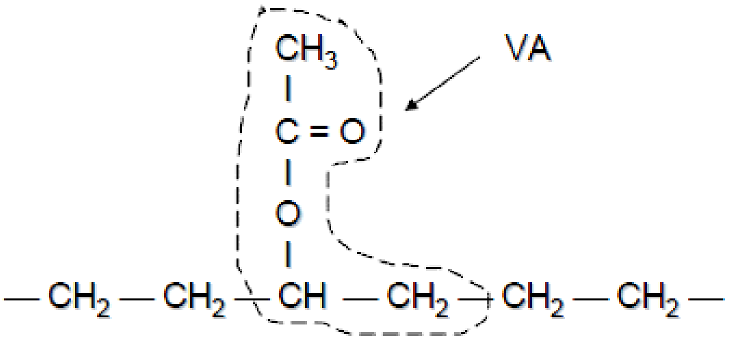
■ Effect of VA content

Increase of VA content gives :



■ Polymer properties

More short chain branching

Less crystalline (More amorphous)

Lower melting temperature

More elastic as solid

Higher density

Increased polarity

■ Application properties

Better adhesion to polar substrate

Increased tackiness

Lower seal initiation temperature

Greater flexibility

Higher clarity & gloss

Increased toughness

Effect of Melt Index

■ Effect of Melt Index

Decrease of MI gives :

▪ Polymer properties

Higher molecular weight

Higher viscosity

▪ Application properties

Lower flowability

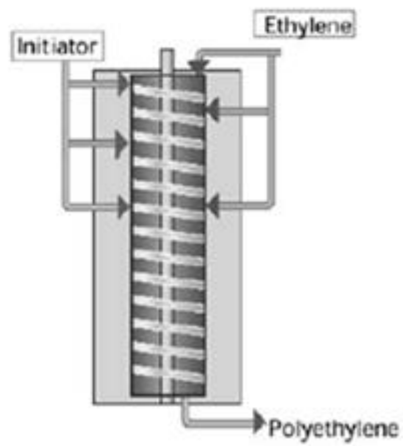
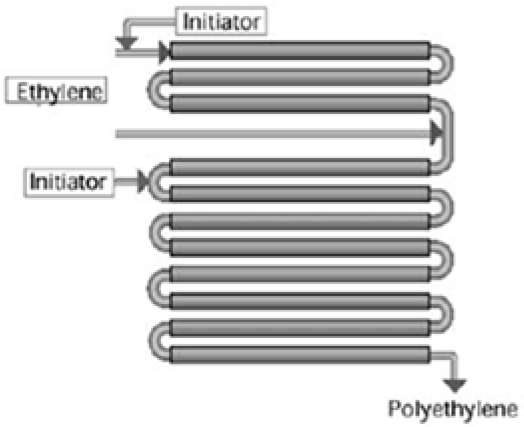
Higher melt strength

Increased impact resistance

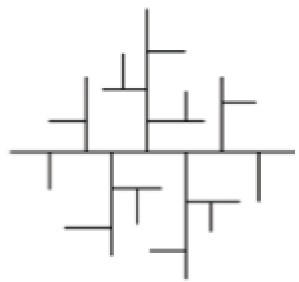
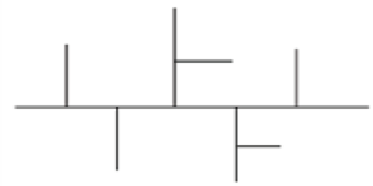
Increased tensile strength

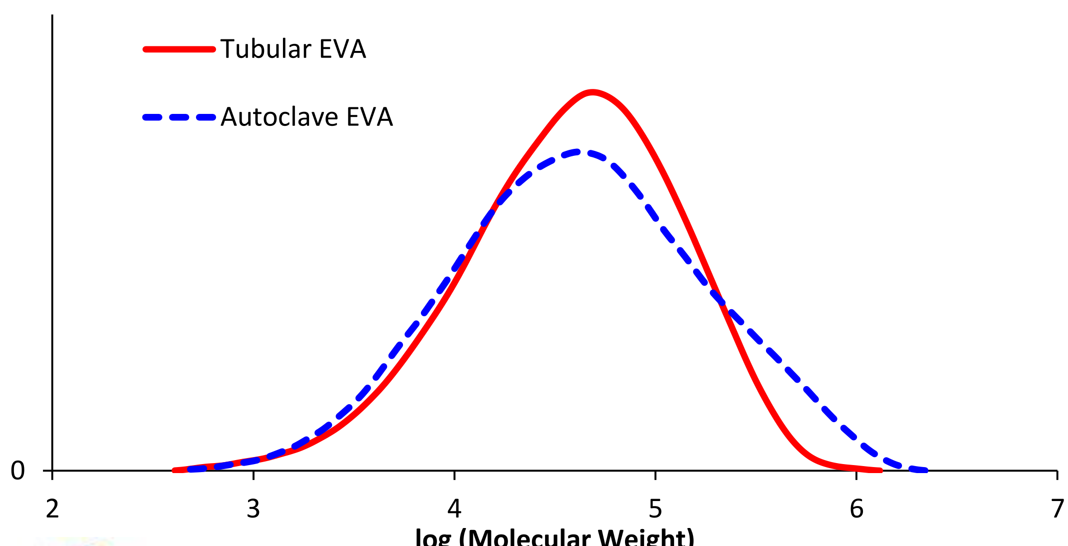
Higher abrasion resistance

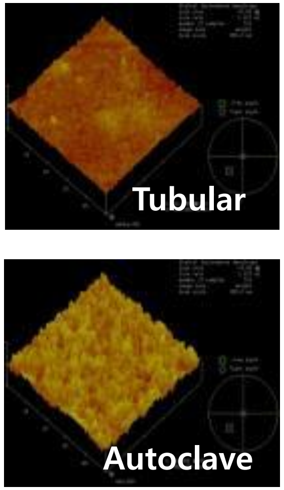
Reactor types

	Autoclave	Tubular
Reactor		
Conversion	Up to 22 %	Up to 36 %
Pressure	1100 ~ 2000 bar	2000 ~ 3500 bar
Temperature	130 ~ 280 ℃	180 ~ 350 ℃
Initiator	peroxide	oxygen, peroxide
Mixing	Stirred/Back Mixing	Plug flow
Residence time distribution	Broad	Narrow
VA content	Possible to produce EVA over 40 %	Max. 10 ~ 30 % (depending on the process)

Characteristics of Tubular EVA

	Autoclave	Tubular
MWD	Broad	Narrow
LCB		





Film surface roughness (AFM)

