A Family of Fluorinated Processing-Aids for Polyolefins

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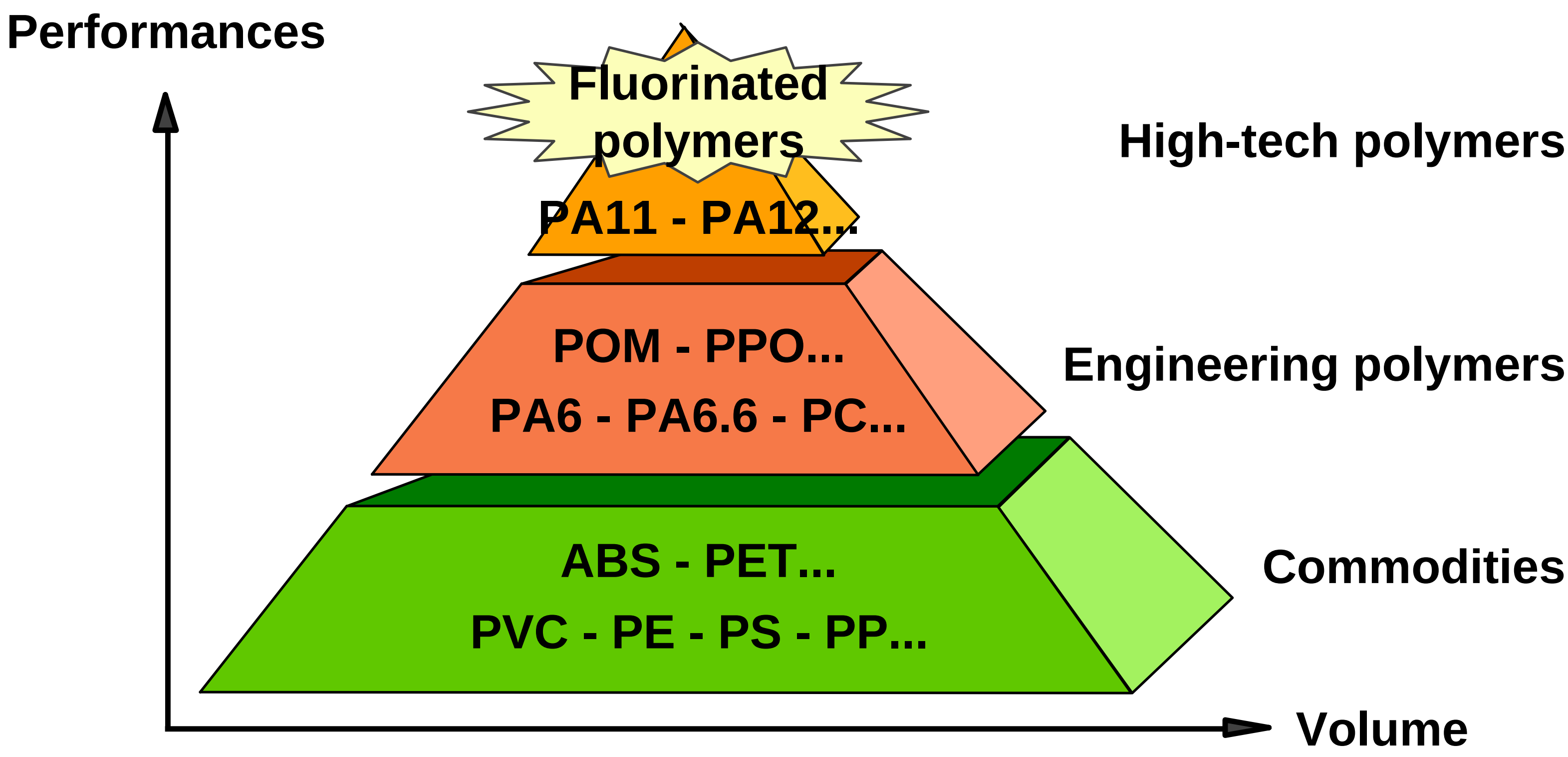
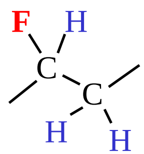
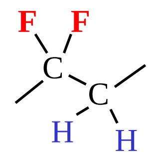
Positioning of fluorinated polymers



