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

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ARKEMA/TPA CERDATAO
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
- 20,060 employees
- A global presence in 55 countries
- 136 production plants
- ~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
Ultra High Performance Poly-ketone
- Key properties: High Temperature Performance and High Strength
- Main Markets: Oil & Gas, Aerospace, 3D Printing

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

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

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

Semi-crystalline

Amorphous

PP – HDPE – LDPE

PBT – POM – PA 6
PA 66 – PET
UHMWPE

PFA / MFA
LEP – PPS
PPA – SPA

KESTAN®

KYNAR®

RILSAN®

PEBAX®

OUR POLYMER PRODUCT RANGE POSITIONING
**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

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

Performances

Impact/Flexibility
- High Chemical resistance
- ZnCl2 sensitivity
- Rigidity
- High moisture sensitivity

Fossil resources

Renewable resources

Short chain PA

Long chain PA
DIFFERENCES BETWEEN PA11 AND PA12: PHYSICAL

**PA11**
- Odd number of C
- Triclinic crystalline cell
- Ringed spherulites

**PA12**
- Even number of C
- Hexagonal crystalline cell
- Coarse spherulites

**XRD - WAXS**
- Triclinic cell
- Hexagonal cell
DIFFERENCES BETWEEN PA11 AND PA12: MECHANICAL

PA11 vs PA12 / Tensile test at 23°C (ISO 527)

Notched Charpy impact @ -30°C

Notched Charpy impact at -40°C
STATE OF THE ART ON PA11 AGEING - API 17TR2

• **RILSAN® USER GROUP - 1997-2002**
  - Informal JIP, theoretical 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 feedback
  - Proposed model with criterion: CIV 1,2 dl/g

• **Mechanical properties**
  - Elongation at break

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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*
**STATE OF THE ART ON PA11 AGEING - API 17TR2**

- **API 17TR2** gives guidelines to assess the lifetime of PA11, dedicated criteria
  \( CIV = 1.2 \text{ dl/g} \) compared to 1.05 dynamic limit (safety)

**Corrected Inherent Viscosity**

![Graph showing the relationship between temperature and time to reach 1.2 dl/g CIV](image)

**REAL CASES**

**LAB TESTS**
CORRECTED INHERENT VISCOSITY VS ELONGATION @ BREAK

Life time model in water pH4 at different temperatures based on 50% strain at break criterion

- 50% strain@b
- 75°C - pH 7
- 70°C - pH 4
- CIV 1.2 dl/g
- 60°C - pH 4

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

<table>
<thead>
<tr>
<th></th>
<th>Temp °C (°F)</th>
<th>MDPE</th>
<th>HDPE</th>
<th>PA11 PA 32316</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDB (psi)</td>
<td>23°C (73°F)</td>
<td>1250</td>
<td>1600</td>
<td>3150</td>
</tr>
<tr>
<td>MAOP (psig)</td>
<td></td>
<td>100</td>
<td>128</td>
<td>252</td>
</tr>
<tr>
<td>MAOP (bars)</td>
<td></td>
<td>7</td>
<td>9</td>
<td>17</td>
</tr>
<tr>
<td>HDB (psi)</td>
<td>81°C (180°F)</td>
<td>Not rated</td>
<td>Not rated</td>
<td>1600</td>
</tr>
<tr>
<td>MAOP (psig)</td>
<td></td>
<td></td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>MAOP (bars)</td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

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)

"Squeeze off - Recovery test"

Better strain recovery of PA11

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>PA11</th>
<th>PA12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>After unloading</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>+3 hours</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>+18 hours @ 80°C</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
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.

ZnCl₂ RESISTANCE OF POLYAMIDES – SAE J 2260 PROTOCOL 23°C

<table>
<thead>
<tr>
<th>Time</th>
<th>PA6</th>
<th>PA610, PA612</th>
<th>PA1010, PA1012, PA11, PA12</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 1 h</td>
<td>Instantaneous cracking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 0.5 h</td>
<td>Risk of leakage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~24 h</td>
<td>Delayed cracking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt; 1000 h</td>
<td>No cracking</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No properties change</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ONLY LONG CHAIN PA’s ARE RESISTANT TO ZnCl₂
**PE-RT or RT-PE**

- Ethylene Octene comonomers
- Imperfection (yellow chain) is pushed out of the crystalline phase
- \(\Rightarrow\) more molecular link between 2 crystalline regions
- Better anti-oxidant package

**Designed for hot water**
**Better creep vs PE100**
**Better SCG resistance**

<table>
<thead>
<tr>
<th></th>
<th>PE-RT</th>
<th>PA 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Tm (°C)</td>
<td>131-135</td>
<td>180</td>
</tr>
<tr>
<td>(\Delta T^\circ)°C = Tm -80°C</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>&lt;-50</td>
<td>0</td>
</tr>
<tr>
<td>Taux de cristallinité</td>
<td>50%</td>
<td>25%</td>
</tr>
</tbody>
</table>

SCG IN CONTACT WITH HOT HYDROCARBON?

Zone A: Elastic to Plastic deformation
- Stretching of amorphous phase
- Shearing of the crystalline 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

Slow Crack Growth

Mass uptake in hot diesel

Ref: 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 initiation time. ENGIE. 2016.
**IN-SITU NOTCHED CREEP TEST IN DIESEL @ 80°C**

Creep tests @ 80°C for fine notched specimens

- **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
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
**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 environments 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**