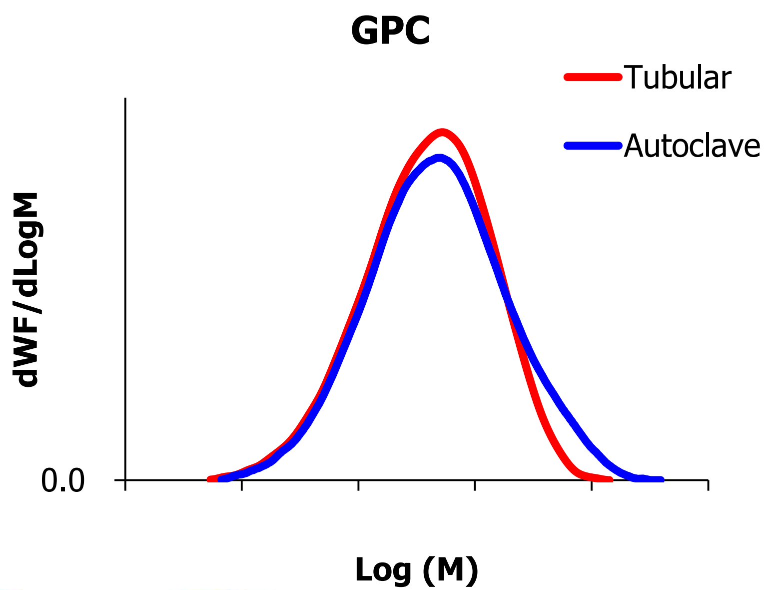
■ Differences originated from Process

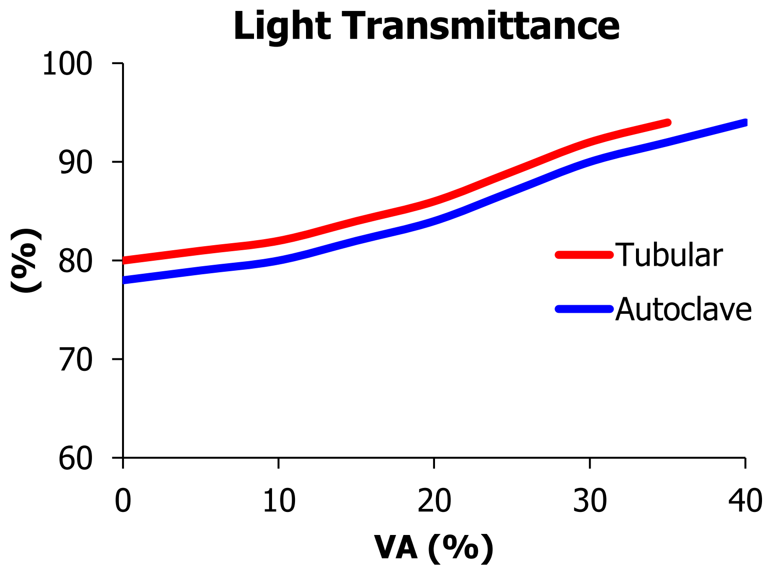
o Autoclave reactor EVA

- Broad MWD, high MW tail, F/E (gel) level increase

o Tubular reactor EVA

- Narrow MWD, high transparent





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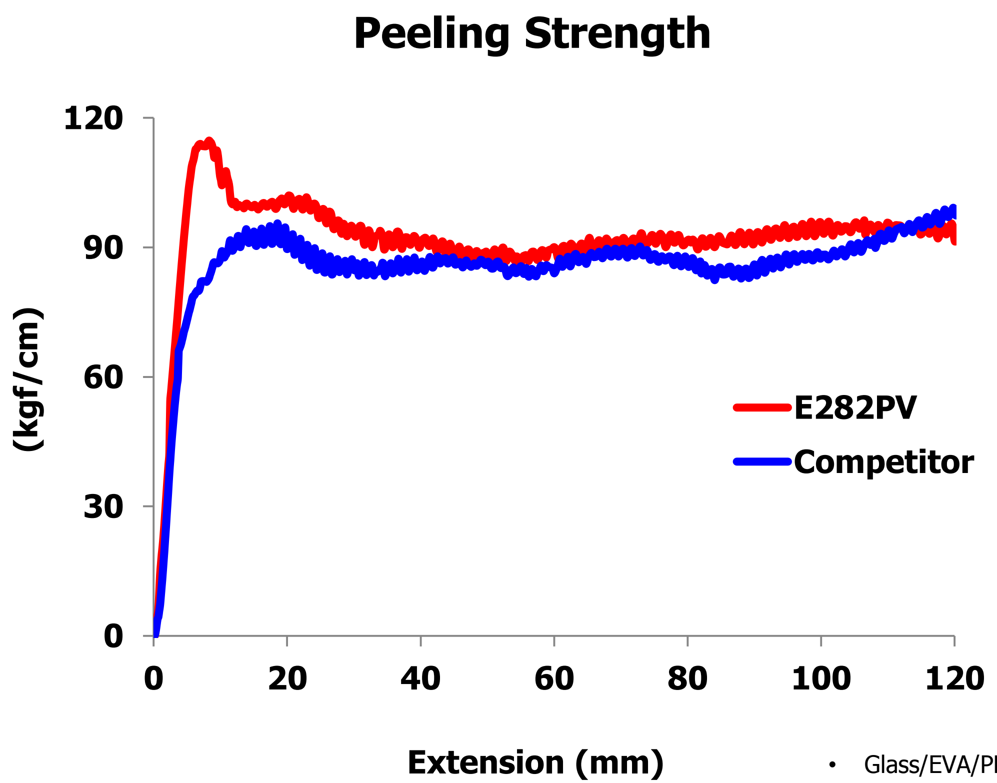
■ Peeling Strength

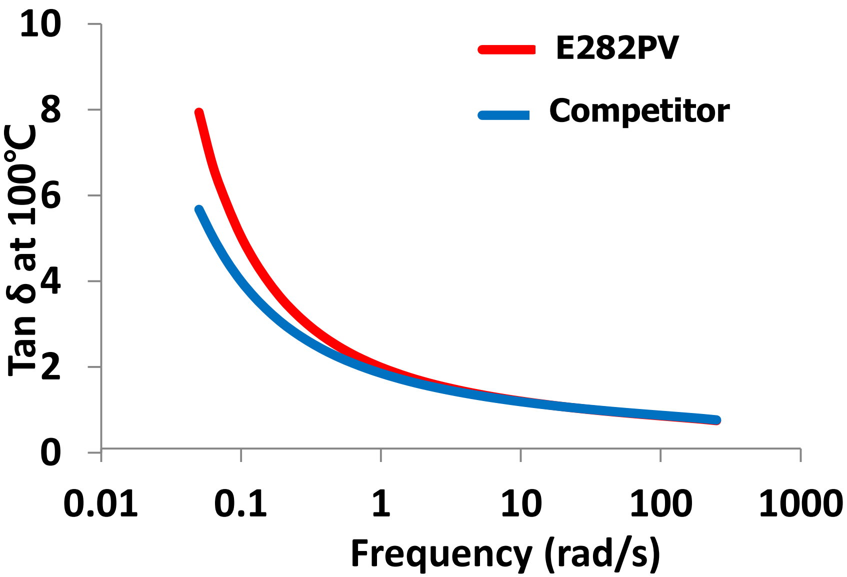
o Higher peeling strength compared to same MI competitor's grade

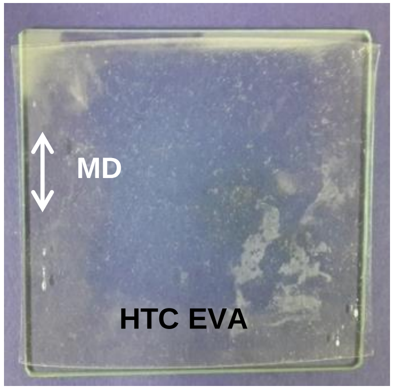


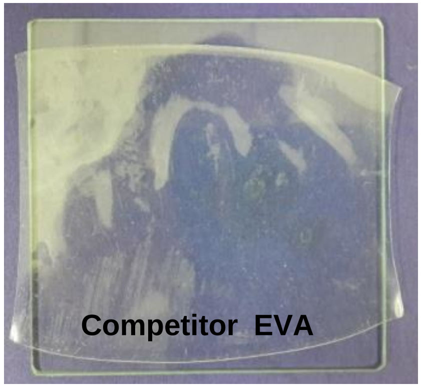
- Glass/EVA/PET lamination
- Lamination Condition : 150 ℃, Vacuum 6 min, Press (100Kpa) 11 min

■ Lower Shrinkage

- o Less melt elasticity and memory effect of HTC EVA leads fast relaxation time
- o Low residual stress in a sheet made from casting or calendering process







