PA 11
A HIGH PERFORMANCE POLYAMIDE FOR OIL AND GAS PIPING APPLICATIONS

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ARKEMA/TPA
CERDATO

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INNOVATIVE CHEMISTRY

OUTLINE

- **INTRODUCTION**
  - ARKEMA in a snapshot
  - Technical Polymers for Oil & Gas Applications

- **POLYAMIDE FAMILY**
  - Main features and differences between short and long chain PA's
  - Differences between PA11 and PA12

- **LONG TERM AGEING PERFORMANCE FOR SURF APPLICATIONS**
  - API17TR2 lifetime model for PA11

- **LONG TERM MECHANICAL PERFORMANCE FOR ONSHORE GAS PIPE**
  - Hydrostatic pressure resistance of PA11 pipe vs HDPE

- **AGEING AND MECHANICAL INTERACTION : STRESS CRACKING**
  - Short chain PA sensitivity to metal salts
  - Slow Crack Growth of PE-RT in hydrocarbon

ARKEMA SNAPSHOT 2018 BASIS

€8.8 billion sales

38 % EU | 31% AP + ROW | 31 % NA

20,060 employees

A global presence in **55 countries**

136 production plants

60 EU | 38 AP + ROW | 39 NA

~3% of sales allocated to R&D

3 R&D and innovation hubs

Spread over 13 R&D centers

1,500 researchers

3 major segments:

High Performance Materials

Industrial Specialties

Coatings Solutions

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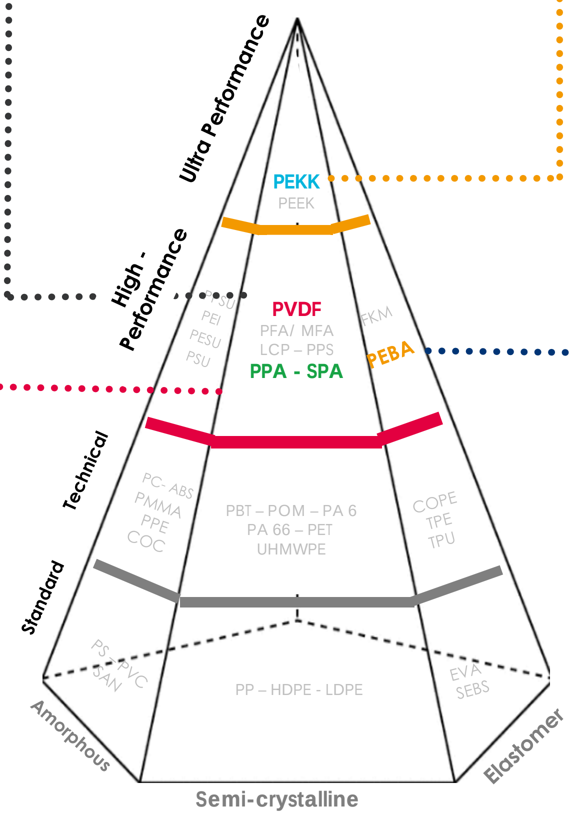
OUR POLYMER PRODUCT RANGE POSITIONING

High Performance Fluoropolymers
- Key properties: Extreme Resistance, Durable and Easy to process
- Markets: Oil & Gas, CPI, Coating

Ultra High Performance Poly-ketone
- Key properties: High Temperature Performance and High Strength
- Main Markets: Oil & Gas, Aerospace, 3D Printing

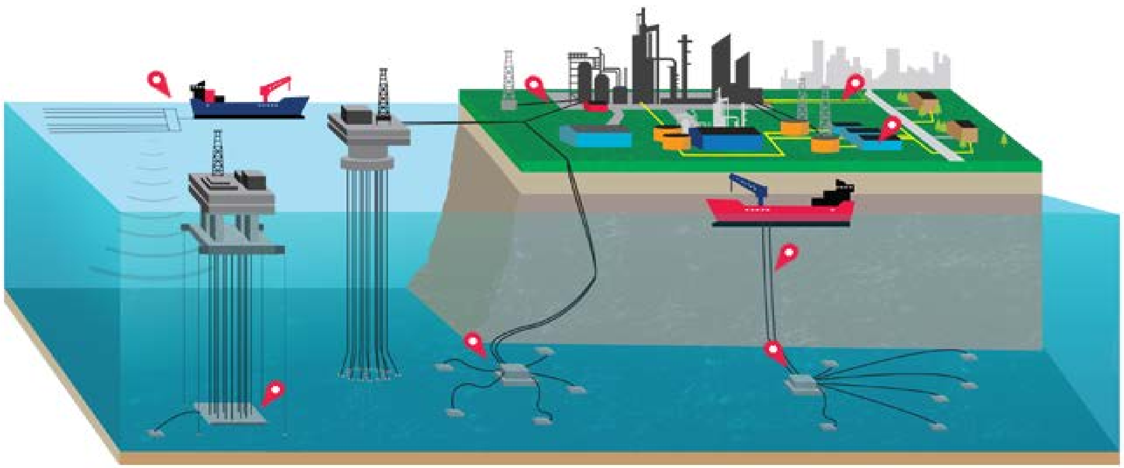
High Performance Specialty Polyamides
- Key properties: Lightweight, Tough, Fatigue resistant
- Markets: Oil & Gas, Transportation, Sports



High Performance Elastomers
- Key properties: Toughness & Flexibility, Lightness, Energy return
- Markets: Sports, Consumer electronics

