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EXPANDING THE APPLICATION RANGE OF HIGH DENSITY POLYETHYLENE FOR USE AS AN INNER-LINER MATERIAL IN REINFORCED THERMOPLASTIC PIPE AND STEEL PIPE

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SHORT SUMMARY

Normal High Density Polyethylene (HDPE) is commonly used as the fluid contacting element, or the “inner-liner”, in Reinforced Thermoplastic Pipes (RTP) and steel pipes up to 65 ºC. Through a modification of the HDPE polymer matrix, by adding nano-particles, the E-modulus can be increased. Research shows that Nano-filled HDPE liners can, as a result, be used in RTP and steel pipe up to 85 ºC, a temperature which could previously only be reached by using rather expensive polyamide 11 and polyamide 12 compounds.

KEYWORDS

High density polyethylene (HDPE)
Nano-filled polyethylene
Polyethylene liner
Reinforced Thermoplastic Pipe (RTP)

ABSTRACT

Normal High Density Polyethylene (HDPE) is nowadays extensively used as a corrosion resistant liner material in Reinforced Thermoplastic Pipes (RTP) and in Carbon Steel Pipes for temperatures up to 65 ºC. Rather than strength, the retention of a certain stiffness (E-modulus) is the design criterion governing the high temperature limitation for plastics as a liner material. Through a modification of the HDPE polymer matrix by adding nano-particles the E-modulus can be increased.

Hydrocarbon fluids tend to absorb in the HDPE matrix, acting as a plasticizer and lowering the E-modulus. Fluid absorption strongly increases with temperature, and also depends on the composition of the fluid. In general, low molecular weight fluids show higher absorption, and aromatic hydrocarbons show more affinity to HDPE than other olefins. The affinity of hydrocarbons towards HDPE can be expressed as the “Hildebrand solubility parameter”. When this parameter closely matches the Hildebrand parameter of the matrix, hydrocarbon absorption, plasticization, and fluid permeation are at maximum. The Hildebrand solubility parameter can be calculated by the arithmetic average of the Hildebrand parameters of the fluid components. When the composition is known, an accurate estimate of the swelling, lowering of the E-modulus, and the level of fluid permeation can be made.

Tests, to assess the modulus retention at high temperature, were conducted with a worst case hydrocarbon fluid composition (based on the Hildebrand solubility parameter): a synthetic gas condensate consisting of 50 % (m/m) of trimethylbenzene and 50 % (m/m) n-decane. HDPE, PE100 was used as a reference material, which has a modulus of around 300 MPa at 65ºC when saturated with the test fluid. The HDPE

based nano-particles filled compound showed a similar modulus as PE100 at a 20 ºC higher temperature.

Results of permeation experiments and slow crack growth tests, support the assumption that HPDE based compound filled with nanoparticles can be used for liner materials in RTP and steel pipe up to 85ºC, a temperature which could previously only be reached by using more expensive polyamide 11 and polyamide 12 compounds.

INTRODUCTION

A thermoplastic material is commonly used as the fluid contacting element, or the "inner-liner", in Reinforced Thermoplastic Pipes (RTP) and steel pipes. In steel pipes, a plastic inner-liner is meant to protect the metal from corrosion, while the steel pipe affords a hydrostatic pressure resistance well beyond the capability of stand-alone solid wall plastic pipes. In RTP, the plastic inner-liner provides a corrosion resistant conduit for the fluid, while the metallic or synthetic fibre reinforcement affords the required hydrostatic strength.

Used as an inner-liner, the hydrostatic pressure resistance of plastic pipe is of secondary importance as this function is performed by the fibre reinforcement or the surrounding steel pipe. Instead, the inner-liner must retain its mechanical integrity, or ring stiffness [1], in contact with the fluid at the maximum allowable operating temperature of the system.
A certain ring stiffness is required to protect the inner-liner from collapse due to potential external loads on the inner-liner pipe.