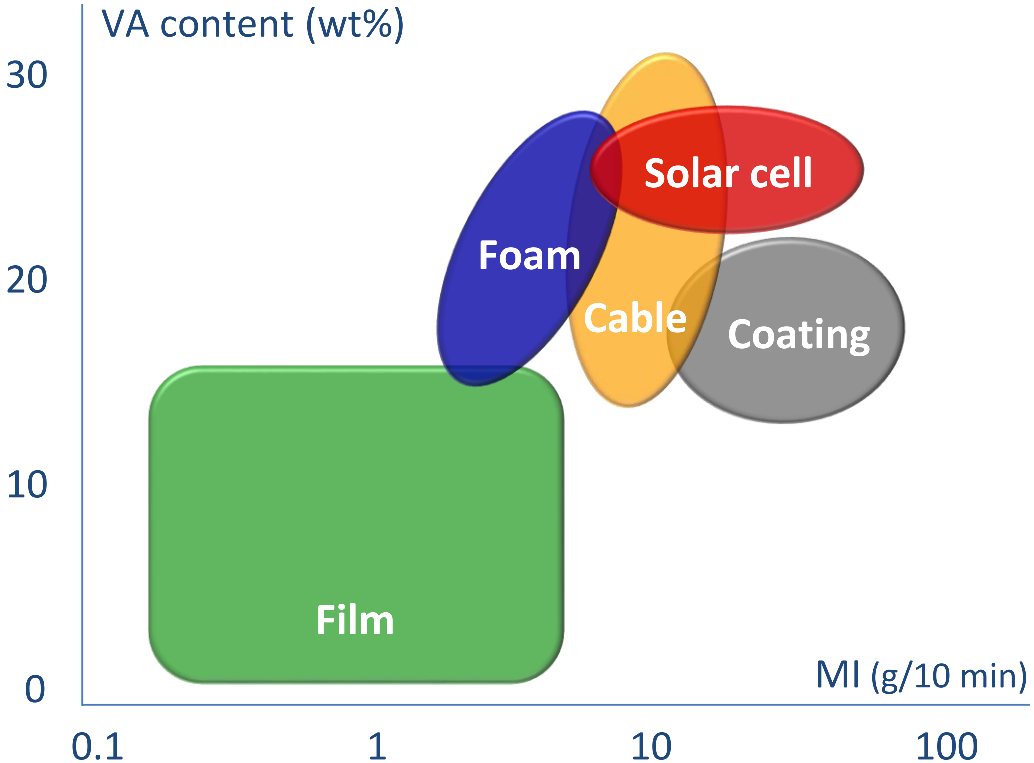
III. Hanwha Total's EVA

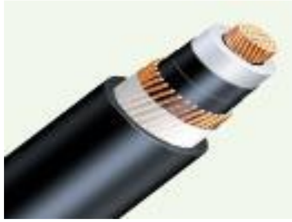
Hanwha Total's EVA Capacity

Plant	Reactor	Licensor	Capacity (KT/Yr)	Start-up
No.1	Tubular	Mitsubishi	155	1991
No.2	Tubular	LyondellBasell	240	2014
Sum			395	

EVA Product Portfolio

- HTC EVA consists of a range of vast array of industrial application such as photovoltaic encapsulant, footwear, food packaging, wire & cable and extrusion coating, agricultrural greenhouse film, stretch hood





IV. Film application

HTC's EVA for Film

■ Grade List

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

■ Agricultural film E032A/E090A/E120A/E150A/E180A

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

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

Greenhouse film (3 layers)

anti-aging layer (outer)	LDPE + mLLDPE
insulation layer(center)	EVA(3~18% VA) + LDPE
anti-droplet layer(inner)	EVA(3~18% VA) + LDPE

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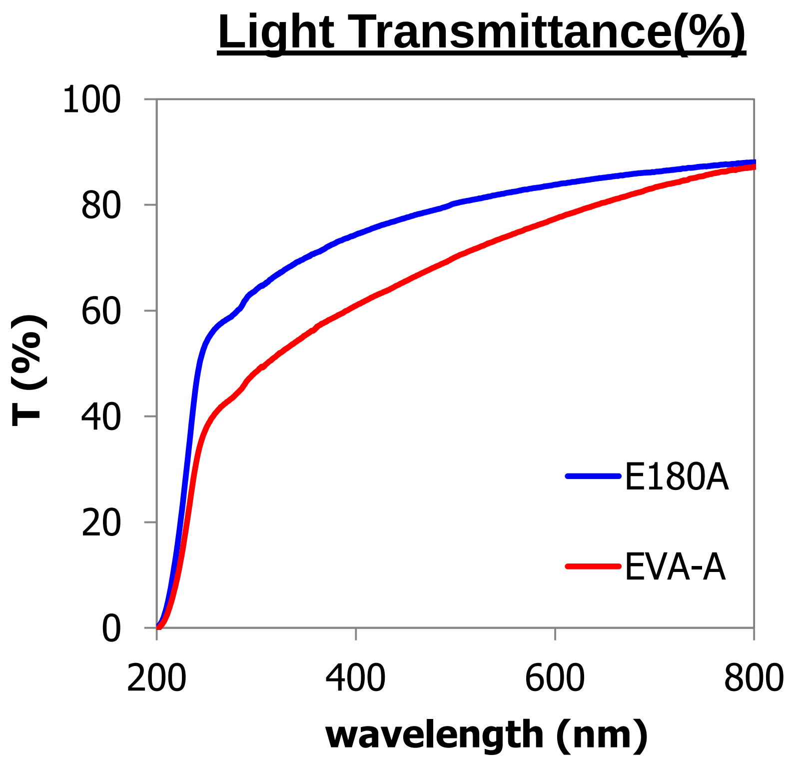
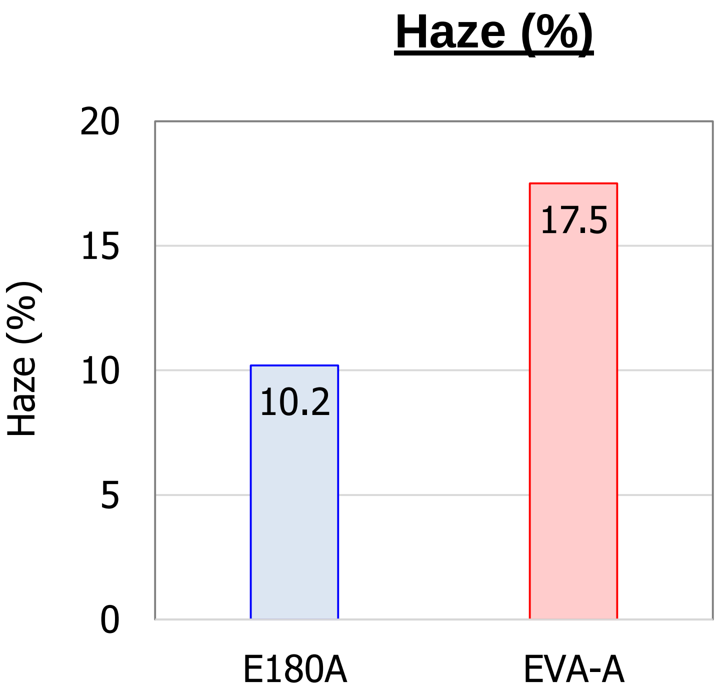
■ Optical property

- Excellent light transmittance
- Lower haze

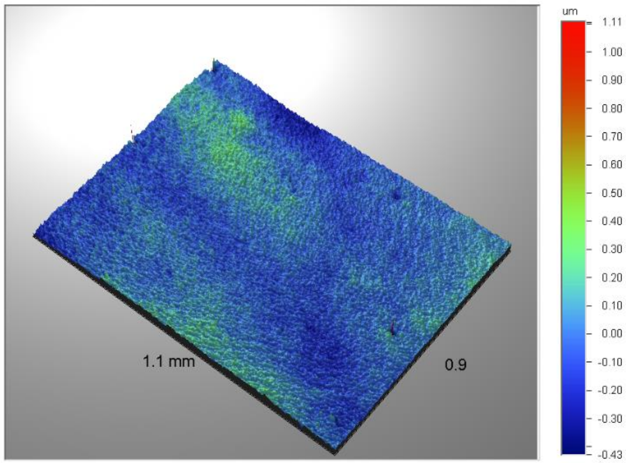
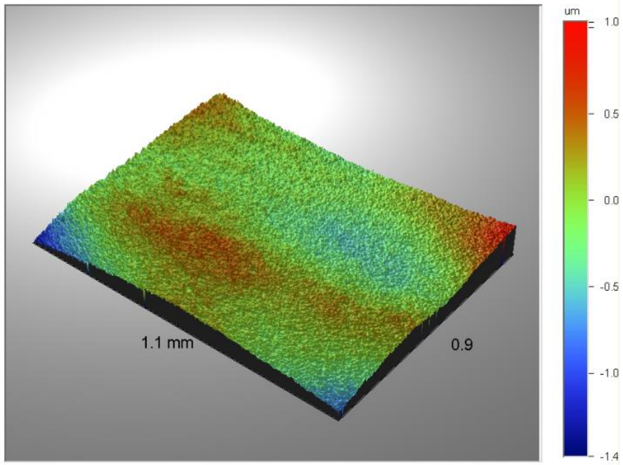




