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# Design of Unplasticized Polyamide 12 Oilfield Line Pipe Based on Published Regression Curves and ASTM F3524

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## ABSTRACT

The long-term strength of unplasticized polyamide 12 (PA-U12) has been characterized using standard methods for plastic pressure pipe during the qualification process for use in buried piping systems for natural gas delivery operating at low ambient temperatures, usually less than 20 to 30°C at pressures previously served only by steel pipe.

The high strength characteristics of the material also made it interesting as a steel substitute for buried and above-ground industrial pressure pipe applications. So far, typical geometries are diameters up to 6 inch (162 mm) with wall thicknesses up to DR9. Assuming a design factor of 0.63 applied to the PPI TR-4 listed HDB, DR9 PA-U12 pipes have a maximum pressure at 23°C of 496 psig (3.4 MPa), although design pressures will typically be lower. These industrial systems can operate at much higher temperatures, up to ~ 50°C for above-ground installations in pipe supports or up to ~ 65°C for surface-laid oilfield pipes. Design engineers need the temperature dependent strength curves to properly design a thermoplastic pressure piping system. Therefore, the regression curves have been extended by LTHS tests up to 120°C. Corresponding test durations enabled to define the location of knees with determination of second branches. These branches are caused by hydrolytic degradation of the polymer resulting in brittleness of the polyamide after long times at elevated temperature in sufficiently wet environments or services. The first appearance of a knee is at 60° C and approximately 44 years.

This paper describes various standards to which PA-U line pipe and materials must conform, and the development of standardized, temperature dependent, long-term strength reference curves for PA-U12 pressure pipe, including the transition from ductile to brittle behavior at long times and high temperatures. These curves have been standardized first in DVS and followed by ISO based on the combined LTHS data of pipes made from two different PA-U12 180 compounds and one PA-U11 180 compound. An example of a typical PA-U12 180 pipe design is presented, applying chemical resistance derating factors for oil and gas applications in the design process.

**Short Summary:** Oilfield pipeline design engineers need temperature dependent strength curves to properly design a thermoplastic pressure piping system for use at temperatures often far above the typical range for natural gas distribution. Therefore, LTHS regression curves have been experimentally developed at temperatures up to 120°C to define the location of knees and characterization of second branches. In this paper we describe various standards to which PA-U line pipe and materials must conform, and the development of standardized, temperature dependent, long-term strength reference curves for PA-U12 pressure pipe, including the transition from ductile to brittle behavior at long times and high temperatures. These curves have been standardized in ISO and DVS and apply to both PA-U12 and PA-U11 [1,2]. For PA-U12 line pipe we also present an example for a typical pipe design, where chemical resistance derating factors are applied for oil and gas applications in the design process.

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## Introduction

Long chain polyamides are polyamides based on at least one monomer having a long alkane segment with 10 or more methylene groups. (e.g.: PA11, PA12, PA6.10, PA10.10) Unplasticized long chain polyamides (i.e., polyamide-12 or PA-U12, and polyamide-11 or PA-U11) have been extensively studied and qualified as pressure piping materials for use in natural gas distribution networks at pressures traditionally served only by steel. They have been standardized ASTM and ISO for natural gas systems [3-7]. ASTM has standardized PA-U12 for industrial linepipe. And standards for industrial piping are in progress at DVS and ISO [8-10]. PA-U12 has been shown to be highly resistant to softening and loss of strength when exposed to liquid hydrocarbons. For these reasons piping system engineers are including PA-U12 as a design option instead of steel in on-shore oil and gas gathering networks and other industrial piping applications [11].

Because of its molecular structure and solid-state morphology these high strength thermoplastic materials are not susceptible to slow crack growth with its characteristic knee in the long-term hydrostatic strength data [12,13].

However, at long times and high temperatures with sufficient water present these polymers exhibit a different type of transition to brittle behavior caused by loss of molecular weight by reaction of the polymer chain with water in a reaction known as hydrolysis. This reaction is the reverse of the polymerization (polycondensation) reaction to make polyamides. See Figure 1. This transition is not a Stage 2 transition (slow crack growth). It is a chemical degradation that would be called Stage 3 in thermoplastic polymer materials that exhibit Stage 2 transitions. The kinetics of hydrolysis depend on the availability of water. Dissolved oxygen, temperature, pH, and the presence of organic acids are of secondary influence.

