PA PIPES FOR 16 BARS GAS PIPELINES

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Presented at "Plastics Pipes 15", 20-22 September 2010, Vancouver, Canada.

ABSTRACT
PA11, PA12 and plasticized PA6.12 pipes are interesting candidates for gas transport and distribution pipelines at 16 bars pressure, which is beyond the maximum pressure for PE100 pipeline systems (10 bars). However, PA pipelines are not meant as an alternative to PE pipelines, but to steel pipelines. Therefore, permeability is important.
Permeability coefficients have been measured at 16 bars methane gas pressure on 110 mm SDR11 PA pipes and compared with the values for PE100 pipes. In comparison to PE100 pipes, PA pipes show a reduction in the methane permeability coefficient of 16 to 90, depending on the PA type. Plasticized PA6.12 shows the largest reduction.
Hydrogen permeability through three brands of PA12 pipe was also assessed.
Special attention was paid to butt fusion and electro fusion jointing. PA materials will absorb some moisture from the surrounding air or from rain and - after installation - from groundwater. During subsequent fusion steam bubbles may be formed which lead to voids at the joint plane.
The worst-case scenario was chosen, meaning butt fusion and electro fusion jointing of water-saturated PA pipes. The maximum water content after immersion ranged from 1.5 to 2.4 weight percent, depending on the PA type.
Despite this, electro fused joints in water-saturated PA12 and plasticized PA6.12 pipes meet the requirements of the Peel Test (ISO 13954), which is required for PA pipe systems (ISO 22621).
Butt fused joints in water-saturated PA pipes were tested at constant load in nitrogen gas at stresses up to 15 MPa and at temperatures up to 100 °C. Failure modes were ductile and no signs of slow crack growth were noted. Results at lower stresses and temperatures were converted to 15 MPa and 100 °C using the Miners Rule. Times to failure converted in this manner range from 153 to more than 2625 hours under these conditions, which is encouraging.
Steam bubbles formed in the joint may be pushed into the weld beads. Joint quality depends on the number and size of the voids at the fusion plane and much less on the presence of voids in the weld beads. Therefore, the process of pushing the steam bubbles into the weld beads is important. It seems possible to optimise joint quality further by changing the fusion temperature, pressure and procedure.

INTRODUCTION
Based on their good internal water pressure resistance, PA11, PA12 and plasticized PA6.12 pipes are considered for gas transport and distribution pipelines at 16 bars pressure. This is clearly above the maximum allowable pressure for PE100 pipeline systems (10 bars). Therefore, PA pipelines are not meant as an alternative to PE pipelines, but to steel pipelines. The use of PA pipes for gas pipelines was evaluated in a

previous publication [1]. For instance, by using modern trench-less installation techniques such as ploughing, cost advantages with respect to steel pipelines may be obtained.

Permeability

PA as a polymeric material shows some gas permeability. Values of the Permeability Coefficient (PC) for methane through PA pipes were published [1, 2]. PA pipes show a reduction in the PC for methane with respect to the PC of PE100 pipe by a factor of 16 to 90, depending on PA type [2], with plasticized PA6.12 showing the lowest PC. PC values for methane at 16 bars of five brands of long-chain PA pipes and PC values for hydrogen of three brands of PA12 pipe are now added.

Water Uptake by PA Pipes

It is well known [3, 4] that Polyamide materials will clearly absorb more moisture than PE materials. Whilst for short-chain PA materials like PA6 water uptake is substantial [4], for long-chain PA types water uptake is moderate. Still, a manufacturer stresses [5]: "It is important for the granules to be kept dry at all times. Necessary precautions should be taken to prevent any moisture pick-up during processing". Another manufacturer mentions [6]: "Moisture control /drying is critical for nylon".
Therefore, pipe extrusion or moulding for fitting production are the moments in the life of PA pipeline materials when the moisture content must be low. This "pivotal" moment is indicated in Figure 1 with the second arrow denoted "extrusion or injection moulding". If the granulate is not dry enough for extrusion or moulding, it must be pre-dried.