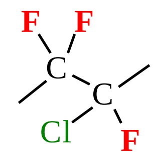
The range of fluorinated polymers



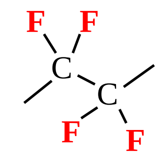
Polyvinyl
fluoride
PVF



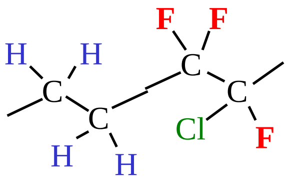
Polyvinylidene
fluoride
PVDF



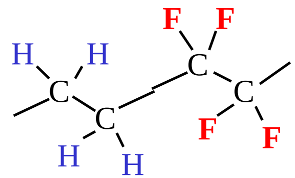
Polychloro-
trifluoroethylene
PCTFE



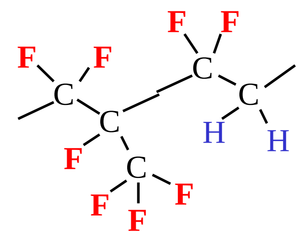
Polytetrafluoro-
ethylene
PTFE



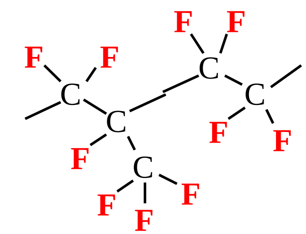
Chlorotrifluoroethylene
+ethylene
ECTFE



Tetrafluoroethylene
+ ethylene
ETFE

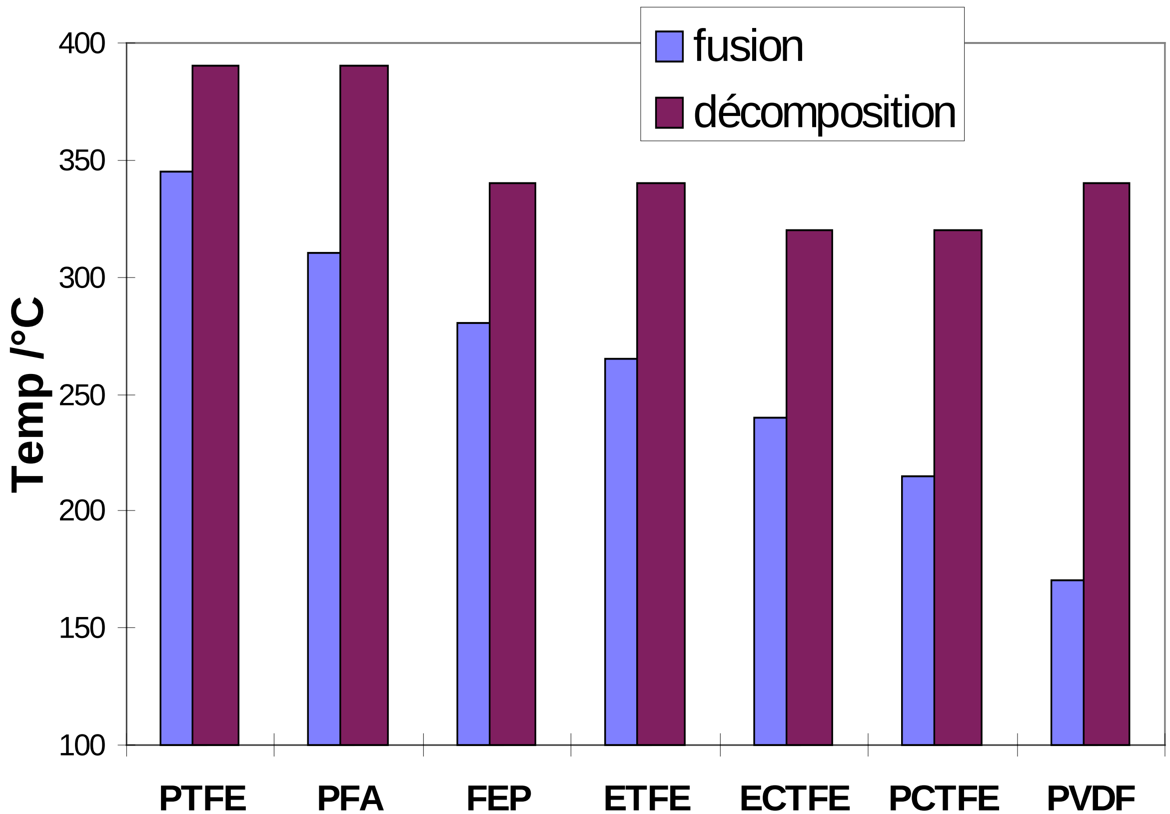


Polyvinylidene