INTRODUCTION : OIL & GAS APPLICATIONS

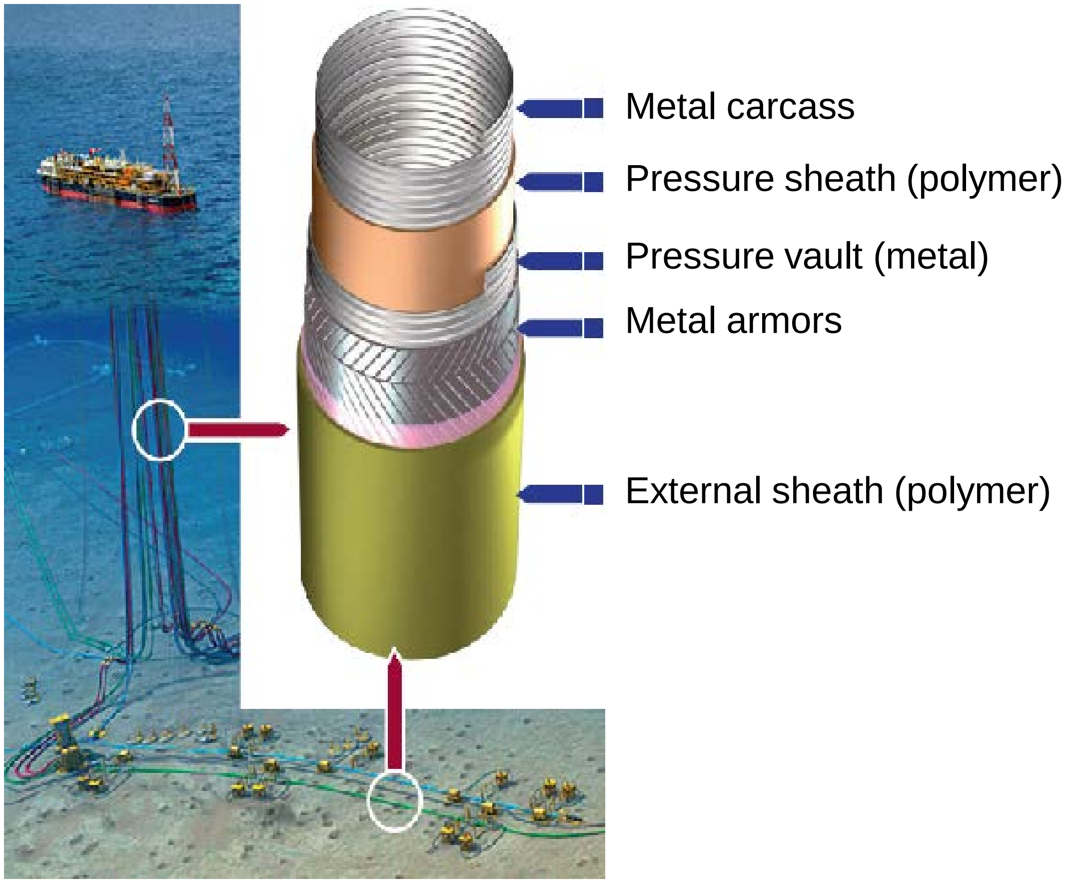
Onshore : gas pipe, service station pipe, composite pipe
PA, PVDF, Steel, HDPE



Offshore : SURF (umbilicals, risers, flowlines)
PA, PVDF, Steel, HDPE

- **API17J unbonded flexibles :** Pressure sheath, Anti-wear tape, External sheath
- **API16C choke & kill :** Pressure sheath
- **API17E umbilicals :** Thermoplastic liner, External sheath

INTRODUCTION : POLYMERS IN FLEXIBLE PIPES



Offshore flexible pipe : Risers & Flowlines

Polymers in flexibles

- **HDPE for water injection**
- **PA11 for gas/crude**
- **PVDF for high temperatures**

Track record

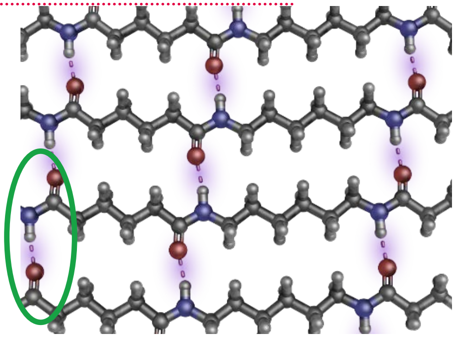
- **PA11 since 1971**
- **PVDF since 1986**

API17TR2

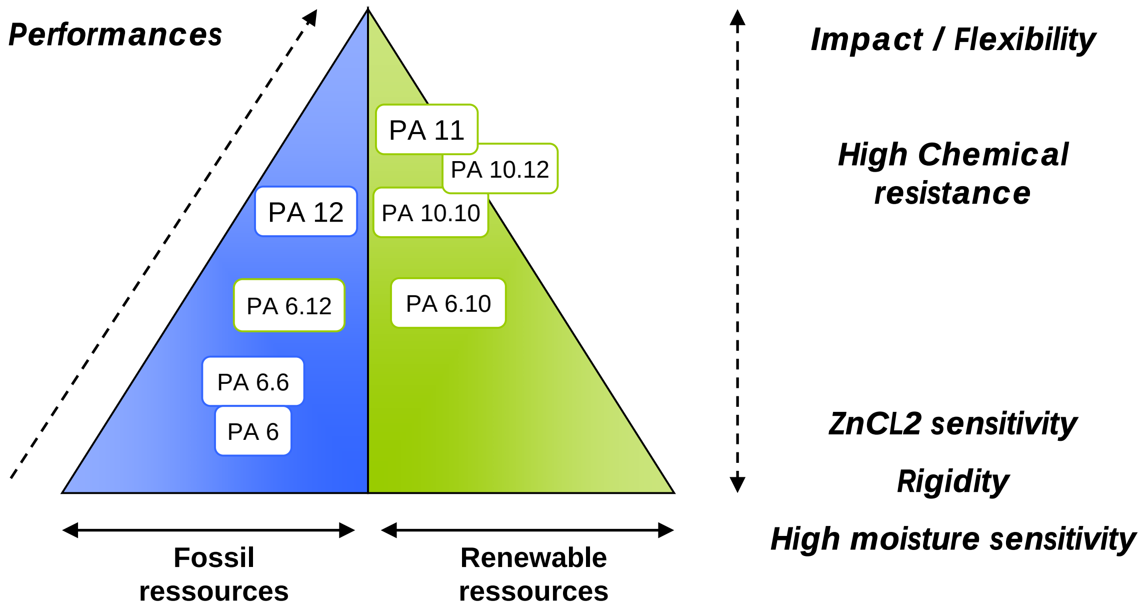
- **PA11 since 2001**

TECHNICAL POSITIONING OF POLYAMIDES

- **Semi-cristalline polymers obtained by polycondensation**
- **Higher chain rigidity vs polyethylene thanks to amide groups**
- **Higher Tg and Tm thanks to hydrogen bonding**