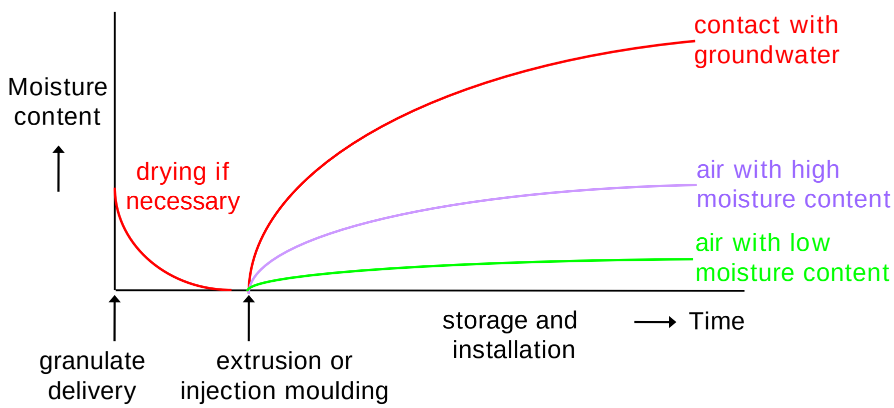

Figure 1. Possible moisture contents of PA materials in different stages of production and use (schematically).

However, once PA pipes are stored outside or installed, the condition of low moisture content is no longer guaranteed and water sorption starts again. Before installation the pipes are subjected to rain and/or the water vapour content of the surrounding atmosphere, which may vary considerably. After installation, the pipes are subjected to the water content of the soil, which may also vary considerably.
Water uptake of PA11, PA12 and plasticized PA6.12 leads to small weight and volume changes [1] and measurable changes in mechanical properties.
Water functions as a plasticizer, reducing stiffness and increasing elongation at break. For instance, Wolf et al report [7] that the tensile strength of PA11 pipe material may be reduced by 19% at a moisture level of 0.6%. Chen [8] noted that the Upper Yield Strength

of PA11 pipe decreases by 29% for an increase in water content up to 1.26%. However, the maximum water uptake of PA11 is 1.9 % [4].
For injection moulded PA12 materials, Goodridge et al [9] noted a reduction of the Ultimate Tensile Strength from about 41 to about 30 MPa and an increase in elongation at break from 10 ± 5 % to about 18% after 52 weeks of water submersion at 20 °C. In their study no water content before and after submersion was reported. They suggest the noted changes could be brought about by physical ageing.

In the present investigation water saturation was attained at 80 °C. Density increases were noted [1]. Therefore, it is also possible that slow re-crystallisation (an increase in crystallinity) of the PA materials occurs. The density of the crystalline phase in PA materials is higher than the density of the amorphous phase. Hence, re-crystallisation leads to an increase in density. DSC experiments were used to study crystallinity.

Fusibility of Water-Saturated PA Pipes

Margolis [3] warns against heat fusion problems that may occur with water-containing PA materials. In his book, on page 117, he writes: "The moisture absorption of nylon polymers affects their ability to be welded. All (…) welding techniques (…) generate molten nylon in the vicinity of the weld (…). Any moisture present in the part will vaporize in the weld area and produce steam. Brittle welds can result from voids and degradation of the molecular structure due to hydrolysis. Parts should be kept in a dry-as-moulded condition or carefully dried prior to welding".
Göring et al have published on fusion of PA12 pipes [10], but have not investigated the influence of water content. Chen [8] performed butt fusion experiments on water-containing PA11 pipes, but only up to a water content of 1.26 %, whilst the maximum water content is 1.9 % [4]. At 1.26 % water content he noted some reduction in the tensile strength and an increase in elongation at break of the joints.

The discussed PA pipe systems for natural gas are intended for operation during a minimum lifetime of 50 years. During this time, the pipes may become water-saturated, depending on the moisture conditions in the soil. However, it must still remain possible to repair PA pipelines after third party damage or in case the network needs to be extended. For repair of existing pipelines, electro fusion is the only practical jointing method. In the case of network extension butt fusion may also be used.
Therefore, for assessing fusibility of existing PA pipelines, the worst-case scenario was adopted, which is water absorption until saturation at 23 °C, attained by complete submersion of pipe segments in water at 80 °C. Next, the influence of the moisture saturation on the fusibility of the pipe materials and on their crystallinity was investigated. The following questions need to be answered:

1. Is the repair by electro fusion of existing – water saturated – PA pipelines possible?
2. Is the extension of water-saturated PA pipelines by butt fusion possible?