+ hexafluoropropene
PVDF-HFP



Tetrafluoroethylene
+ hexafluoropropene
FEP

PVDF among other fluorinated polymers

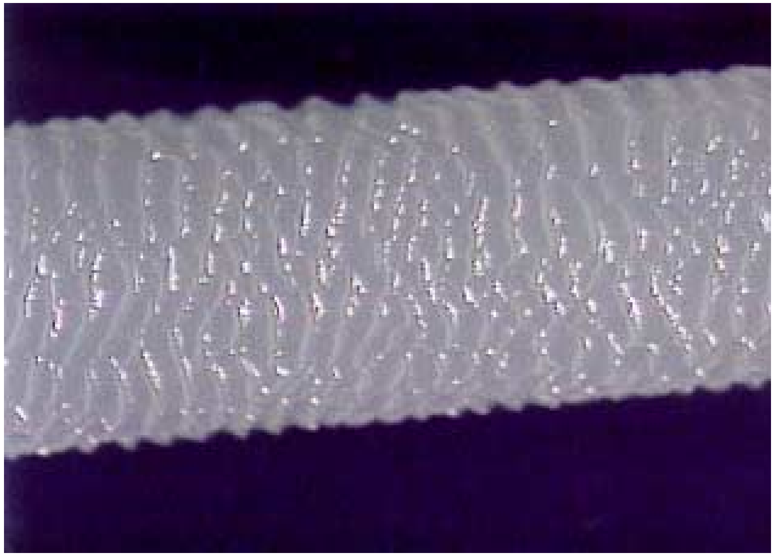


What makes PVDF or PVDF-HFP attractive ?

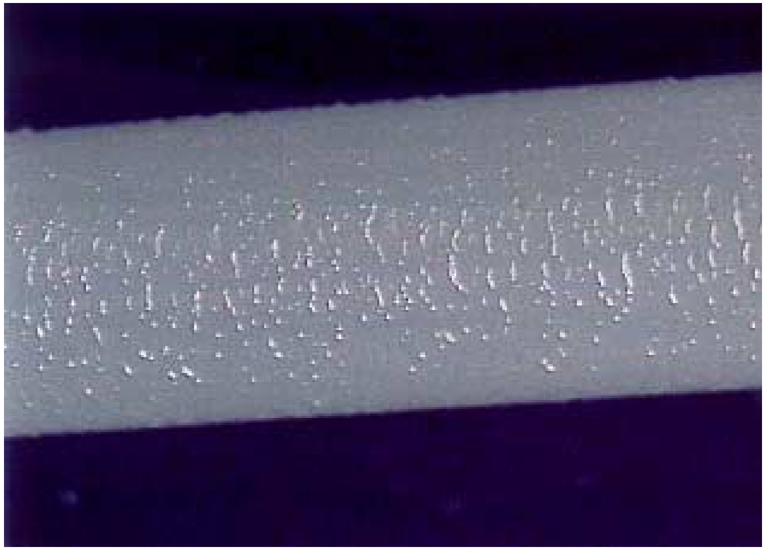
- *Chemical & thermal stability* of fluoropolymers
- *Processability* of thermoplastics
- *Large melting point range* between 115°C and 175°C
  - The higher HFP content, the lower T_m
- Among the *cheapest fluoropolymers*

Kynar®
Kynar Flex®
Kynar Superflex®

Why is PVDF-HFP attractive for you ?