Over time hydrolysis and recombination reach an equilibrium molecular weight that is lower than the initial molecular weight. Crystallinity increases because the shorter chains have higher mobility in the solid state than longer chains and can organize into crystals. At the same time, chain entanglement decreases. Eventually, brittle behavior dominates the mechanical properties. Because this is a gradual process no sudden loss of strength occurs [14-16].

This reaction and its effects have been extensively studied by academics, major oil companies, offshore oil and gas production equipment manufacturers, and long-chain polyamide suppliers since the late 1990s. That research has been centered on predicting the lifetime of long-chain polyamides used as the fluid barrier in complex multilayer steel-polymer composite high pressure flexible pipes used extensively in deepwater offshore oil and gas production.

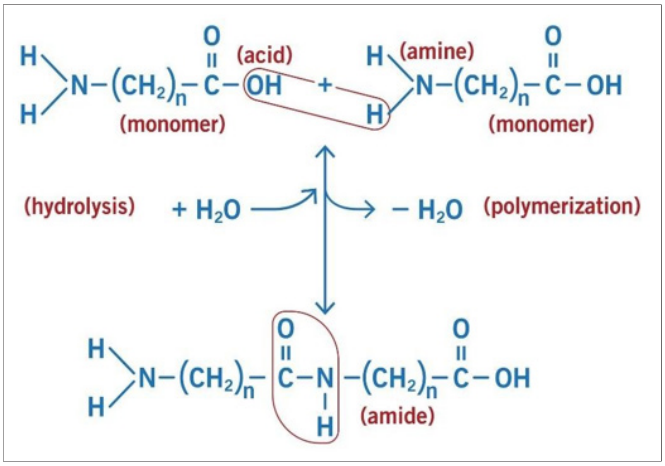


**Figure 1:** Polymerization (Condensation) and Hydrolysis of Polyamides

The transition time from ductile to brittle at any given set of conditions can be measured in the laboratory using tensile bars and a suitable exposure vessel, and if conducted at multiple temperatures the Arrhenius activation energy for the reaction can be derived, then used to predict the rate at any other temperature. A comprehensive review of the literature and procedures to carry out these hydrolysis studies are presented in an API technical report, a book on polymer stability, and an academic thesis [14-16].

The design of an industrial PA-U12 pipeline must account for conditions such as pressure, temperature, chemical environment, and required service life. Based on the LTHS regression curves, the pipe can be designed as required.

**Experimental**

Long chain polyamides are hydrophilic and can absorb up to about 3 weight percent water. The absorbed water slightly reduces the stiffness of the polyamide material and can affect the long-term hydrostatic strength. Therefore, the pipes used in this study were saturated with water to the equilibrium concentration by immersion in water prior to starting the stress rupture testing. The studies described in this paper were caried out on a specific PA-U12 180 compound, VESTAMID® NRG 2101 manufactured by Evonik.

Stress rupture curves were developed for 2-inch (50 mm) SDR11 pipes at 20° C, 60° C, 80° C, and 93.3° C; and 32mm SDR11 pipes at 110° C and 120° C according to ISO 1167-1 and ISO 1167-2. The pipes were pressurized with water and kept in a constant temperature water bath except for the 120° C test in which the pipes were kept at the test temperature in a constant temperature oven using water as the internal pressurizing medium [17,18].

Stress rupture data were analyzed according to ISO 9080 with a certainty of at least 97.5 % using Pipeson Analyzer version 3.2.7 [19]. The first and second branches were identified and the equations describing them were calculated.


**Figure 2:** PA-U12 180 pipes in the test chamber for LTHS testing

**Discussion**

During stress rupture testing at 80° C and lower temperatures the ruptures were all ductile through the 10 000 hours required to establish the long-term hydrostatic strength. Brittle ruptures were first observed at 93.3°C (200°F) around 10 000 hours. (Figure 3) A transition to brittle rupture was observed at 110°C and 120°C at progressively shorter times. The time to reach brittle behavior in the LTHS tests of PA-U12 180 at 110° C was the same as the time required to reach brittle behavior of water-immersed tensile bars of PA- U12 180 at 110° C, confirming that the transition to brittle behavior is the result of the same mechanism and the same hydrolysis kinetics.