* Processing conditions : PLACO 50mmΦ Blown film M/C (Die Gap 2.5mm)
Temperature 180 ℃, Screw rpm 50, Film thickness 50 ㎛

■ Surface property

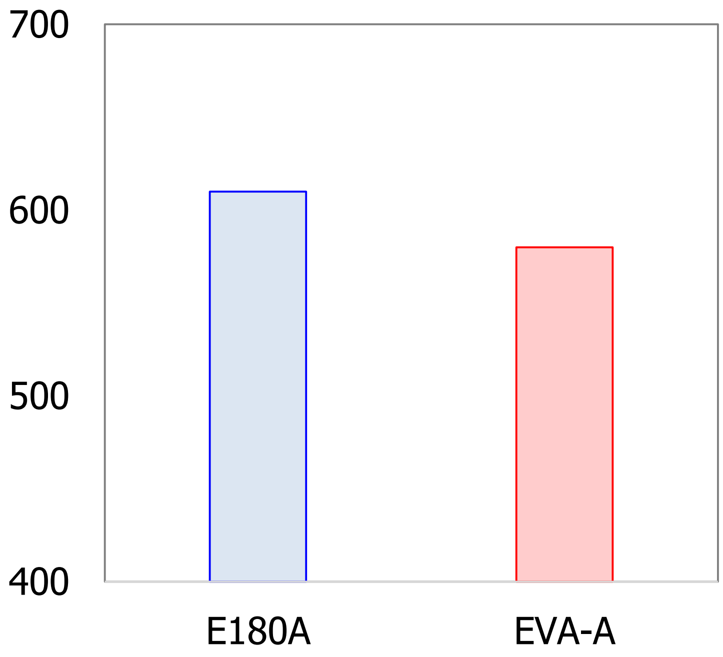
- Better clarity due to uniform surface

	E180A	EVA-A
Roughness (nm)	98	246
Haze (%)	10.2	17.5
3D Image		

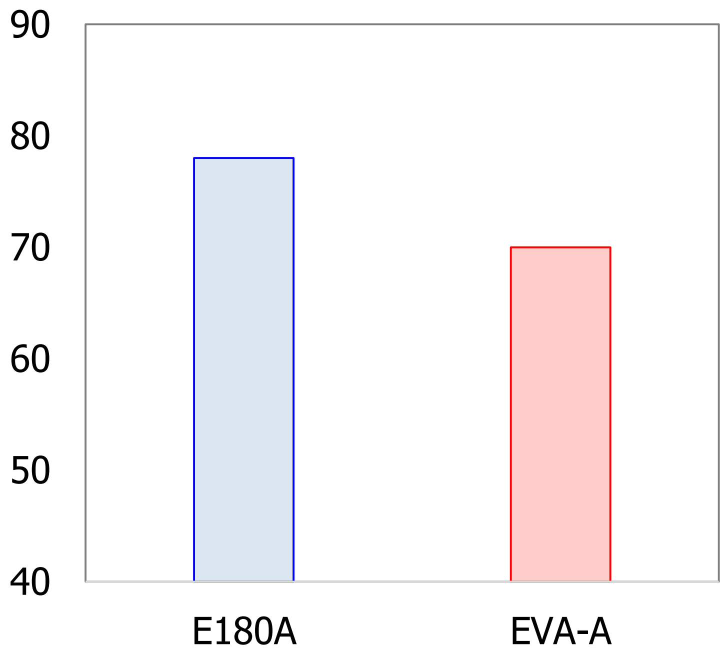
■ Physical property

- o Excellent impact strength, puncture strength, etc

Impact strength (g)



Puncture resistance (N)



Agricultural film

Resin type	LDPE	LLDPE	HDPE	EVA				
Grade	**310A**	**4220U**	**F120U**	**E032A**	**E090A**	**E120A**	**E150A**	**E180A**
Basic property								
MI (g/10min)	0.8	1.0	0.044	0.5	0.8	1.0	1.0	0.8
Density (g/cm^3)	0.922	0.921	0.956	0.923	0.928	0.931	0.936	0.940
VA (wt%)	-	-	-	3	9	12	15	18
Additives								
Anti-oxidant agent	●	●	●	●	●	●	●	●
Anti-block agent	●	●		●				
Slip agent	●	●		●				
UV agent		●	●					
Applications								
Greenhouse	●			●	●	●	●	●
Mulching		●	●					

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

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

■ Automatic fisheye counter (AFC)

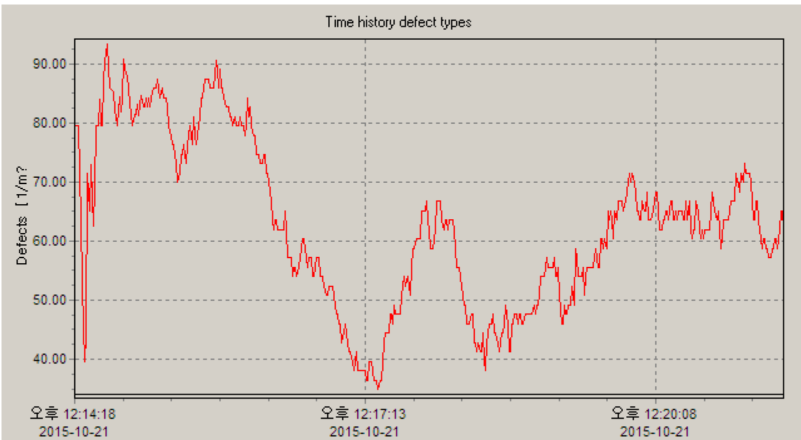
- Advantage
  - cover large area
  - analysis fisheye trend, size distribution
- Disadvantage
  - limitation on distinguishing fisheye type
  - resolution limited by measuring area
- Type : online measure, offline measure

■ Identification of fisheye

- Visual inspection
- Microscope & hot stage melting test
- Instrumental analysis : material & element analysis

Analysis with AFC

■ Time trend, position & frequency, shape of fisheye



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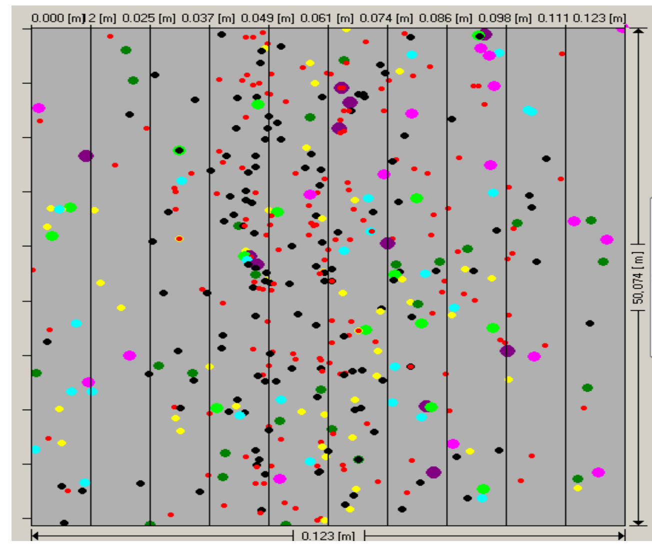