without
PPA additive



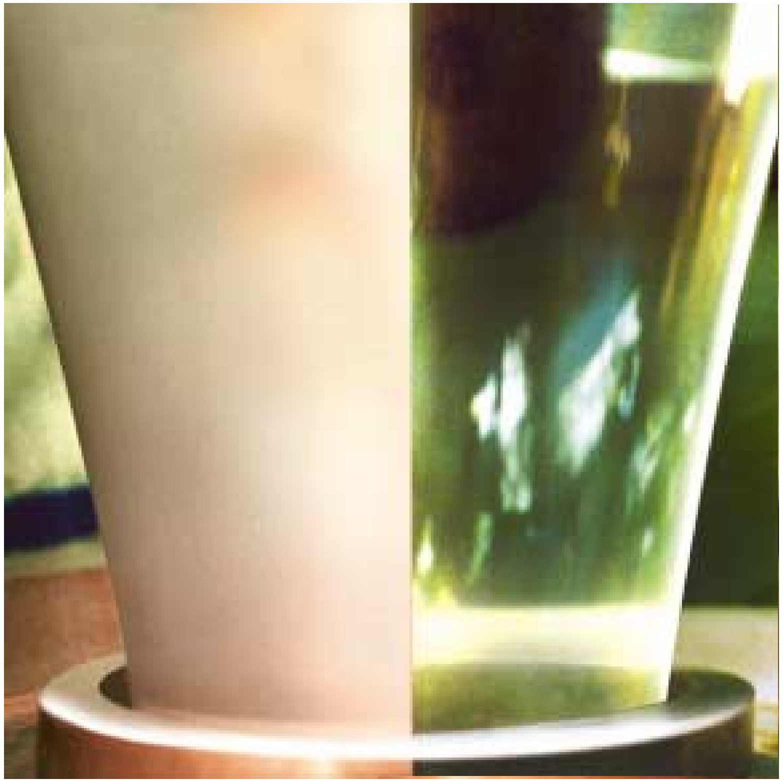
with
500 ppm of PPA additive

Tube, cable extrusion - Blow molding process

… gets better surface aspect !

Why is PVDF-HFP attractive for you ?

without
Kynar Flex® PPA

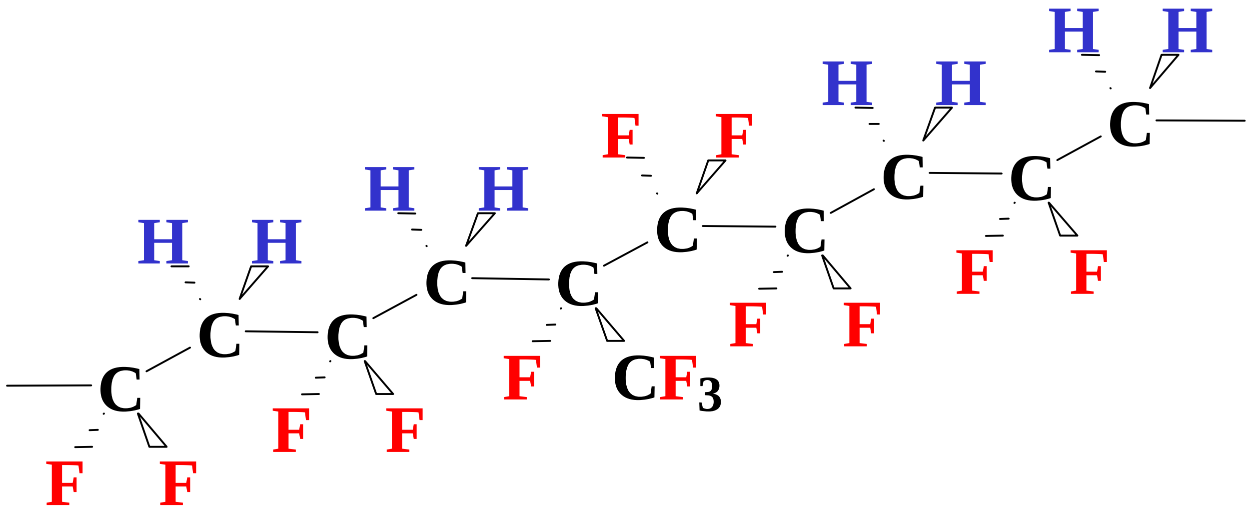


with
500 ppm of
Kynar Flex® PPA

Blown film extrusion

… gets better surface aspect also !