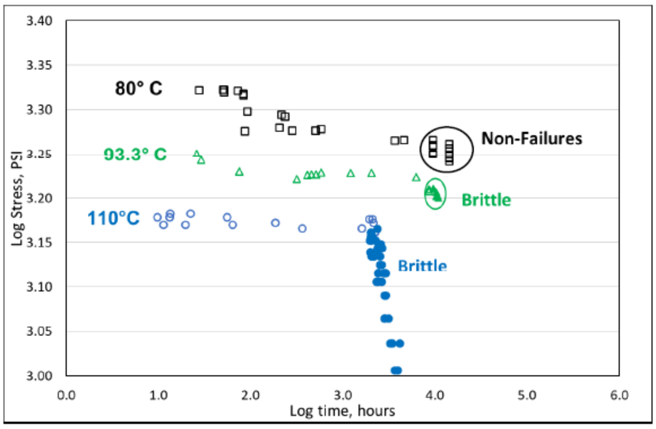


**Figure 3:** Example of stress rupture data for a specific PA-U12 180 compound showing brittle transition at high temperatures. Data points beyond 10 000 hours at 80°C were nonfailures

Figure 4 shows the appearance of a ductile rupture and a brittle rupture of pipes tested at 120° C. The ductile failure appearance is characteristic of the first branch. The brittle rupture appearance is characteristic of the second branch.


**Figure 4:** Examples of ductile (left) and brittle (right) failures of PA-U12 180 pipes from LTHS tests at 120° C

The ductile-brittle transition times at multiple temperatures were used to calculate the activation energy for the embrittlement process responsible for the knee. The activation energy for PA-U12 180 was 108 kcal/mol.

Equations for the first and second branches of the PA-U12 180 stress rupture lower predictive limit (LPL) curves were developed. The first branch is described by a 4-coefficient model. The second branch is described by a 3-coefficient model.

First branch: $$\log_{10} t = A_1 + \frac{B_1}{T}\log_{10}\sigma + \frac{C_1}{T} + D_1 \log_{10}\sigma$$

Second Branch: $$\log_{10} t = A_2 + \frac{B_2}{T}\log_{10}\sigma + \frac{C_2}{T}$$

Where:
$t$ = time in hours
$T$ = temperature in Kelvin
$\sigma$ = hoop stress in MPa

$A_1$ = -34.909 $A_2$ = -12.752
$B_1$ = -7240.036 $B_2$ = -618.358
$C_1$ = 24234.068 $C_2$ = 6753.180
$D_1$ = -8.855

Based on these LTHS measurements and the calculated fit equations, reference curves over a broad temperature range have been developed for PA-U12 180 (Figure 5) and standardized as DVS 2205- 1 supplement 8 [2].

**Application of the Reference Lines**

Industrial piping systems such as those use in oil and gas gathering often operate at elevated temperatures. Designers can use the reference lines to determine the long-term strength at the use temperature. Most industrial piping systems operate in an environment or fluid service with sufficient water that hydrolysis and transition to brittle behavior should be considered in the design. Both the long-term strength and transition to brittle behavior are temperature dependent. The reference lines in Figure 5 show that a transition to brittle behavior happens after 25 years at temperatures of 60° C and below. At 70°C and 80° C the transition happens around 12 and 5 years, respectively. It is important to recognize that these reference lines and the time to appearance of the second branch assume that the temperature has been constant for the entire time. Knowing these times helps the designer decide when to use a PA-U 180. Based on the reference lines, the 25-year and 50-year minimum expected strength (MES) values can be calculated for the first branch. See Table 1.