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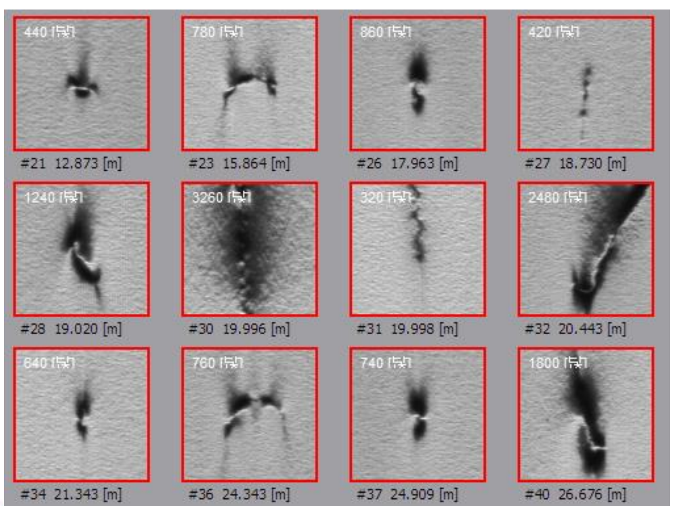
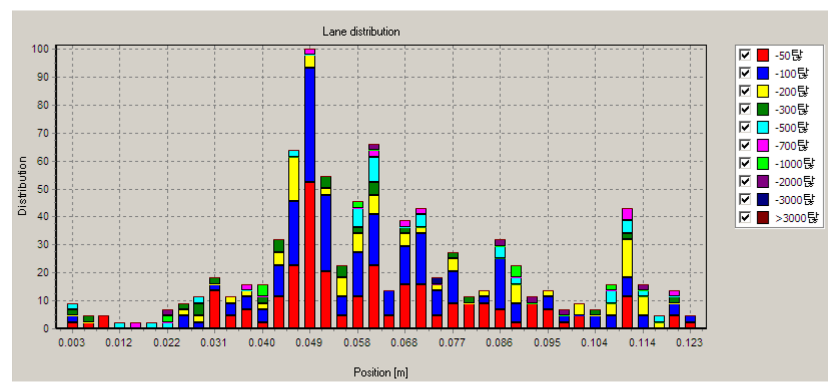
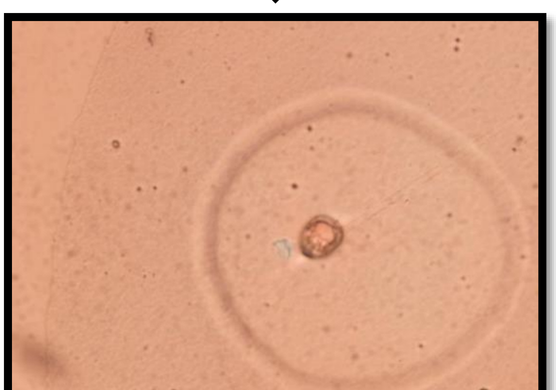




Identification of fisheye

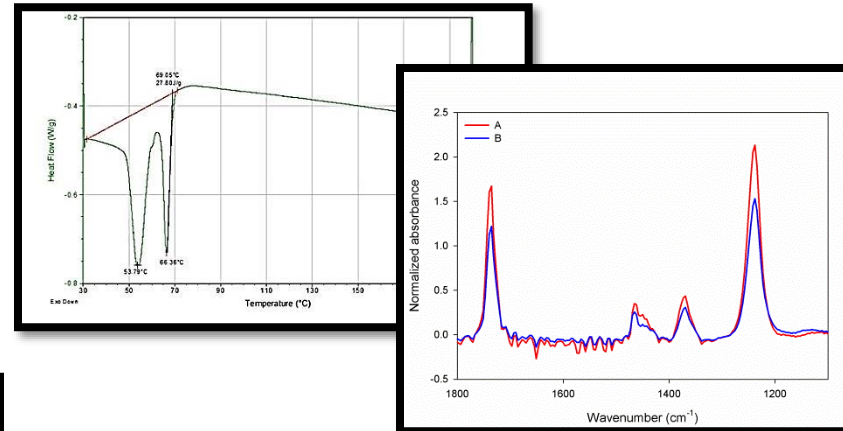
Visual inspection

OM & Hot stage



Organic

DSC & FT-IR



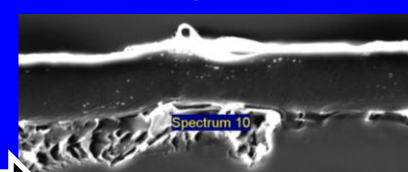
Inorganic

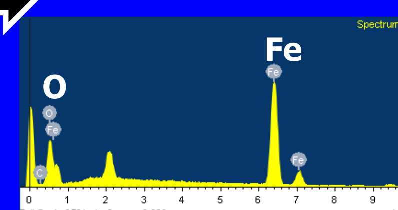
SEM / EDS

Cross-sectioning

microtoming

SEM



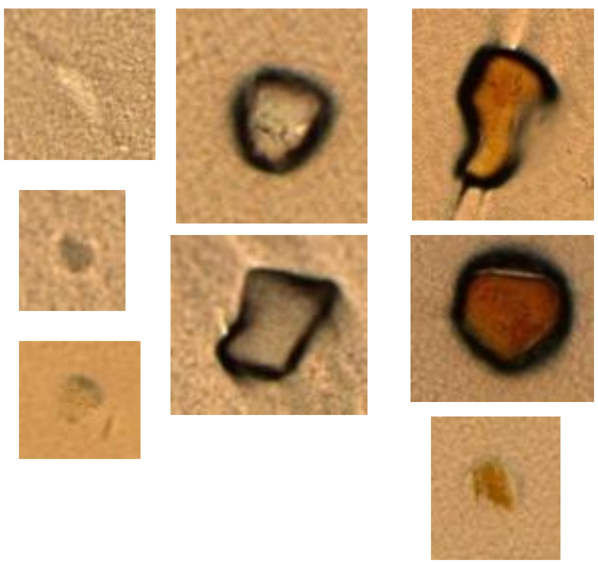


EDS

Classification of fisheye

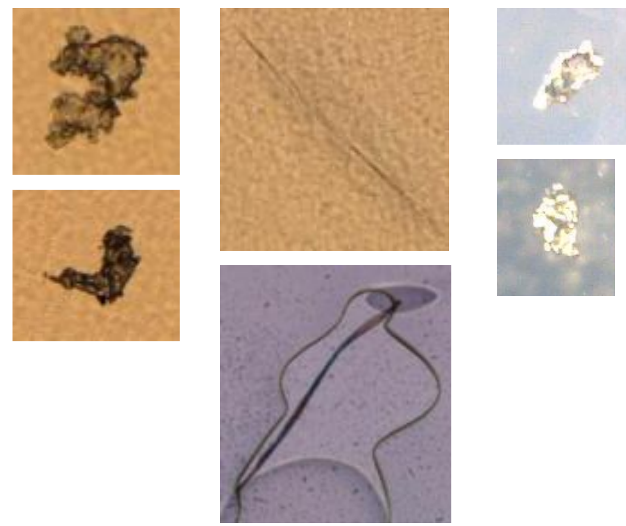
■ **Degradation, crosslinking, oxidation of polymer**

- **During polymerization and extrusion**
- **Crosslinked gel, oxidized gel**



■ **Contamination**

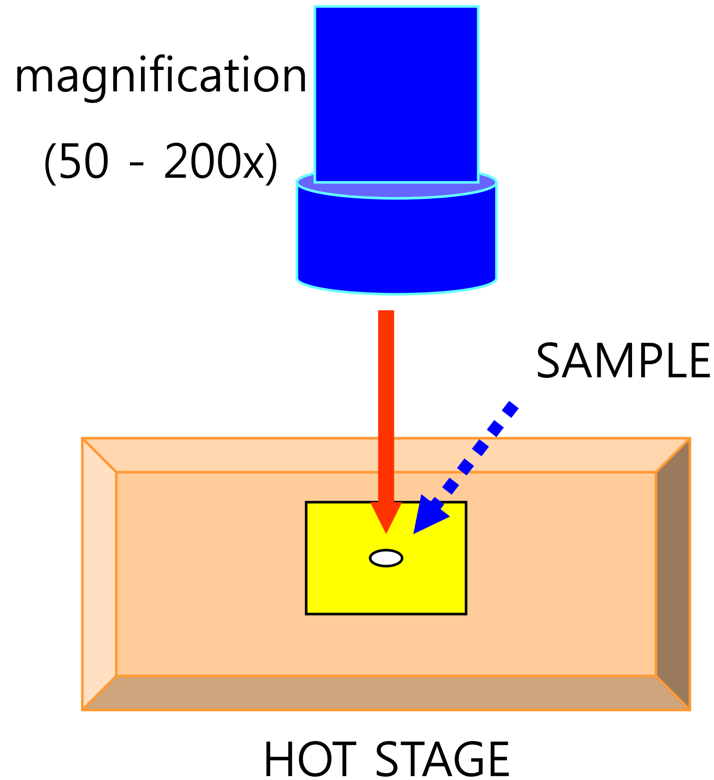
- **Fiber : gloves, clothes, dust**
- **Inorganic material : additives**
- **Metal**
- **Foreign resin**