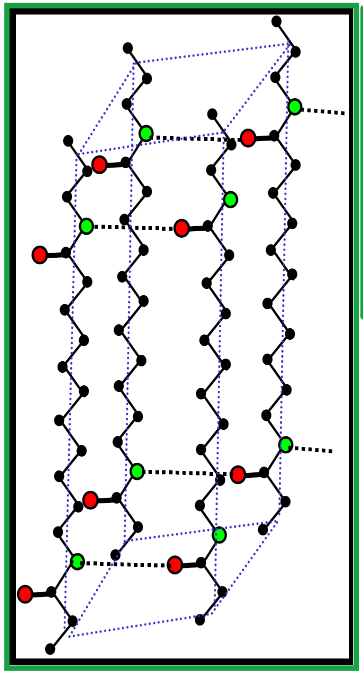


Long chain PA



Short chain PA

DIFFERENCES BETWEEN PA11 AND PA12 : PHYSICAL

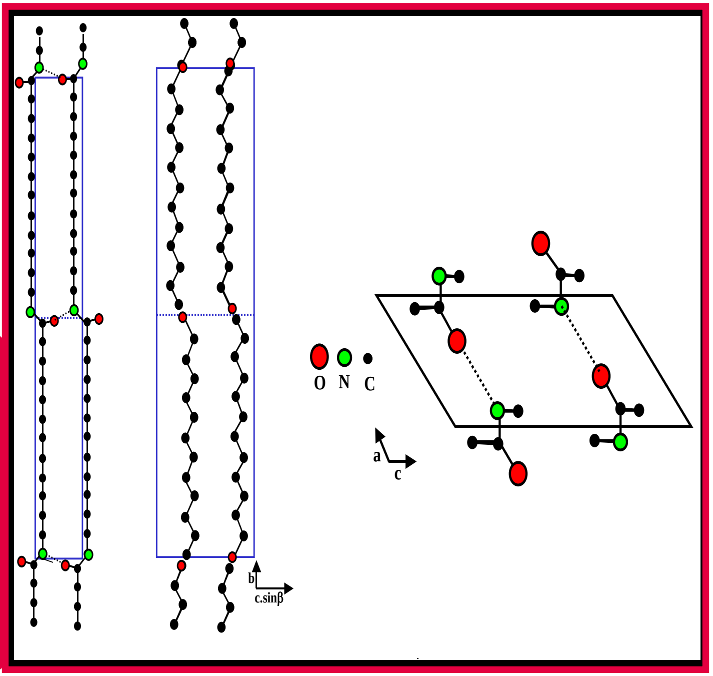


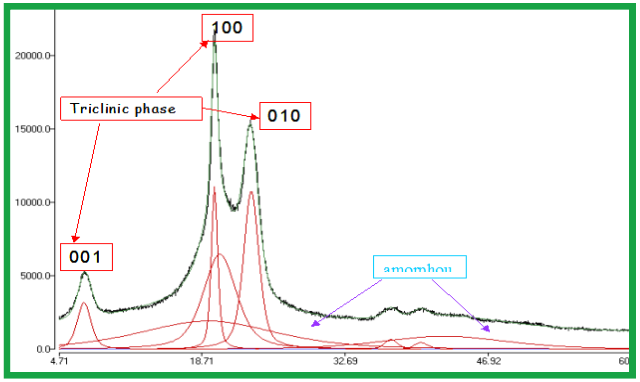
PA11

- Odd number of C
- Triclinic cristalline cell
- Ringed spherulites

PA12

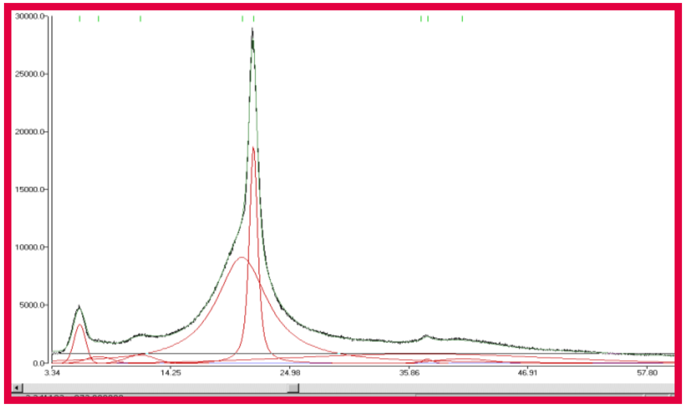
- Even number of C
- Hexagonal cristalline cell
- Coarse spherulites