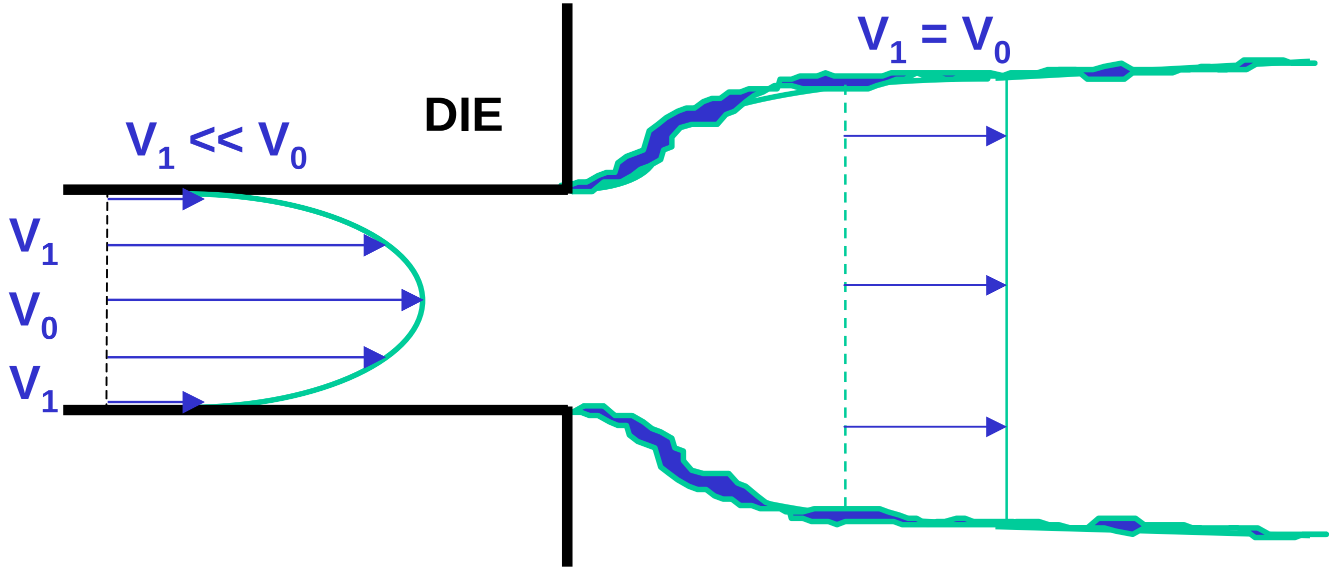
Kynar Flex® PPA Chemical Structure



- PVDF-HFP copolymer, fluorine content of ~ 0.615
- Two key properties :
  - incompatible with polyolefins
  - very low surface tension

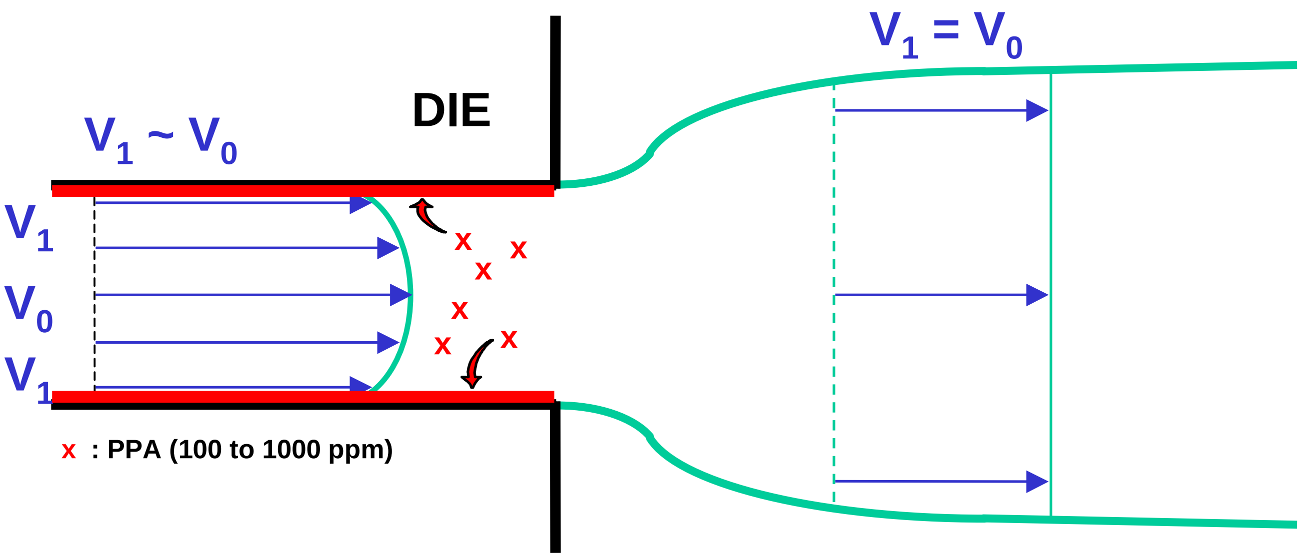
Without PPA : Melt fracture

- Narrow dies / high extrusion outputs brings *high shear rates*
- Change of velocity at the die exit brings *melt fracture* (also referred as *sharkskin*)