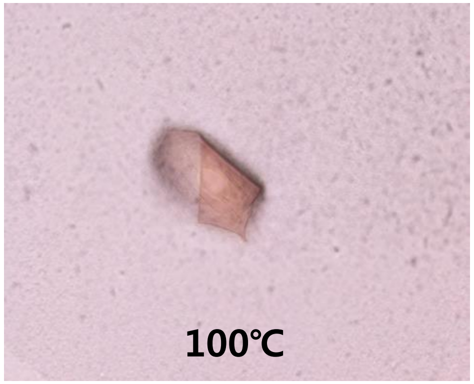
Microscope & Hot stage

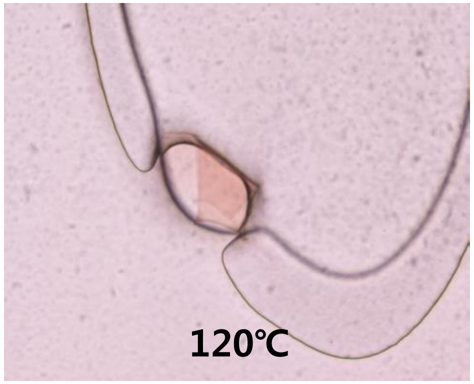
■ Fisheye analysis using microscope

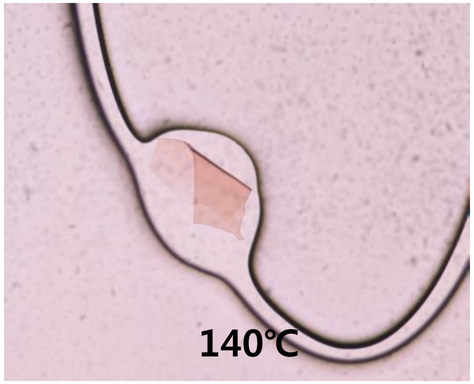
- **shape, size**
- **melting or unmelting**
- **measuring Tm**

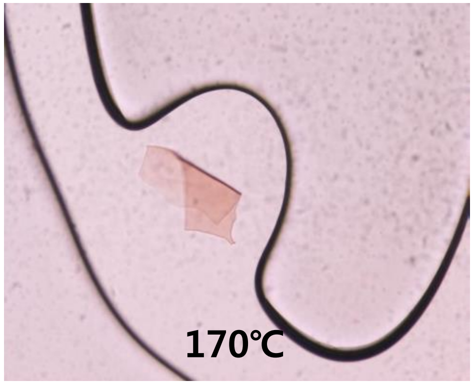


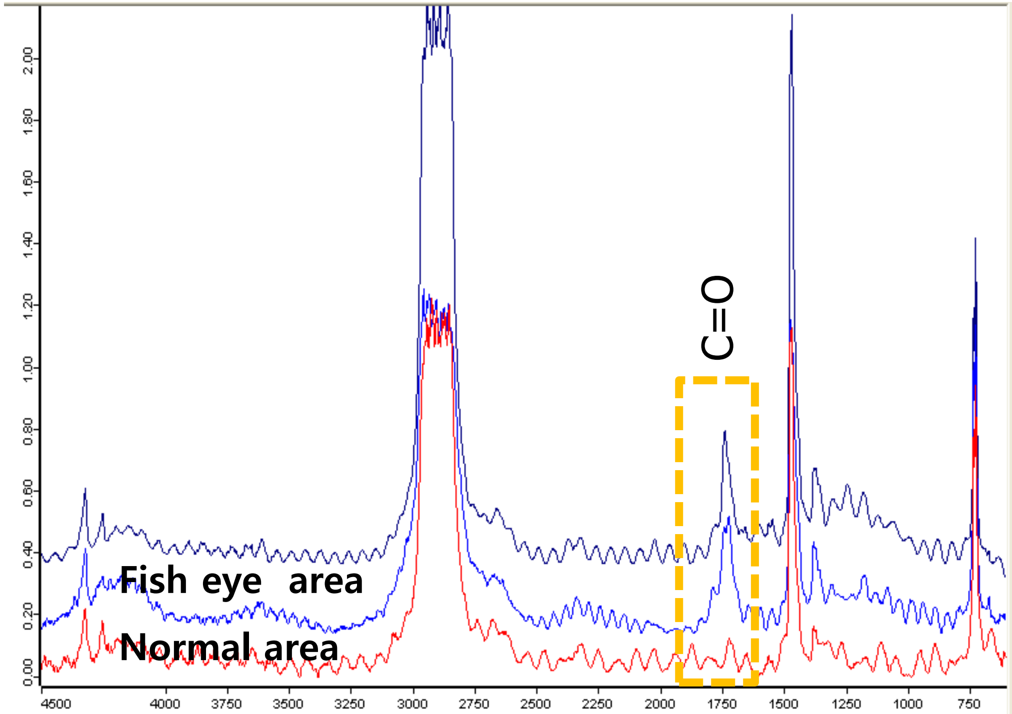
Examples : Oxidized fish-eye











- **Observed fish-eye seed after melting. Fish-eye is not melted in high temp**
- **C=O peak is observed in FT-IR**

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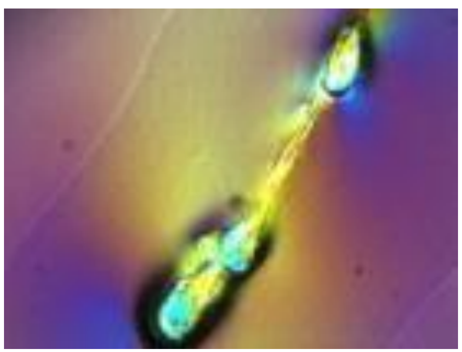
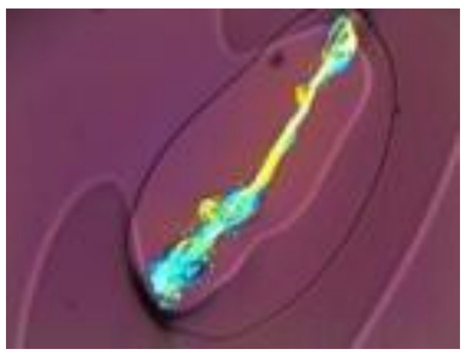
Examples : other resin contamination

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

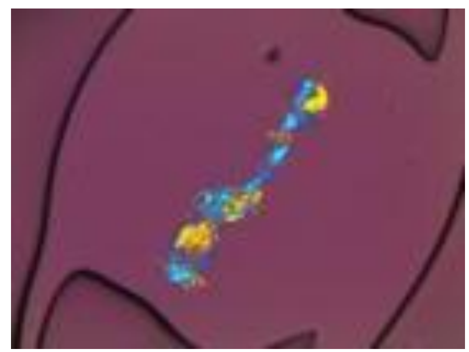
30℃



80℃



110℃



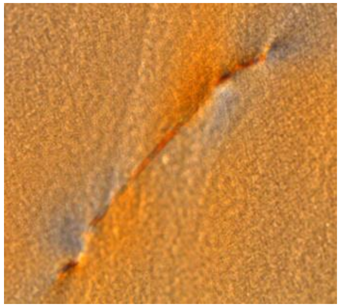
115℃

Examples : Fiber

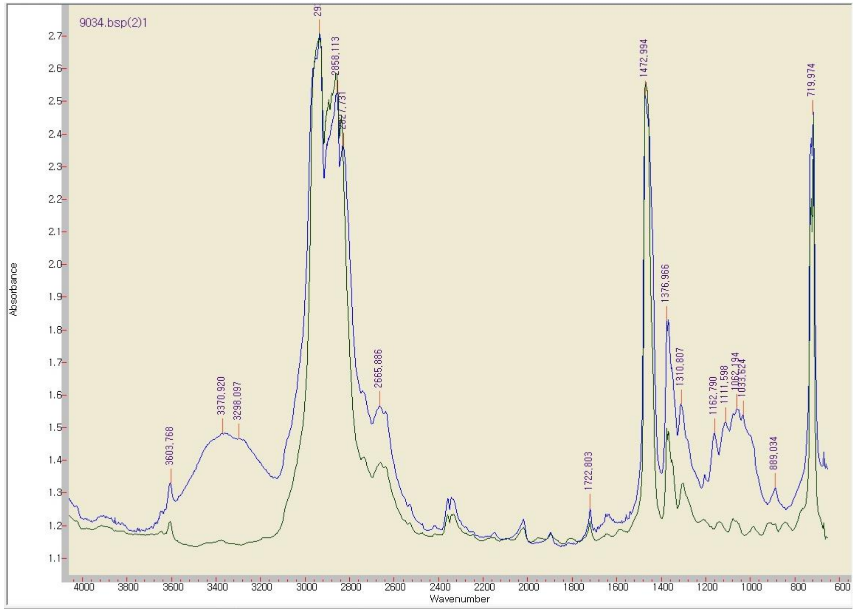
■ **Fiber can be classified by shape, and identified with FT-IR analysis**