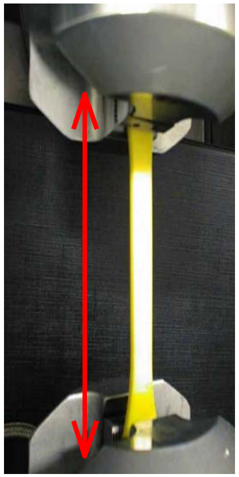


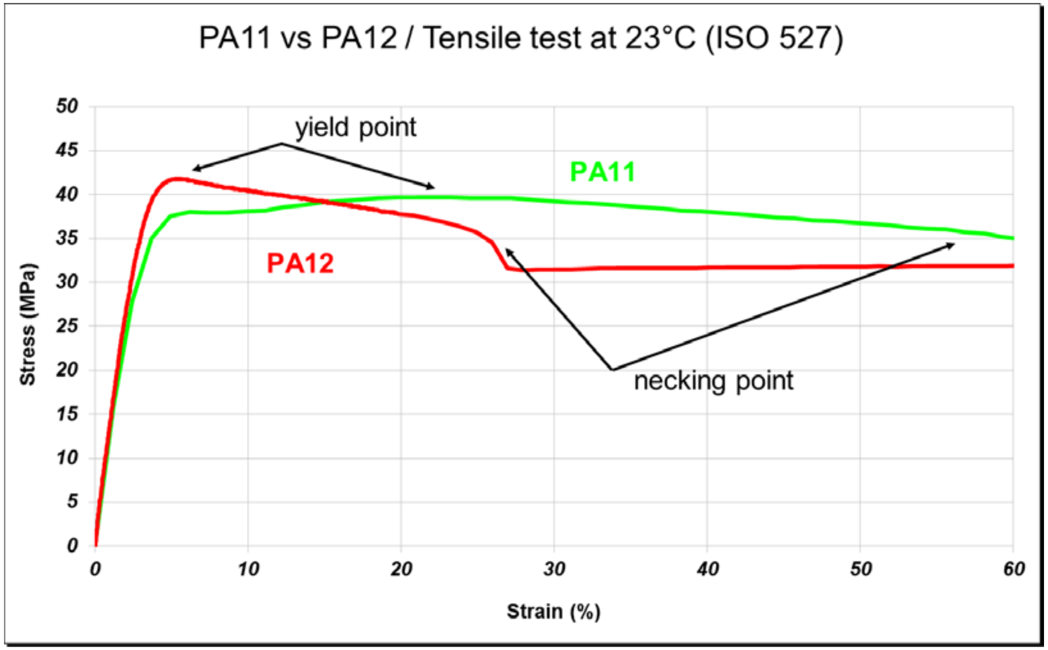
XRD – WAXS

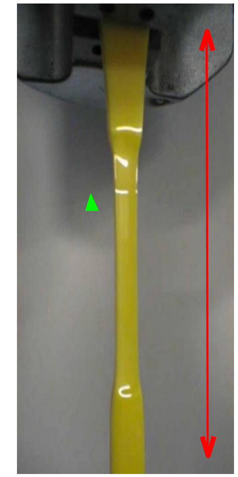
- Triclinic cell
- Hexagonal cell

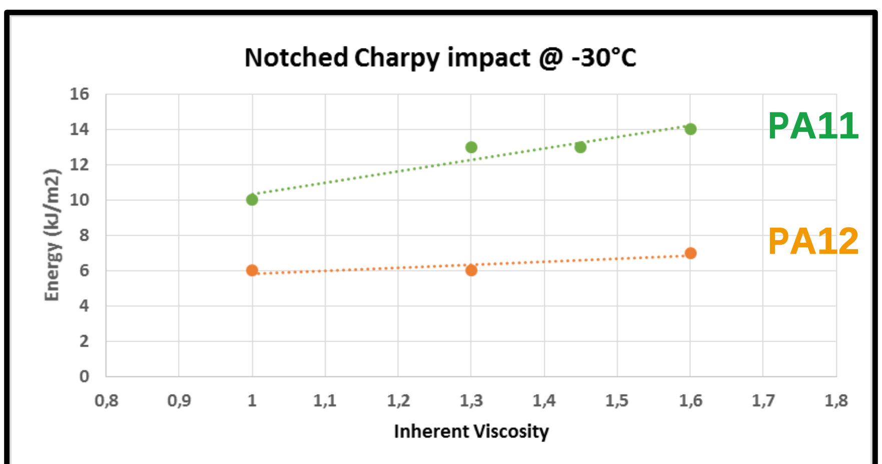


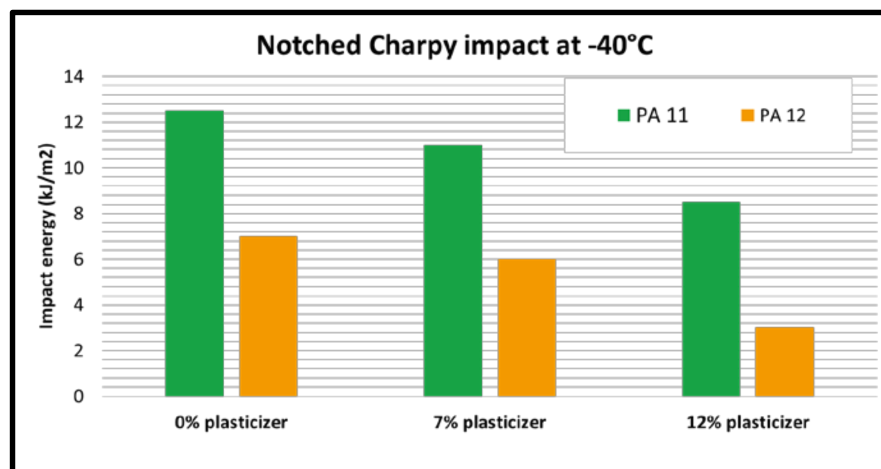
DIFFERENCES BETWEEN PA11 AND PA12 : MECHANICAL











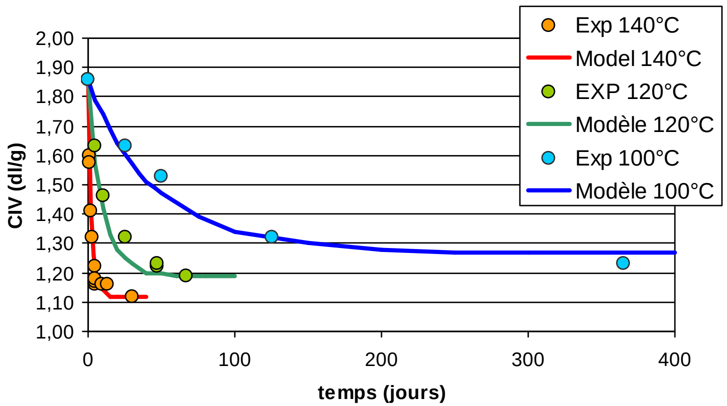
STATE OF THE ART ON PA11 AGEING - API 17TR2

- **RILSAN® USER GROUP – 1997-2002**
  - **Informal JIP , theroretical approach+real cases, all Majors O&G, all flexibles manufacturers**
  - **Publishing of API 17 TR2 document**

- **Hydrolysis kinetics**
  - **The Molecular Weight / Corrected Inherent Viscosity decreases with time**
  - **Temperature effect : the higher T°C / the faster the ageing rate**
  - **Effect of pH : the more acid / the faster the ageing rate**

- **End of life criteria : CIV**
  - **Based on 30 years experience**
  - **Both Lab studies and Field feed back**
  - **Proposed model with criterion : CIV 1,2 dl/g**