**Table 1: Expected strength of PA-U12 180 for various values of time and temperature**

| Temperature | Design Life (years) | Minimum Expected Strength MPa (psi) |
|---|---|---|
| 20° C (68° F) | 25 | 18.4 (2668) |
| | 50 | 18.0 (2610) |
| 30° C (86° F) | 25 | 16.3 (2363) |
| | 50 | 16.0 (2320) |
| 40° C (106° F) | 25 | 14.5 (2102) |
| | 50 | 14.2 (2059) |
| 50° C (122° F) | 25 | 13.0 (1885) |
| | 50 | 12.6 (1827) |
| 60° C (140° F) | 25 | 11.6 (1682) |
| | 50 | Not recommended |
| 65° C (149° F) | 25 | 10.9 (1580) |

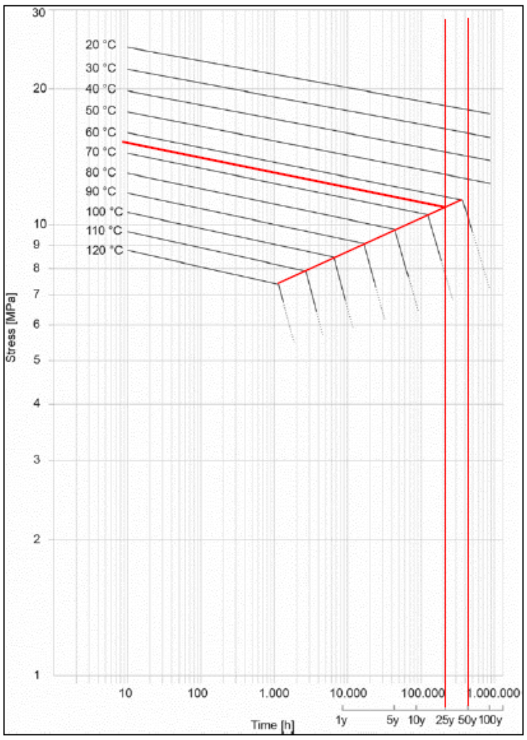


**Figure 5:** Expected strength of PA-U12 180 pipes with equations for the first and second branches according to DVS 2205-1 supplement 8 [2].

**Pipeline Design Examples**

ASTM F3524 - Specification for Polyamide-12 (PA12) Line Pipe was developed to address applications of polyamide-12 in industrial piping applications, especially applications in oil and gas production [8]. The standard requires that a compliant polyamide-12 compound used to make pipe shall have the long-term hydrostatic strength determined according either of two internationally recognized methods: ISO 9080 or ASTM D2837 [19, 20]. It is common for onshore oilfield piping to be designed for a 25-year service life. This is different from the case for natural gas distribution systems which are designed to a 50 or 100-year service life.

**Design Using Minimum Expected Strength (MES)**

PA-U12 180 pipes can be designed for a specific combination of temperature and design life using the MES values in Table 1 and the standard design equations. Given a design pressure and temperature we can calculate the wall thickness or nearest SDR that matches the pressure requirements. For this example, we will use the following conditions for a PA-U12 pipeline transporting a liquid hydrocarbon mixture:

Maximum Design Pressure: 20 bars
Maximum Design Temperature: 65° C (149° F)

Design Equation: $DR = \frac{20 \times MES \times FSF}{MOP \times S_{min}} + 1$

$$\boldsymbol{DR} = \frac{20 \times 10.9\, MPa \times 0.95}{20\, bars \times 1.25} + 1 = \mathbf{9.3}$$

Where:
*DR* = dimension ratio = OD/wall
*MES* = 25-years expected strength at temperature from Table 1
FSF = fluid service factor (1.0 for water, 0.95 for liquid hydrocarbons)
*MOP* = maximum operating pressure in bars
$S_{min}$ = design safety factor (typically 1.25 for liquids)

The more common size is SDR 9, which is slightly over-designed for this application.

A paper presented at PPXX showed that the long-term strength of PA-U12 should be derated 5% in liquid hydrocarbon service. To calculate the DR for pipes intended for hydrocarbon service the Minimum Expected Strength in Table 1 should be multiplied by 0.95 [9].