- **Cotton, polyester, nylon, etc.**

Cotton



Polyester



FT-IR: Cotton, Cellulose

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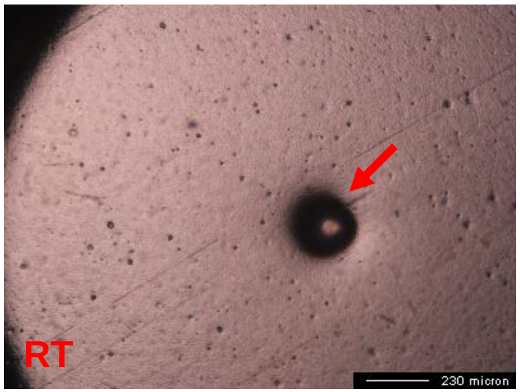
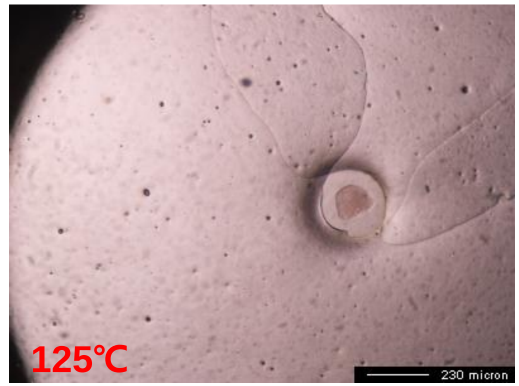
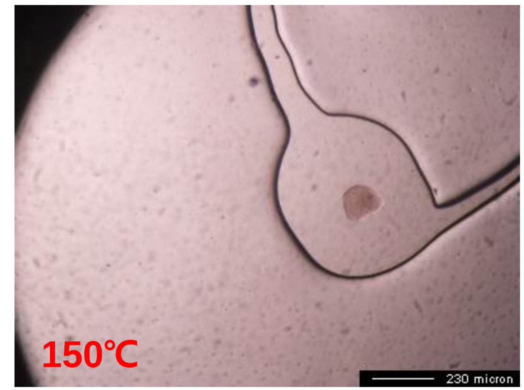
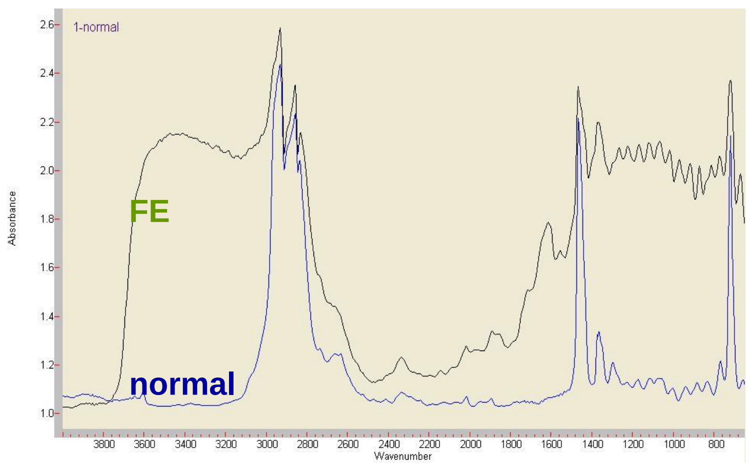
Examples : inorganic material

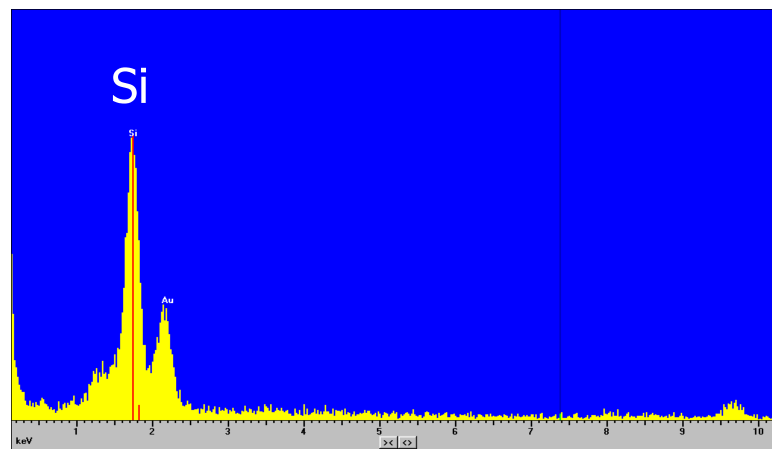
■ **Inorganic material can be identified with elemental analysis**











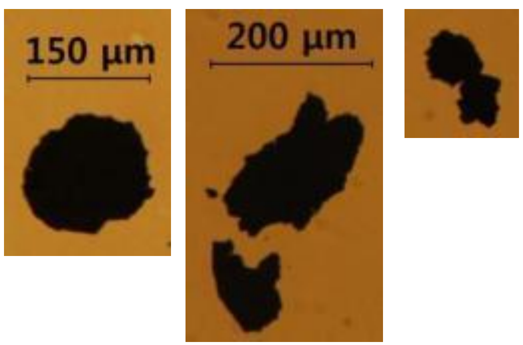
=> identified as anti-blocking agent

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

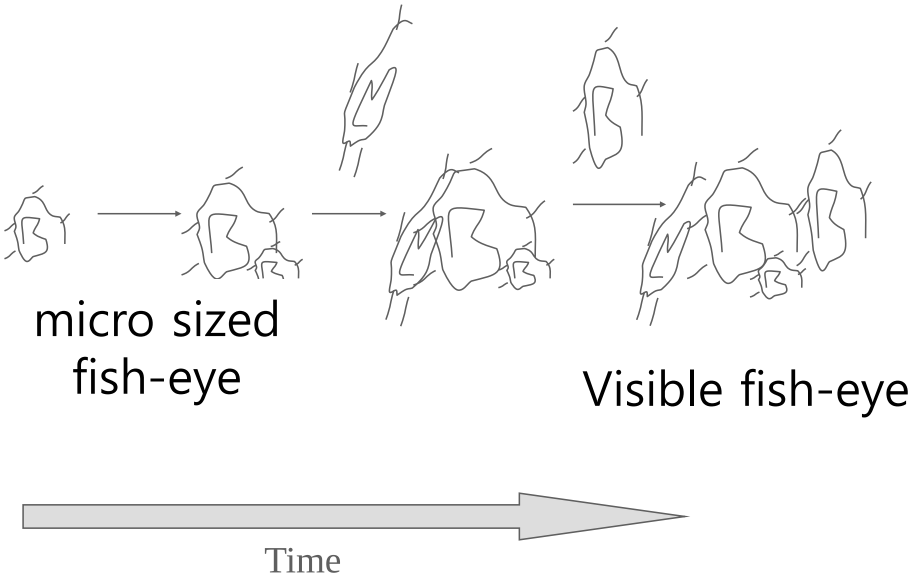
transmission microscope



reflection microscope

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

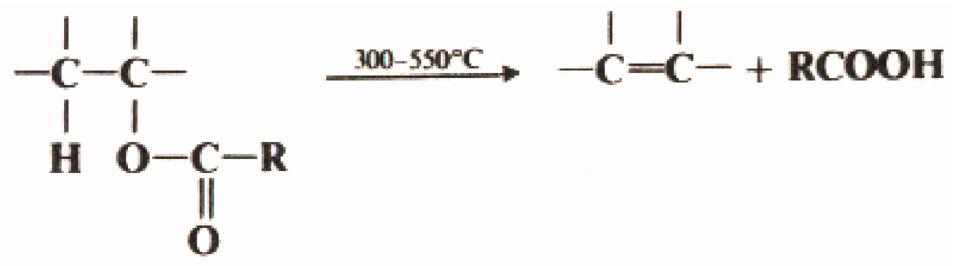
Degradation of EVA

■ Thermal stability of olefin copolymer

- o (stable) HDPE > LDPE > LLDPE > EVA (unstable)