- **Mechanical properties**
  - **Elongation at break**



Hydrolysis Ageing of Polyamide 11 – 1. Hydrolysis kinetics in water

B. Jacques, M. Werth, I. Merdas, F. Thominette and J. Verdu

Polymer 2002; **43**,6439-47

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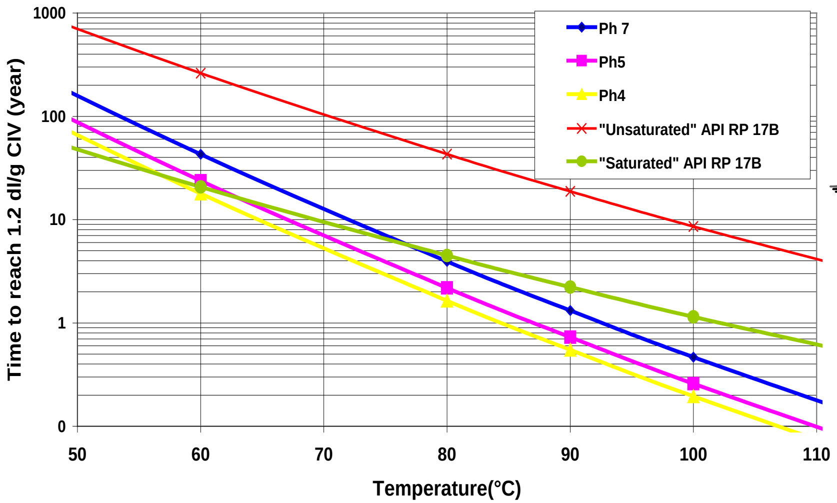
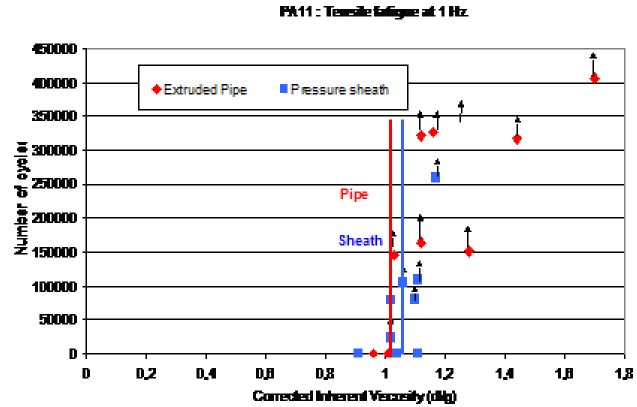
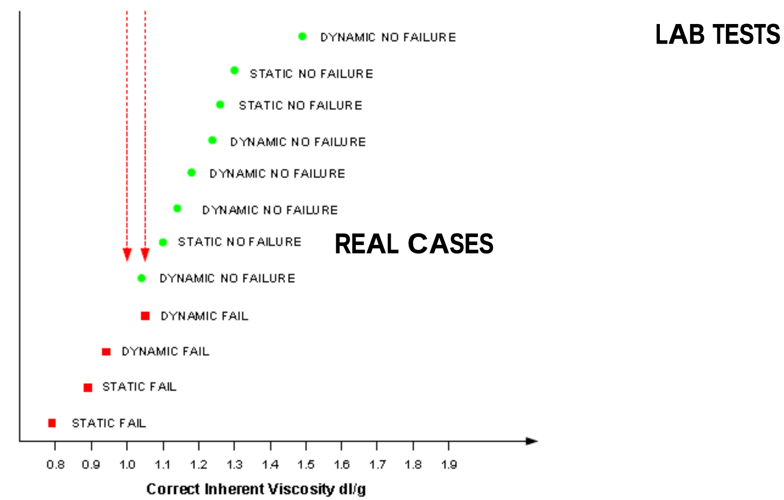
STATE OF THE ART ON PA11 AGEING - API 17TR2

- **API17TR2 gives guidelines to assess the lifetime of PA11, dedicated criteria CIV = 1.2 dl/g compared to 1,05 dynamic limit (safety)**