With PPA : No melt fracture

- Makes a *coating* on barrel & die extruder inner surface
- Reduces shear rate / viscous drag in the die :
  - ***occurrence of melt fracture is delayed / extruder output is increased***
  - ***surface aspect is improved !***



How to use the fluorinated PPA ?

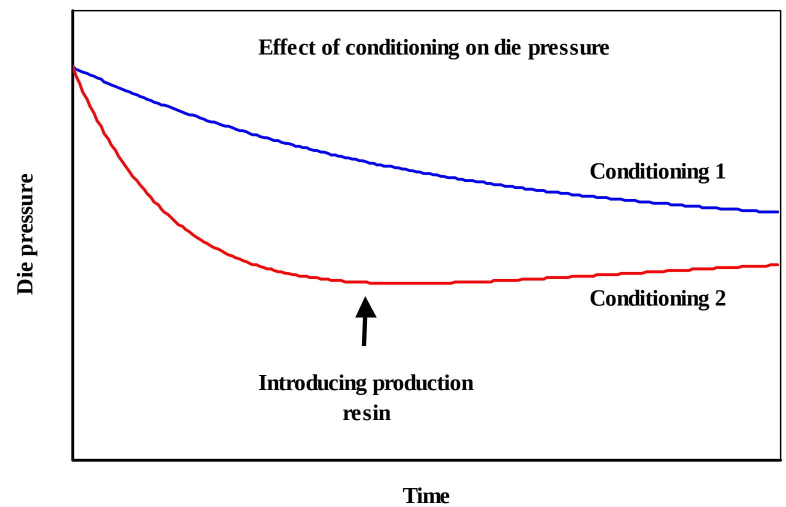
- ***1st Step*** : Conditioning of the extruder
  - objective is to coat the surface of the extruder with fluoropolymers
  - can be seen either by a *drop of pressure* in the extruder head or by *elimination of melt fracture*
  - use of a masterbatch is recommended
- ***2nd step*** : Maintain the fluoro-coating during the extrusion
  - coating is slowly removed by the abrasive action of the melt
  - 200 - 800 ppm of PPA is needed to maintain it
  - pressure is maintained low when amount of PPA is enough

Conditioning time

- Depend on the *host polymer*, the *level of PPA* and *tooling*
- Fast conditioning is obtained when :
  - **concentration** of PPA is **high**
  - **dispersion** of PPA in the host matrix is **fine** (< 2 µm)
  - viscosity of host matrix is low
  - shear rate in the extruder is high