MATERIALS AND METHODS

Materials

Commercially available pipes and fittings were investigated. They were provided by five important resin producers, Evonik Degussa in Germany, UBE in Germany, EMS

GRIVORY in Switserland, DuPont in Germany and Arkema in France. Table 1 lists the resin types and the resin codes A until F.
Not all investigations were performed on all materials. PA pipes E and F were only used for permeability measurements, whilst on PA pipe D, no permeability measurements and no electro fusion experiments were performed.
For PA pipes A and D no electro fusion fittings were delivered. Fittings of PA type B (also made from PA12 resin) were used for electro fusion experiments on PA pipes A.

Table 1. Investigated 110 mm SDR11 PA pipes and electro fusion fittings.

Product	**PA code**	**Product**	**PA code**
PA12 pipe	A	PA11 pipe	D
PA12 coupler	not delivered	PA11 coupler	not delivered
PA12 pipe	B	“long-chain PA” pipe	E
PA12 coupler	B	PA12 pipe	F
PA6.12 pipe	C		
PA6.12 coupler	C		

Methods

Permeability measurements were performed on 110 mm SDR11 pipes, using the methods described earlier [1, 2]. It is emphasized that the pipe diameter was taken as the “median pipe diameter”, halfway between the external and internal pipe diameter, as explained previously [2]. It was later proven that this approximation leads to negligible errors [11].
Methane permeation was measured at 16 bars gas pressure, whilst hydrogen permeation was measured at 10 bars.
Electro fused joints were tested using the Peel Test according to ISO 13954.
Butt fusion was performed in the conditions published before [1], at either 230 or 260 °C.
To avoid the use of a detergent the butt fused joints were tested at constant load at 90 and 100 °C in air at stresses up to 15 MPa. Because the most optimal testing temperature and stress were unknown beforehand, the tests were started at 8 MPa and 90 °C. Every week the stress was increased by 2 MPa up to 15 MPa. After ± 1,100 hours in the latter condition only some test bars had failed. Therefore, the testing temperature was increased to 100 °C for additional testing during ± 2,200 hours at 15 MPa.
The failures data were converted to the harshest condition of 15 MPa and 100 °C using the Miners Rule [12]. Activation energies and the influence of the testing stress were derived from results of internal water pressure tests published by the manufacturers of materials B and D. The data of material B was used for A as well, because both are PA12 resins. For material C no data were available and conversion was not possible.

RESULTS

Permeability for Methane and Hydrogen

Results obtained on five brands of PA pipe with 16 bars methane are shown in Table 2.

Figure 2 shows the results of the permeability measurements using hydrogen gas at 10 bars. Steady state permeation already starts after 1 day or less. This is too short to determine the breakthrough time reliably. This is in clear contrast with the results for methane permeation when breakthrough times of 220 to 250 days were found [2].

Table 2. Permeability coefficient (PC) at 21 °C for methane and hydrogen of PA pipes and their ratio and comparison to PE100 pipe [2] and HPDE film [13].

Pipe nr.	Resin type	PC ($ml.mm/m^2$/bara/day) CH_4	H_2	Factor H_2/CH_4
A	PA12	1.64	84.2	51
B	PA12	1.81	79.1	44
C	PA6.12	0.38	-	-
E	"long-chain PA" pipe	5.76	-	-
F	PA12	2.37	95.8	40
	PE100 pipe	35.7 [2]	166 (a)	4.6
	HDPE film	-	156 (b)	-

a: measured at the author's lab in another project. b: at 25 °C [13]

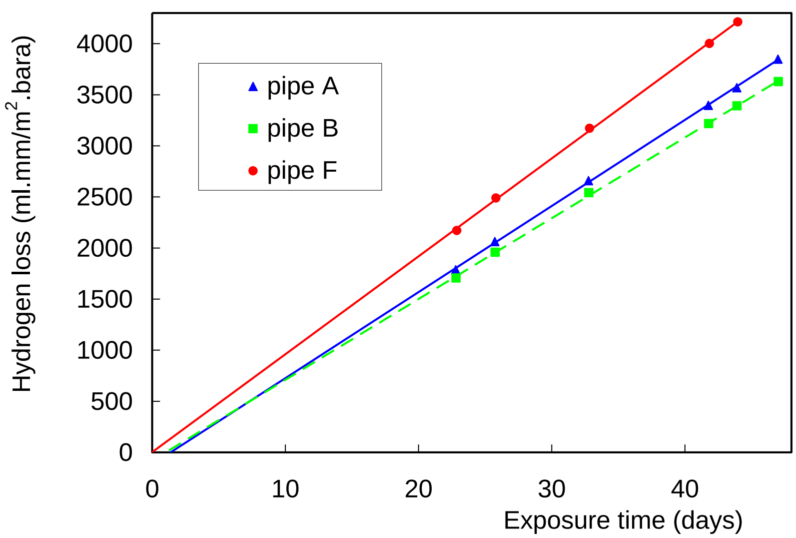

Figure 2. Permeation of hydrogen through the wall of PA12 pipe types A, B and F. As with methane [2] pipe F shows the highest permeability of the three types.