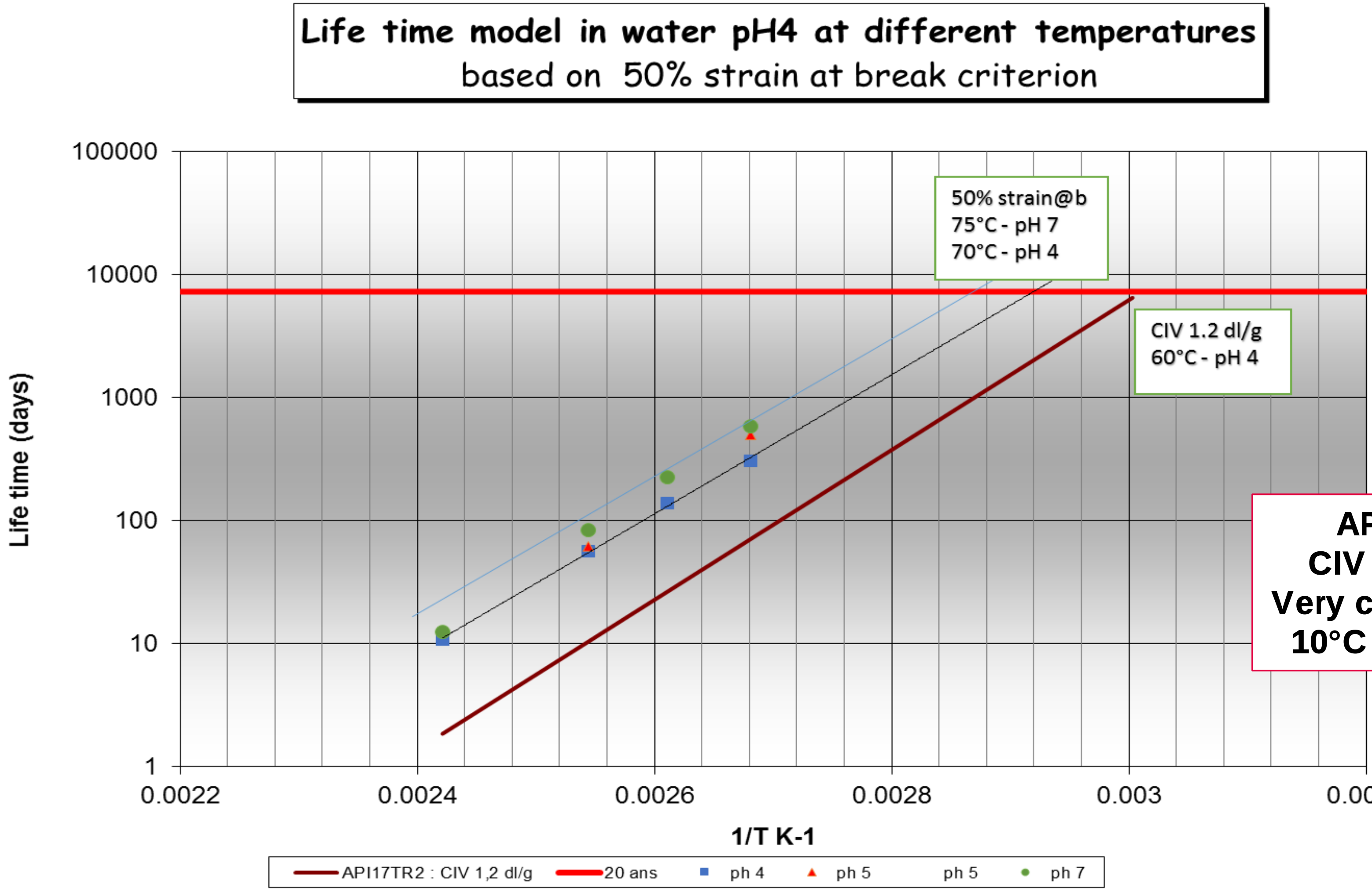
Corrected Inherent Viscosity







CORRECTED INHERENT VICSOSITY VS ELONGATION @ BREAK



API 17TR2
CIV : 1.2 dl/g
Very conservative
10°C difference

POLYAMIDE 11 FOR ONSHORE NATURAL GAS PIPE

- **1980s- Australian Gas Company – use of low pressure PA-11**
- **1995 - High pressure Rilsan pipe project initiated**
- **2004 - Complete 2-inch piping system available**
- **2009 – DOT Permitted – 200 psi, 4in, DR11 or thicker, DF 0.4**
- **2011 - Over 35 miles of 4in DR11 installed, in-service at 200 psi**
- **2018 - DOT Permitted – 250 psi, 6in, DR11 or thicker, DF 0.4**

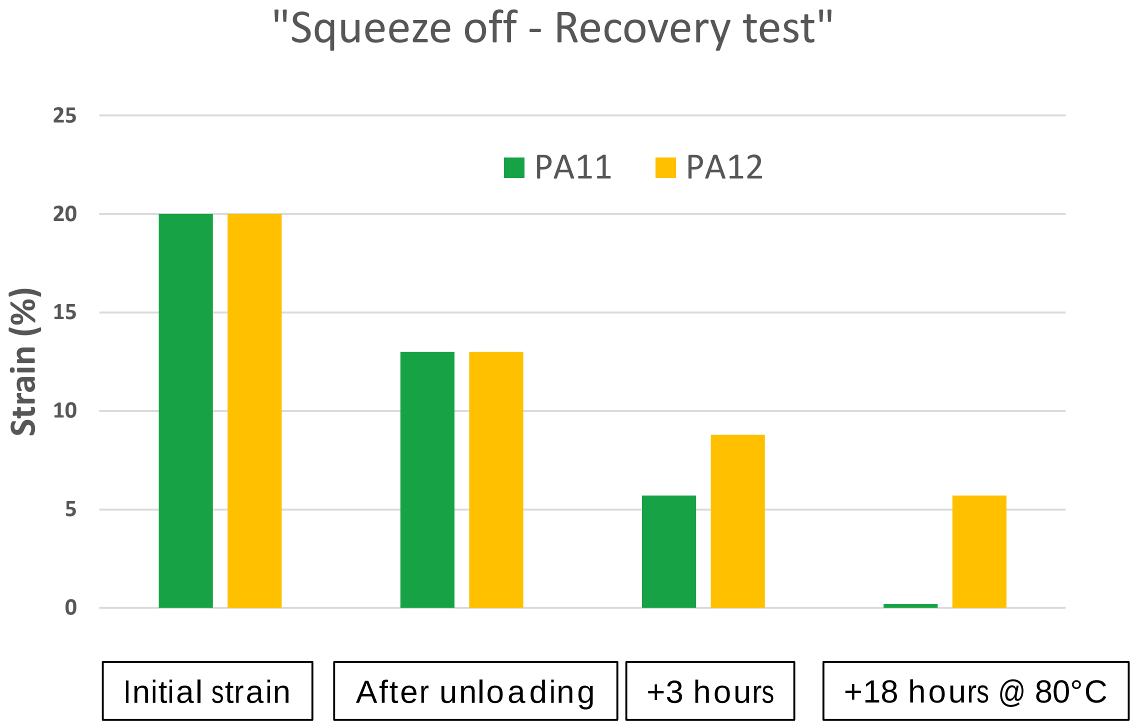
	Temp °C (°F)	MDPE	HDPE	PA11 PA 32316
HDB (psi)	23°C (73°F)	1250	1600	3150
MAOP (psig)		100	128	252
MAOP (bars)		***7***	***9***	***17***
HDB (psi)	81°C (180°F)	Not rated	Not rated	1600
MAOP (psig)				125
MAOP (bars)				***9***

Higher pressure resistance Vs HDPE

Higher temperature resistance Vs HDPE

INTRINSIC ELASTICITY OF POLYAMIDE 11

- Squeeze off for gas flow stop
- Simulation by applying a 20% tensile strain @ 23°C
- Record residual strain with time after unloading
- Recovery acceleration by heating above Tg (glass transition temperature)



Better strain recovery of PA11

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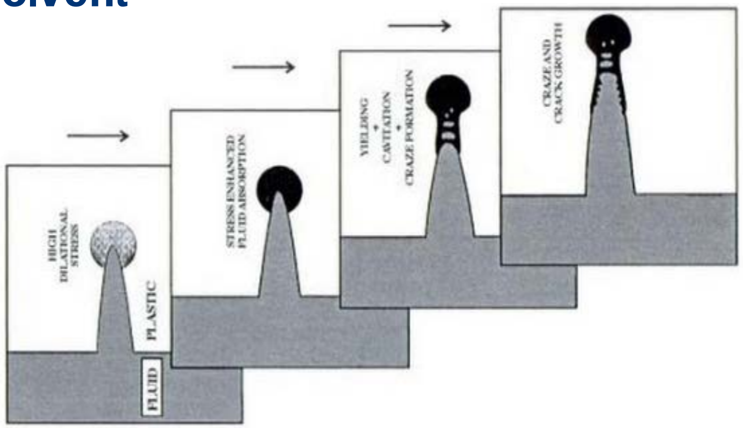
ENVIRONMENTAL STRESS CRACKING OF POLYMERS

Environmental Stress Cracking (ESC)

Failure by a crack propagation caused by the action of a load or stress and the swelling by a fluid or solvent



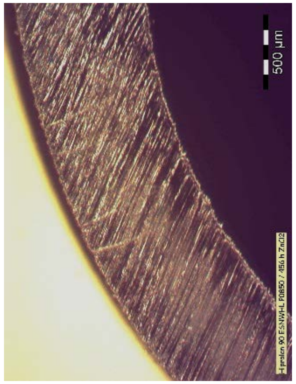
- **The more the swelling by solvent , the more the drop of the yield stress**
- **Any initial crack or defect can be the source of ESC**

<u>Réf</u>: Wright, David. Environmental stresse stress craking of plastics. s.l. : Rapra technology LTD, 1996.