**Design Using Hydrostatic Design Basis (HDB)**

The HDB is the categorized long-term strength of a polymeric pipe material determined at a single temperature, typically at 73, 140, and 180° F (23, 60, 82° C). Recommended HDBs are published in PPI TR-4. Table 2 shows the PPI TR-4 recommended HDB values for the PA-U12 180 compound used in this study [21].

Stress regression data is accumulated through 10 000 hours and the mean regression line is extrapolated to 100 000 hours (11.4 years) to find the long-term hydrostatic strength (LTHS). The resultant value of the LTHS determines the HDB strength category to which the material is assigned. ASTM D2837 defines the ranges of long-term strength for each HDB strength category. The HDB can be established at multiple temperatures for each individual compound. If the HDB is determined at the design temperature, that HDB is used in the design equation. If the design temperature is between two temperatures for which the 100 000-hour LTHS is known, the interpolation method of PPI TR-3, Part D.2 can be used to determine the appropriate HDB for the design temperature. The actual LTHS should be used for the interpolation, not the HDB values because the HDB is a categorized strength based on the LTHS [22]. If the LTHS is near the upper or lower limit of one or both HDB categories, the interpolation might not give an accurate interpolated HDB.

The same design case that was used with the minimum expected strength example is shown below using the HDB-based design equation.

Maximum Design Pressure: 290 psig (20 bars)
Maximum Design Temperature: 149° F (65° C)

Design Equation: $DR = \frac{2 \times HDB \times DF \times FSF}{MOP} + 1$

$$\boldsymbol{DR} = \frac{2 \times 2000\,psi \times 0.63 \times 0.95}{290\,psi} + 1 = \mathbf{9.3}$$

Where:
*DR* = dimension ratio = OD/wall
*HDB* = TR-3 interpolated hydrostatic design basis at 149° F (65° C)
*DF* = design factor (0.63)
*FSF* = fluid service factor (1.0 for water, 0.95 for liquid hydrocarbons)
*MOP* = maximum operating pressure in psi

**Table 2: Recommended HDB for the PPI TR-4 Listed PA-U12 180 compound used in this study**

| Temperature, °F (°C) | HDB, psi (MPa) |
|---|---|
| 73 (23) | 3150 (21.7) |
| 140 (60) | 2000 (13.8) |
| 180 (82) | 1600 (11.0) |

Using a DF=0.63 instead of 0.50 at 65°and below is justified by the following characteristics of the specific PPI TR-4 listed PA-U12 180 used in this study:

1. The regression curve is linear through the 25-year intercept at 65° C and below. (Figure 5)
2. PA-U12 180 is highly resistant to conventional slow crack growth [12,13].
3. LCL/LTHS ratio of regression data submitted is at least 90%. (97% at 23° C, 95% at 60° C, 97% at 80°C)

Again, the more common manufactured size is SDR 9. Both design methods result in DR=9 for the same temperature and operating pressure.

## Conclusions

The hydrocarbon resistance and long-term hydrostatic strength of PA-U12 180 makes it an attractive option for surface-laid and buried oilfield piping systems. Because all polyamides are susceptible to hydrolytic degradation at high temperature and long times with sufficient water present, the long-term properties of PA-U materials, including the effects of hydrolytic degradation have been standardized in as DVS 2205-1 supplement 8. The reference curves identify the temperature and time at which a second branch appears, and the minimum expected strength at 25 and 50 years. The first appearance of a second branch is at 60° C and approximately 44 years. These long-term strength values can be used with conventional plastic pipe design equations to determine the wall thickness needed for the design pressure.

When designing pipes to the requirements of ASTM F3524 the PPI TR-4 listed HDB can be used in the design equation to calculate the required wall thickness. Since the HDB design method does not use reference curves it is helpful if the designer refers to the ISO reference curves to confirm that the design lifetime is less than the time needed to reach the second branch at the design temperature. The designer may choose to use the minimum expected strength at the design temperature shown in Table 1 instead of the HDB or an interpolated HDB.

Oilfield pipelines rarely operate at a constant temperature throughout the design life. The PA-U12 reference lines can be used with a cumulative damage model like Miner's Rule to estimate remaining life of a pipe that has been used at more than one temperature for known periods of time [23].

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