A very low breakthrough time means [2] that the diffusion coefficient of hydrogen through PA12 pipes is too high to be reliably measured using this setup.
Table 2 also shows the PC values for hydrogen through three PA12 pipes and the ratio between both. The PC values for hydrogen are 40 to 51 times higher than for methane. A comparison with hydrogen permeability through PE100 pipe is also made. A previously unpublished value for PE100 pipe is included in Table 2.
The PC for hydrogen through PA12 pipes is only 1.8 to 2.2 times lower than the PC for hydrogen through PE100 pipe. This difference is much smaller than for methane permeability. A similar value for hydrogen permeability through HDPE film with an unspecified density was added to Table 2. The above results are not further discussed.

Effects of Water Saturation

DSC measurements were performed on the water-saturated pipes (Table 3). Most pipes show a decrease in volume and a weight increase [1], hence a density increase. However, the volume reduction of pipe C is influenced by plasticizer loss.

An increase in melting enthalpy (crystallinity) of 8-9% was noted, with B showing an even higher increase of 19%. It is unknown why B behaves differently. The melting (peak) temperatures are not influenced.

Table 3. Changes in volume and DSC parameters of water-saturated PA samples.

		Melting enthalpy (Joule/g)			Melting temp. (°C)	
PA type	Volume change (%)	ΔHa as-received	ΔHw water-saturated	ΔHw/ΔHa	Tm as-received	Tm water-saturated
A	-2.1	72.0	78.6	1.09	176.7	176.4
B	-1.1	74.3	88.3	1.19	177.7	178.0
C	-4.3	88.8	95.8	1.08	209.4	209.7
D	-1.1	73.2	80.1	1.09	189.0	189.4

Table 4. Average properties of Peel tested electro fused joints in water-saturated (w) and as-received (a), PA pipes and their ratio. Smax: maximum Stress based on the pipe wall thickness. EaY: elongation at yield, EaB: elongation at break.

PA type	Pipe condition	Water content (%)		S_{max} (MPa)	EaY (%)	EaB (%)	Acceptable test bars
A	w-w	1.5	Average	7.51	8.3	25.0	4 out of 4
	a-a		Average	8.56	7.2	23.8	4 out of 4
			Ratio (%)	88	115	105	
B	w-w	1.5	Average	7.44	8.6	27.1	4 out of 4
	a-a		Average	8.80	8.0	26.1	4 out of 4
			Ratio (%)	85	108	104	
C	w-w	2.3	Average	5.67	29.5	46.9	3 out of 4
	a-a		Average	7.11	15.4	36.1	4 out of 4
			Ratio (%)	80	192	130	

Electro Fusion Jointing of Water-Saturated Pipes

The mechanical characteristics of the electro fused joints are given in Table 4. Most joints fail in the pipe or in the fitting wall. Both failure modes are acceptable. The column on the right shows the number of acceptable test bars. In general the results of the electro fusion experiments on water-saturated PA pipes are good. One test bar of PA type C shows brittle failure in the joint plane and this particular result is not acceptable. However, this is considered as a non-systematic exception.

Butt Fusion Jointing of Water-Saturated Pipes

Because relatively few samples from water-saturated butt fused PA pipes were tested, the results in Table 5 should be evaluated with some caution.

After the tests the failed and intact test bars were examined for voids in either the beads or at the fusion plane. Figure 3 and Figure 4 show an example of a failed and an intact test bar. All test bars were evaluated for such voids (Table 5).