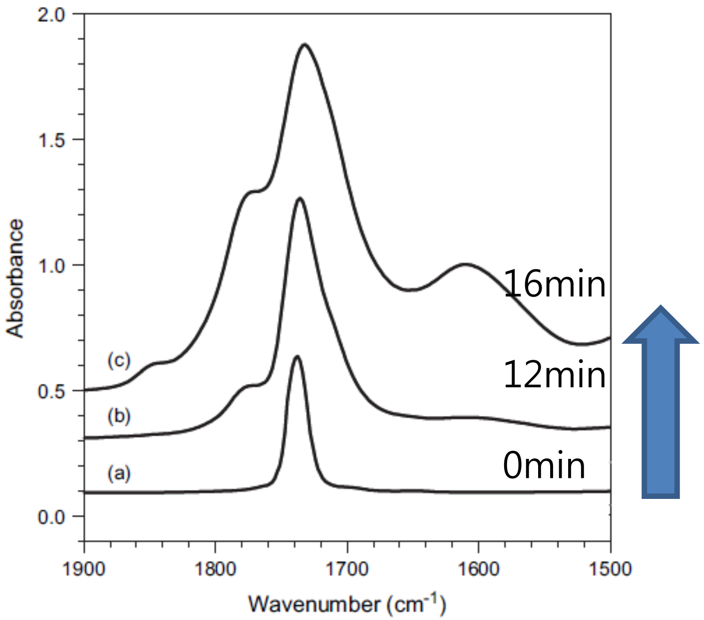
■ Degradation by thermal radical

- o degradation rate increases,
  - at excessive high temperature
  - by oxygen contact
  - by impurities such as acid, oxides, metal ion
- o High VA EVA degrades faster



degradation of EVA, releasing acetic acid

EVA in Air, 180℃

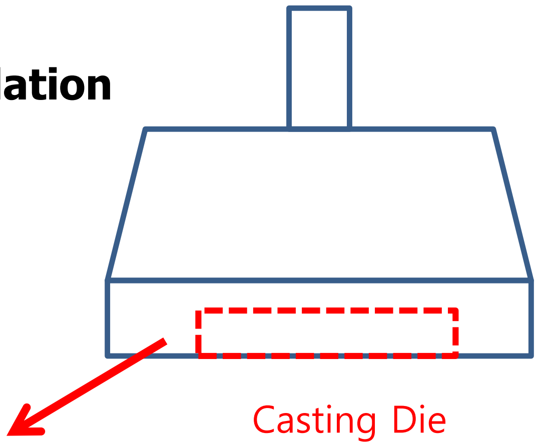


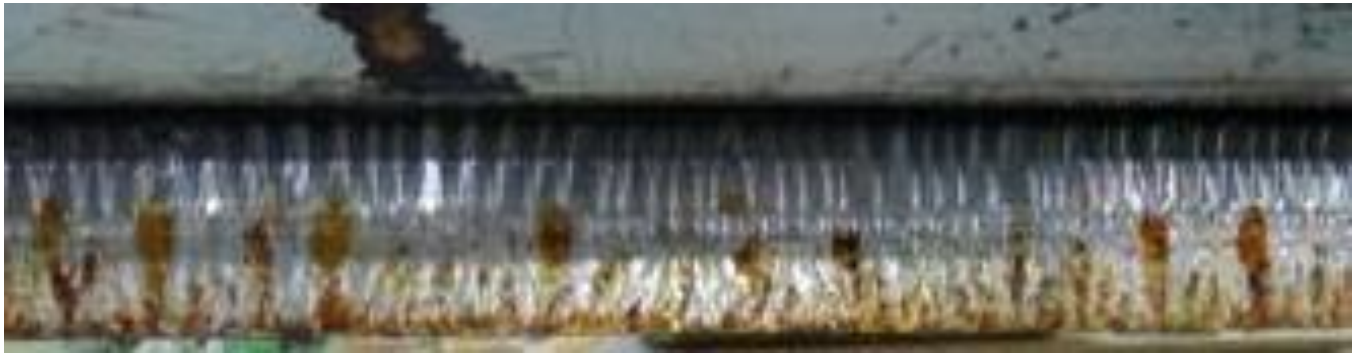
FT-IR : oxidation peak

Aging inside the die

- **After finishing film extrusion, machine stopped and the EVA (VA 18%) had exposed to excessive high temperature 240 ℃ 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

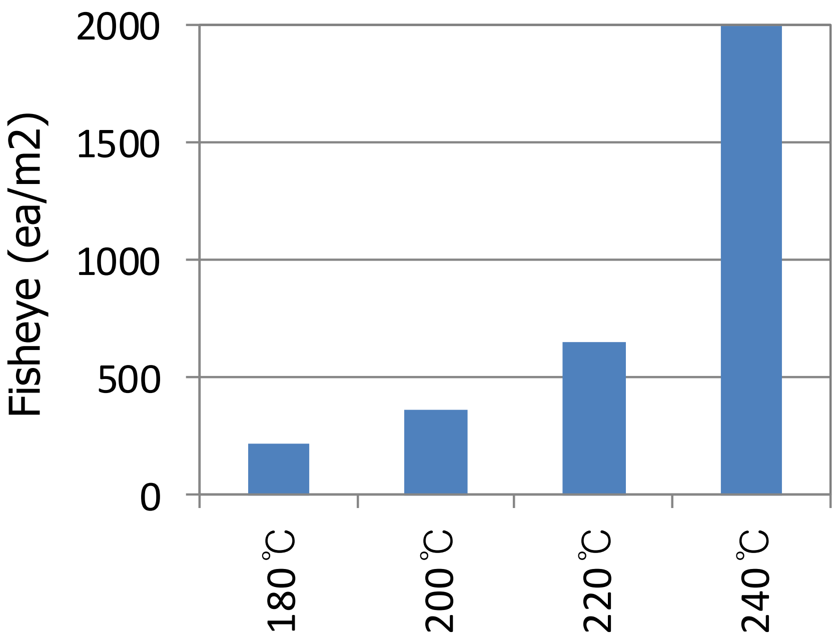


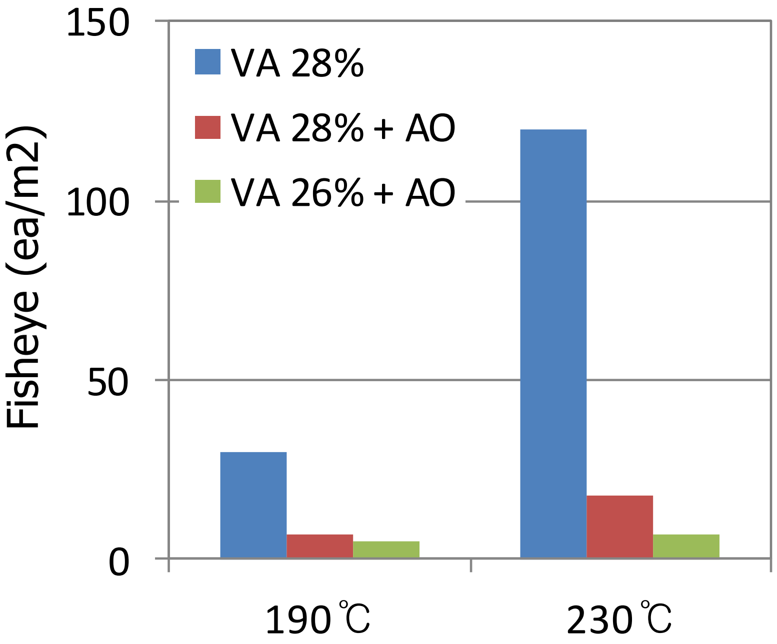


Inside the die;
after 5 hours aging
at 240℃

Processing temperature and antioxidant

- **Crosslinking reaction become 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**





Countermeasure

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

Disclaimer