$ZnCl_2$ RESISTANCE OF POLYAMIDES – SAE J 2260 PROTOCOL 23°C

< 1 h < 0.5 h

~24 h



> 1000 h

PA6

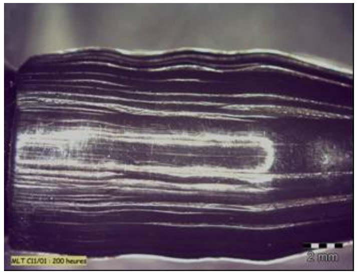
PA610, PA612

PA1010, PA1012, PA11, PA12

Instantaneous cracking
Risk of leakage

Delayed cracking
Risk of long term leakage

No cracking
No properties change



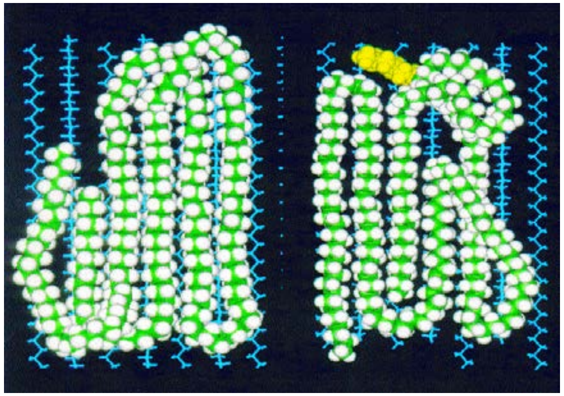
Leakage in fitting area

Normal burst

ONLY LONG CHAIN PA's ARE RESISTANT TO $ZnCl_2$

IS RAISED TEMPERATURE POLYETHYLENE GOOD FOR HC PROD ?

PE-RT or RT-PE



Standard HDPE (left) and PE-RT (right)

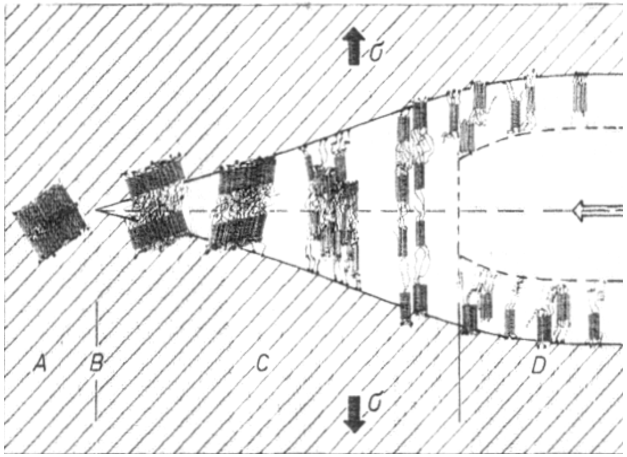
- **Ethylene Octene comonomers**
- **Imperfection (yellow chain) is pushed out of the cristalline phase**
- **=> more melecular link between 2 cristalline regions**
- **Better anti oxydant package**

Designed for hot water
Better creep vs PE100
Better SCG resistance

	PE-RT	PA 11
Melt Tm (°C)	**131-135**	180
ΔT°C = Tm -80°C	**50**	100
Tg (°C)	**<-50**	0
Taux de cristallinité	**50%**	25%

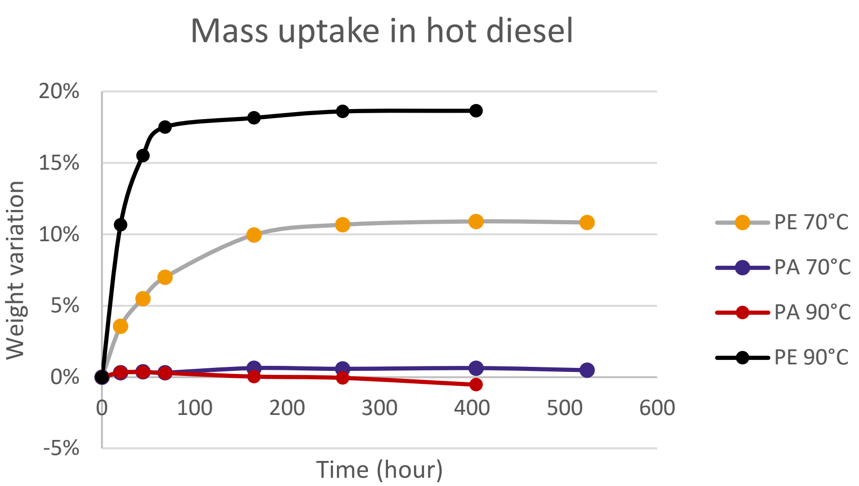
Réf: SCHARMM, Detlef et JERUZAL, Mark. PE-RT, a new classe of polyethylene for industrial pipes. [En ligne] http://plasticpipe.org/pdf/pe_rt_new_class_polyethylene.pdf.

SCG IN CONTACT WITH HOT HYDROCARBON ?

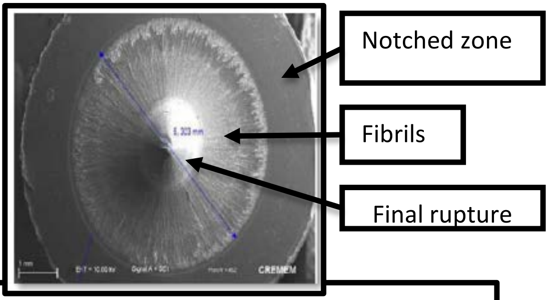


Slow Crack Growth

- **Zone A: Elastic to Plastic deformation**
  - **Stretching of amorphous phase**
  - **Shearing of the cristalline phase**
- **Zone B: Fibrils creation zone and initiation of voiding , start of crazing**
- **Zone C: Growth of the craze due to fibril elongation**
- **Zone D: Craze turns into crack propagation as fibrils break under tension creep**