Table 5. Failure times (FT) and their geometrical mean [14] *of butt fused joints in previously water-saturated PA pipes converted to 15 MPa and 100 °C using the Miner's Rule* [12]*. One test bar of PA type C already failed at 90 °C.*

PA code	Test bar	FT (h) at 100 °C and 15 MPa	Result	Geometrical Mean (h)	Voids in beads	Voids at fusion plane
A	B7	2624	intact		many	few
A	B8	153	failed		many	many
A	B9	1120	failed	> 767	many	many
B	B5	519	(a)		very many	few
B	B6	2625	intact	> 1168	very many	few
C	B1	913 (b)	failed		few	very many
C	B3	2132	failed	-	few	very many
D	B10	2312	intact		many	very few
D	B11	2312	intact	> 2312	many	very few

a: failed 15 mm from the fusion plane. *b: failed at 90 °C*

There is a qualitative correlation between voiding at the fusion plane and joint quality. The voids in the beads are not relevant. The voids in the failed joints in pipe C are largest near the weld beads. However, voids are nearly absent in the beads.

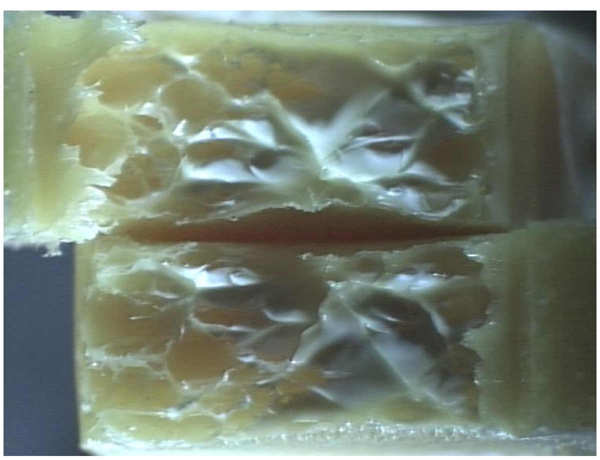

Figure 3. Broken test bar B8 from a previously water-saturated butt fused PA pipe (type A) after 153 hours of Constant Load testing at 15 MPa and 100 °C.

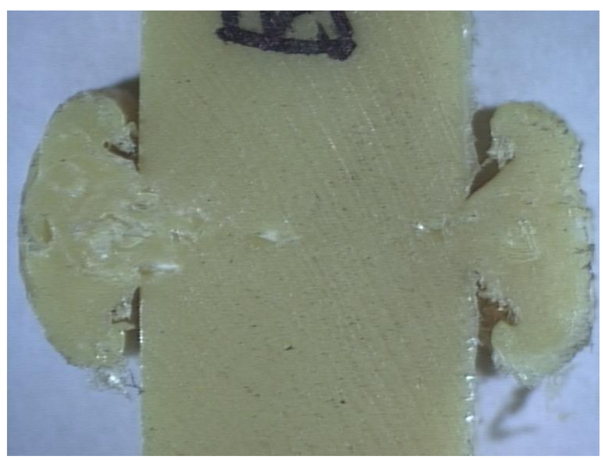

Figure 4. Intact test bar B7 from a previously water-saturated butt fused PA pipe (type A) after 2640 hours of Constant Load testing at 15 MPa and 100 °C.

In those cases where the voids were pushed into the weld beads during butt fusion the best test results were obtained. For pipe C this process was not completed and the voids are near, but not in the weld beads (Figure 5). This leads to less optimal properties.

It was investigated using Thermo Gravimetric Analysis (TGA) at which temperature all water in a water-saturated PA sample is lost. This temperature is derived from the minimum in the derivative TGA curve (not shown). The results are shown in Figure 6. For each of the four PA types, the "water loss temperature" is shown in the left column and the applied fusion temperature in the right column. For material D, the difference between both temperatures is highest and for C it is lowest.

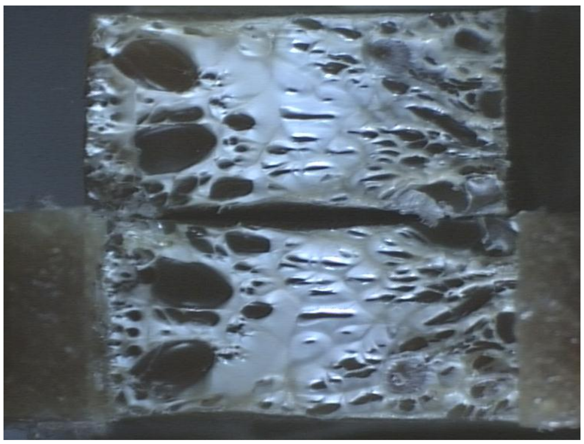

Figure 5. Failure surfaces of test bar B3 from a previously water-saturated butt fused PA pipe (type C) showing orientation of the voids in the direction of the weld beads (left and right).