Conditioning 1 = Use of a resin with 500 ppm of KYNAR FLEX® PPA

Conditioning 2 = Use of a masterbatch with 2% of KYNAR FLEX® PPA



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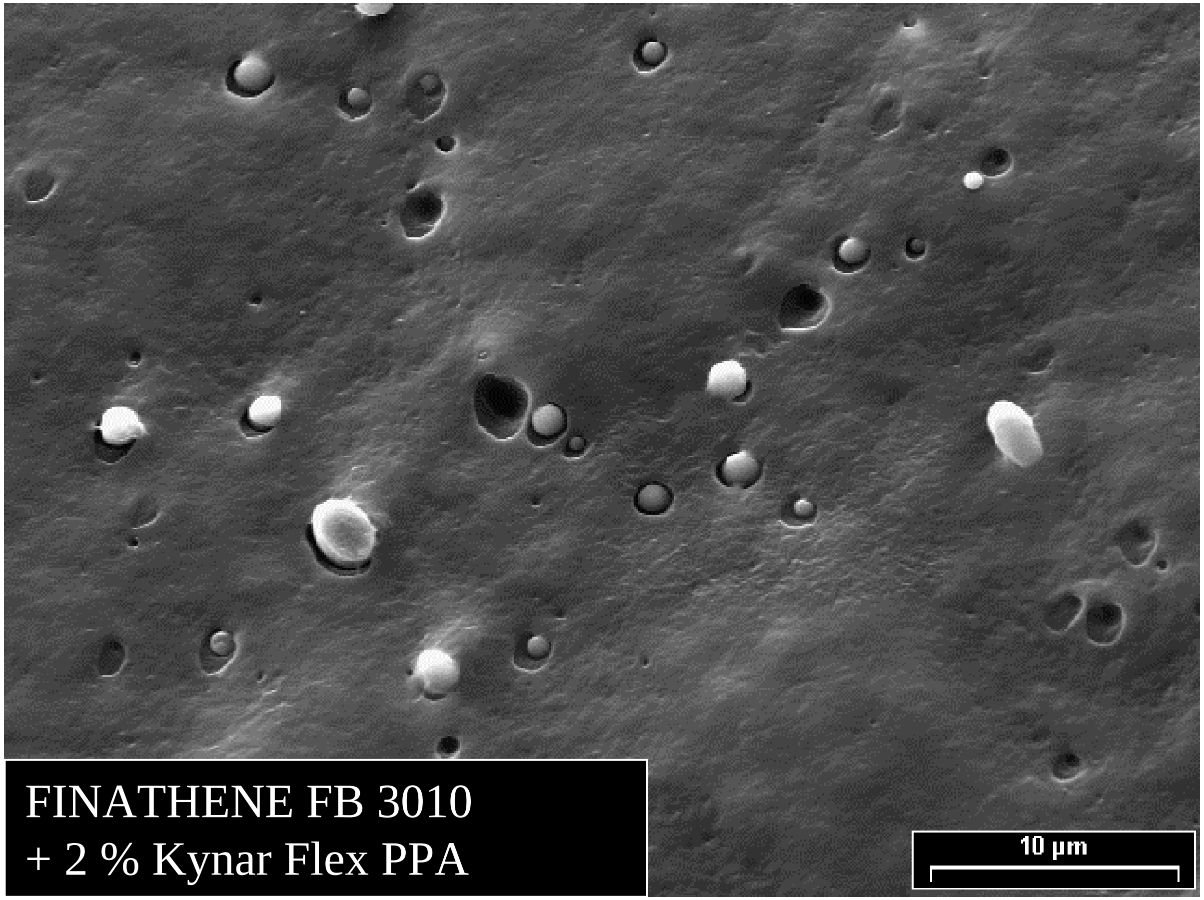
Masterbatch preparation

- Typical concentration = 2% of PPA in host matrix
- Goal : ensure a fine dispersion of PPA in the host matrix (particles diameter < 2 µm)
- Addition of other additives possible, unless specified
- Processing aid of similar viscosity than the matrix + high shear tooling is recommended
- Can be handled by most single-screw extruders

SEM picture of a masterbatch



Average diameter
1.5 µm

Experiments on LLDPE strands

Apparent shear rate (s^{-1})	100	150	210	420	630	840	1050	1260	1500	1700
Without PA	Green	Green	Yellow	Yellow	Yellow	Yellow	Red	Red	Red	Red
Fluoroelastomer V	Green	Green	Green	Yellow	Yellow	Yellow	Red	Red	Red	Red
Fluoroelastomer D	Green	Green	Green	Green	Green	Yellow	Yellow	Red	Red	Red
KYNAR FLEX PPA 2801	Green	Green	Green	Green	Green	Yellow	Yellow	Red	Red	Red
KYNAR FLEX PPA 2821	Green	Green	Green	Green	Green	Yellow	Yellow	Yellow	Red	Red