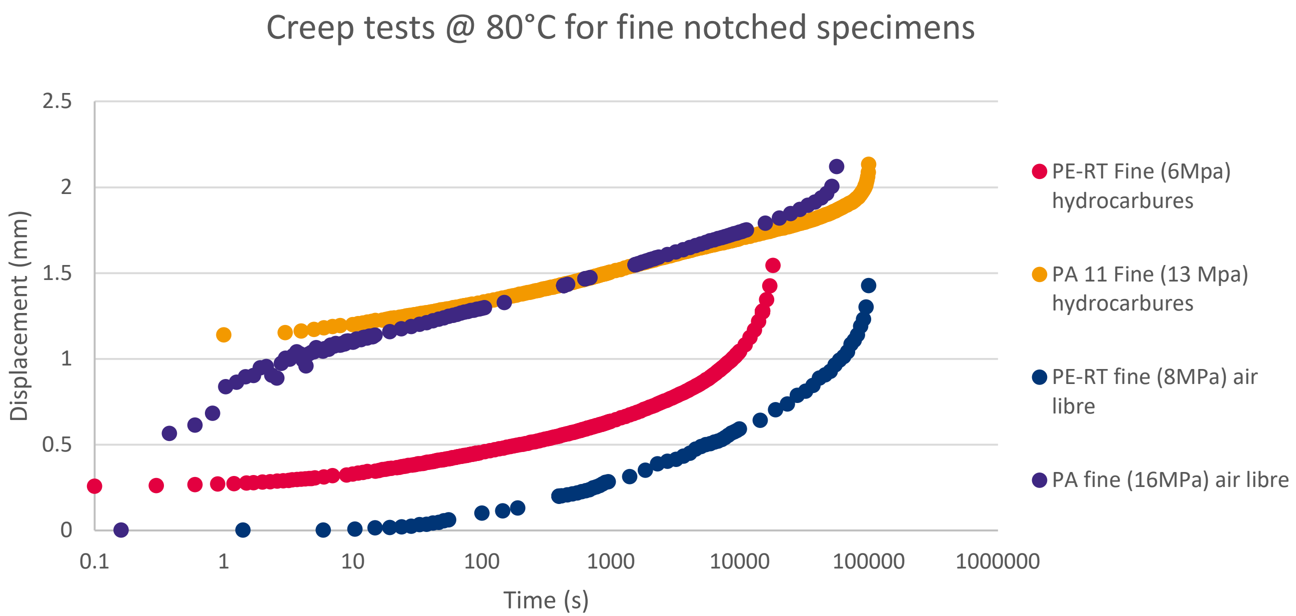
Cylindrical sample With notch



Surface observation after a fracture under creep

Réf: GUEUGNAUT, et al. The "notched cylindrical bars under constant load test" (NCBT) for assessing the resistance to initiation of PE100 and PE100RC : determination of the initoation time. ENGIE. 2016.

IN-SITU NOTCHED CREEP TEST IN DIESEL @ 80°C

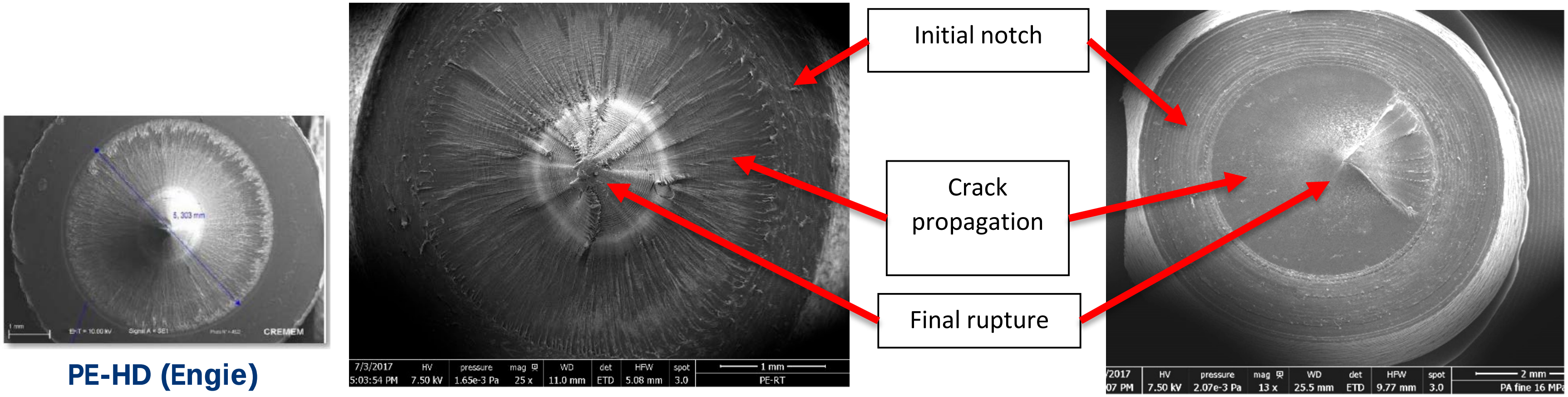


- **For PE-RT under 8MPa immediate failure during loading for Fine notched**

- **Diesel makes the failure faster and decreases the strength of PE-RT : 6MPa Diesel is much faster than 8MPa air – (4MPa Diesel would be equivalent) ------------ 50% loss**

- **Better resistance of PA11 : 13MPa Diesel is like 16MPa in air ------------only 19% loss**

OBSERVATIONS UNDER SEM



PE-HD (Engie)

PE-RT

PA11

- Same fracture morphology between PE-RT (that study) and HDPE from ENGIE paper
- 3 different zones on the fracture surface for both PE-RT and PA11
- For PE-RT (and HDPE) high amount of « wrinkles » caused by the rupture of the fibrils in the craze – PA11 is smoother indicating plastic flow rather than SCG

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CONCLUSIONS

- The family of polyamide is wide and care should be taken when choosing the right polyamide for the right and safe application.
- Long chain polyamides are better vs short chain in term of hydrolysis resistance and stress cracking resistance to metal salts.
- Among the long chain, PA11 has some specifics that make it the best choice for mechanical resistance and ageing performance especially in subsea applications but also for onshore piping.
- It can be challenging to extend the use of polymers in environements where other physical mechanisms can highly degrade the performance – PE-RT in liquid HC

- PA11 « The right material at the right place – Safety first »

THANK YOU FOR YOUR ATTENTION