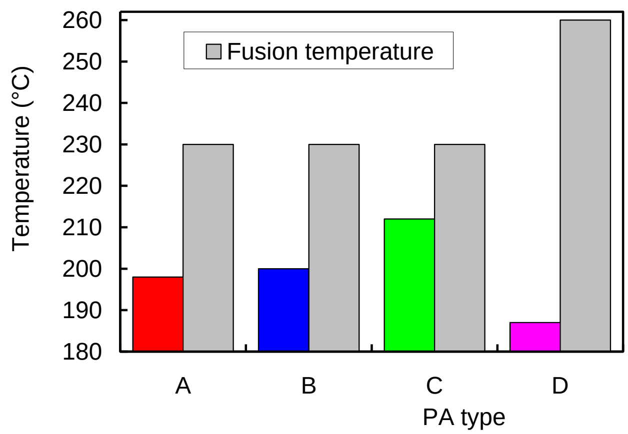

Figure 6. Temperature at which all water in four water-saturated PA samples is lost (TGA) and the applied fusion temperature [1]*.The difference between both temperatures is important.*

DISCUSSION

Water Saturation and Crystallinity

Table 3 confirms that volume reduction and density increase of the PA pipe segments noted before [1] is explained by an increase in crystallinity of the PA pipes that were water-saturated at 80 °C. It is likely that temperature is more important than water content.

Electro Fusion Jointing of Water-Saturated PA Pipes

In water-saturated condition the average Maximum Load during the Peel test is reduced by more than 10% with respect to the "relatively dry" pipe condition (Table 4). Elongation at Yield and the Elongation at Break both increase by water saturation. These effects are most pronounced for pipe material C of which the saturated water content (see also Table 4) is highest. This corresponds with earlier findings [7, 8, 9].

Butt Fusion Jointing of Water-Saturated PA Pipes

Constant Load testing in air up to 100 °C and 15 MPa is attractive for long-term testing of butt fused joints in PA pipes, because the use of thermally unstable detergents [15, 16] is

avoided. Times to failure are several thousands of hours. This guarantees assessment of the long-term joint properties.
There seems to be a general correlation between the butt fusion joint quality and the difference between the fusion temperature and the temperature at which all water is lost (Figure 6). The larger this difference, the more water is lost from the pipe ends before the actual butt fusion process takes place. This stresses the importance of removing all water before fusion.

Practical Considerations
Voids in the fusion plane of water-saturated PA pipes are very important. Even in partially water saturated PA pipes, voids are present in the weld beads [1]. On the other hand, voids in PE pipes do not normally occur. When they are formed a reduction of joint strength or premature failure is often noted. Such voids usually lead to in-depth disputes between constructors, pipe manufacturers and pipeline owners. To avoid void formation, EN 1555 demands that PE pipes may not contain more water than 300 ppm (0.03%).

How should the real danger of void formation in butt fused joints in water-containing PA pipes be treated in practical guidelines?

- The gas industry has trained the “men in the trench” very thoroughly to be critical about bead shape and size and any irregularities in the beads of butt fused PE pipes.
- It is unwanted that any steam bubbles should be ignored for butt fused PA pipes “because for PA pipes this is normal”, whilst no check of the fusion plane is possible.
- Making a distinction between different fusion behaviours of different polymer pipes is only possible by highly skilled and separately trained staff. More work in this area needs to be done. Welders of PA pipes should have a special certificate for fusing high-pressure PA gas pipelines.

CONCLUSIONS AND RECOMMENDATIONS

1. Re-crystallisation of all four PA pipe materials is responsible for volume and diameter reduction of the PA pipes after water-saturation by immersion at 80 °C. It is unknown how quickly this process occurs at ambient temperature.
2. Electro fusion jointing can be used for repair after third party damage of water-saturated PA12 and plasticized PA6.12 pipelines and for network extensions. Electro fused joints in water-saturated PA11 pipes were not tested.
3. In water-saturated PA pipes, but also in PA pipes that contain less absorbed water, steam bubbles are formed during butt fusion. These steam bubbles may remain at the fusion plane or can be pushed into the weld beads, or both.
4. There is a qualitative correlation between the extent of voiding at the butt fusion plane and the quality of the joints as assessed by constant load testing at 15 MPa and 100 °C. Large and many steam bubbles at the fusion plane provide the greatest threat to butt fusion joint quality. Steam bubbles in the beads are unimportant.
5. For water-saturated PA pipes, the butt fused joint in PA11 pipe contains fewer voids at the fusion plane and shows a better mechanical quality than joints in one type of PA12 pipe and in plasticized PA6.12 pipe, which contain more voids at the fusion plane. The other type of PA12 pipe also contains fewer voids at the fusion plane.