Green = Smooth   Yellow = Rough surface (sharkskin)   Red = Gross melt fracture

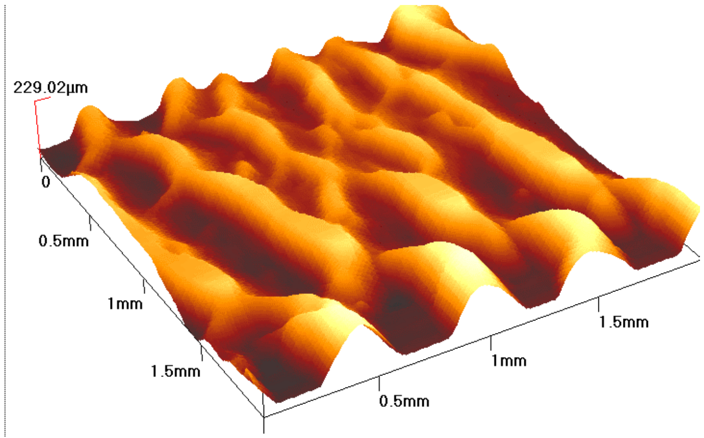
Extrusion conditions: - LLDPE of a 1.0 MFR, 400 ppm of processing aid
- HAAKE RHEOLEX extruder
- 30 mm diameter, 25 L/D screw
- 3 mm diameter, 18 mm long capillary die, horizontal entry
- 220 °C die temperature.

Experiments on LLDPE films

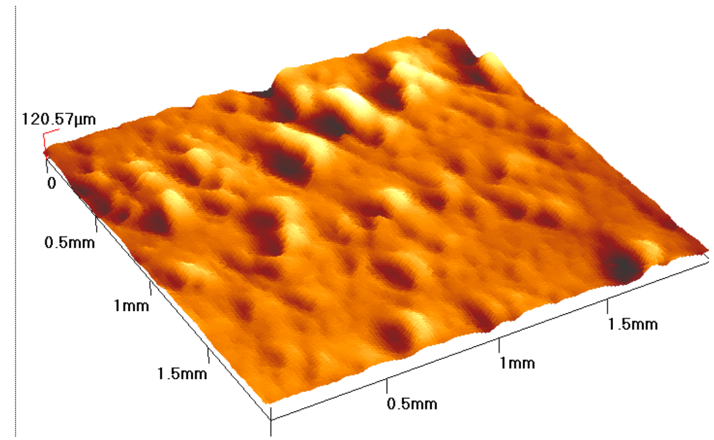
After 3 hours…	Transparency (%)	Pressure (bars)	Power (amps)
Without PA	15	255	66
Fluoroelastomer V	34	248	65
Fluoroelastomer D	62	236	64
KYNAR FLEX PPA 2821	70	235	64

Extrusion conditions:
- Butene LLDPE of a 1.0 MFR, 400 ppm of processing aid
- KIEFEL blown film extruder
- 63.5 mm diameter, 28 L/D screw
- 150 mm diameter, 0.8 mm die gap, 20 mm land length
- dual lip air ring, 190 s^{-1} apparent shear rate at die wall
- 210 °C die temperature.

Surface analysis on LLDPE films



Pure LLDPE



LLDPE + 500 ppm Kynar Flex® PPA

Surface roughness probed by a 3D profilometer (Dektak from VEECO)

- Surface roughness divided by 4 !
- Fluorine content measured < 1000 ppm by ESCA
  - No adverse effect on printability and sealability

Food and pharmaceutical contact

- Being 100% pure fluoropolymer, the whole Kynar Flex® range is rated USP class VI for pharmaceutical contact.
- In **Europe**, Kynar Flex® PPA complies with directives EC 90/128 and 92/39 for food contact.
- In the **USA**, Kynar Flex® PPA is listed in FDA chapters for use in olefin polymers and EVA copolymers with a limit of 1% by weight.
- Conclusion : Kynar Flex® PPA is ***clear for use*** *in food contact & pharmaceutical applications* !

Interactions

- PPA is *chemically inert* (ex. strong bases)
- Some *physical interactions* may exist with other additives :
  - "positive" interactions (effect of PPA is increased) with erucamide or some anti-oxidants
  - "negative" interactions (effect of PPA is decreased) with some anti-block agents, fillers and inorganic pigments like stearates, talc, silica and TiO_2
- No interactions with UV stabilizers, antistatic and slip agents

Summary

- Kynar Flex® PPA allows a **wider operating window** of process parameters by delaying occurrence of melt fracture (addition rates of 200 - 800 ppm)
- Designed to eliminate surface defects & increase output
  - especially for LLDPE, metallocene PE and PP *film extrusion*
  - also for *blow molding* and *tube extrusion* of polyolefins
  - can work in other thermoplastic polymers
- At levels of 200 - 400 ppm, PPA can eliminate die build-up
- Cost of 400 ppm of Kynar Flex® PPA < 1 cent of € / kg

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