6. During butt fusion of PA pipes in the field only steam bubbles in the surface of weld beads can be readily observed. It is difficult to assess whether voids are also present at the most dangerous location, the fusion plane. This needs further attention.
7. Butt fusion procedures for water-containing PA pipes may be further optimised by removing absorbed water by pre-heating. Optimising the flow process in radial pipe direction into the bead is another option. Heating plate temperature and welding pressure may be optimised, because various values were applied.
8. In view of the voids that may occur in butt fused PA pipes it is recommended that welders should have a special certificate for fusing high pressure PA gas pipelines.
9. The hydrogen permeability of three investigated PA12 pipes is 1.7 to 2.1 times as low as the hydrogen permeability of PE100 pipe. Methane permeability of the investigated PA pipes is 16 to 90 times lower in comparison to PE100 pipes, depending on the PA type.

ACKNOWLEDGEMENTS

The authors wish to thank E.ON Ruhrgas (Germany) and GdF Suez (France) and the PA resin manufacturers Evonik Degussa, EMS GRIVORY, UBE, DuPont and Arkema for financial support and permission to publish these results. Mr. Kim van Oers and Mr. Matthijs Schrijver are thanked for carefully performing the experiments.

REFERENCES

1. Scholten F.L. and Wolters M., “Polyamide 11, 12 and 6.12 for High-Pressure Gas Pipelines”, Proc. Int. Gas Research Conf. 2008, 8-10 October, Paris.
2. Scholten F.L. and Wolters M., “Methane Permeation through Advanced High-Pressure Plastics and Composite Pipes”, Proc. Plastics Pipes XIV Conference, Budapest, 2008.
3. Margolis J.M., “Engineering Thermoplastics”- Properties and Applications”, Volume 8, Marcel Dekker, Inc., (1985), ISBN 0–8247–7294–6.
4. Kohan M.I. ed., “Nylon Plastics Handbook”, (1995), ISBN 3-446-17048-0.
5. Brochure 738, “RILSAN PA 11: Created from a Renewable Source”, 2007, Arkema.
6. “Pipelon extrusion epromotion_1.3”, 2007, DuPont.
7. Wolf R., Dang P., Patadia H., “Evaluation of PA11 for use in Natural Gas Distribution Systems operating at high Pressures and Temperatures”, Plastics Pipes XI, Munich, 2001.
8. Chen J., “Optimization of Parameters Influencing Butt Fusion Integrity in Polyamide 11 Pipe”, Proc. Natural Gas Technologies 2005, Jan. 30 – Feb. 2, 2005.
9. Goodridge R.D., Hague R.J.M. and Tuck C.J., Polymer Testing 29 (2010), 483-493.
10. Göring R., Dowe A., Lohmar J., “Joining technology for Polyamide pipes (PA12) in the gas high-pressure range”, Joining Plastics, DVS (Germany), 2 (2007), 164-174 (in German).
11. van der Stok E.J.W., Scholten F.L. and Dalmolen L.G.P., “Cover Blow-off Resistance of Reinforced Thermoplastic Pipes for Gas Service”, Plastics Pipes XV, Vancouver, 2010.
12. ISO 13760:1998 “Plastics pipes for the conveyance of fluids under pressure -- Miner's rule -- Calculation method for cumulative damage”.
13. Massey L.K., “Permeability Properties of Plastics and Elastomers”, 2nd Edition, Plastics Design Laboratory, Norwich, NY, USA, (2003), ISBN 1-884207-97-9.
14. http://en.wikipedia.org/wiki/Geometric_mean and http://www.buzzardsbay.org/geomean.htm
15. Scholten F.L., Pisters J. and Venema B., “A more reliable detergent for Constant Load testing experiments on Polyethylene”, Polym. Testing, 8, (1989), 385-405.
16. Scholten F.L., Gueugnaut D. and Berthier F., “A more reliable detergent for Cone and Full Notch Creep testing of PE pipe materials”, Plastics Pipes XI, Munich, 2001.