The resistance against collapse of the inner-liner is determined by its ring stiffness which, in turn, is determined by its dimensions and the E-modulus of the plastic material.The E-modulus of the plastic material is strongly influenced by temperature and by absorption of fluid components, in particular by hydrocarbons.

High density polyethylene (HDPE) liners are used in the oil and gas industry for water, oil, and gas pipelines for temperatures up to 65 ºC. For higher temperatures, other materials are required, such as polyamide 11 (PA11) or polyamide 12 (PA12) (up to about 85 ºC) or PVDF (for temperatures up to about 120 ºC). However, these materials are considered significantly more expensive than HDPE.

To improve the temperature performance of HDPE, for it to reach the level of PA11 and PA12, several modifications have been made such as PEX and PE-RT. Most recently also a nanoparticle filled HDPE compound has been developed. These nano-particles are high aspect ratio particles, with an average length of 5 micrometers. This nanoparticle filled HDPE fulfils the most essential criteria for inner-liner application at higher temperatures.

All of these PE modifications were considered a potential solution to improve the inner-liner resistance to temperature. Using the E-modulus of HDPE, saturated with a hydrocarbon test fluid, at 65 ºC as a benchmark, the relative improvement of the temperature performance of these compounds was assessed. After the assessment of the E-modules when saturated with a hydrocarbon test fluid, the best PE modification was chosen for further testing on other critical aspects.

As hydrocarbon permeation can also be a major consideration for HDPE inner-liners, permeation tests were performed for both the original HDPE material and the best PE modification, the HDPE containing nanoparticles. A mixture which has a Hildebrandt solubility [2] parameter which closely matches the solubility parameter of HDPE and therefore is expected to show the highest solubility and permeability, has been used and serves as a “worst case scenario”. The permeability coefficients have been determined experimentally at 23 ºC and 65 ºC, respectively, according to the test method mentioned in EN 14125:2013 (paragraph 7.2.9) [3].

Another concern for inner-liner applications is the resistance against slow crack propagation under constant strain. This has been assessed by measuring the strain hardening modulus [4,5] of both materials. Used as an inner-liner, rather than exposed to a situation of constant hydrostatic stress, the inner-liner is exposed to a situation of constant strain, the strain level being imposed by the deformation of the surrounding steel pipe or reinforcement under hydrostatic internal pressure. While strained, the inner-liner material should not rupture due to slow crack propagation. Resistance to slow crack growth is therefore also a design criterion. The selected PE modification containing nanoparticles was compared to standard HDPE, type PE100 material by performing the strain hardening test in accordance to ISO 18488 [6].

RESULTS

The following materials (Table 1) were compared with regard to the performance as an inner-liner pipe for oil and gas applications:

Table 1. Polyethylene based resins used in the experiments.

ID	Description
	HDPE based
HDPE	PE 100
HDPE-F	PE100 with nano-particles
PE-RT1	Octene copolymer based PE-RT, manufacturer 1
PE-RT2	Octene copolymer based PE-RT, manufacturer 2
	Crosslinked PE
PEX-1	PEX from medium density PE
PEX-2	PEX from high density PE
PEX-2 NX	Same as PEX-2, but not yet cross-linked

Modulus retention immersed in synthetic gas condensate.

The polyethylene materials in Table 1 were selected for the comparative study of the secant modulus at elevated temperature. Prior to Dynamic Mechanical Analysis (DMA) [7] testing, the samples were immersed at 65 ºC in synthetic gas condensate until the absorption of the fluid has reached equilibrium. The gas condensate consists of 50 % (mole/mole) of 1,3,5 trimethylbenzene and 50 % (m/m) n-decane, as per ISO 4437 [8]. The dissolved gas condensate in the polymer matrix acts as a plasticizer, lowering the secant modulus.

The secant modulus of HDPE, as a function of temperature in dry condition, and immersed in gas condensate are depicted in Figure 1.

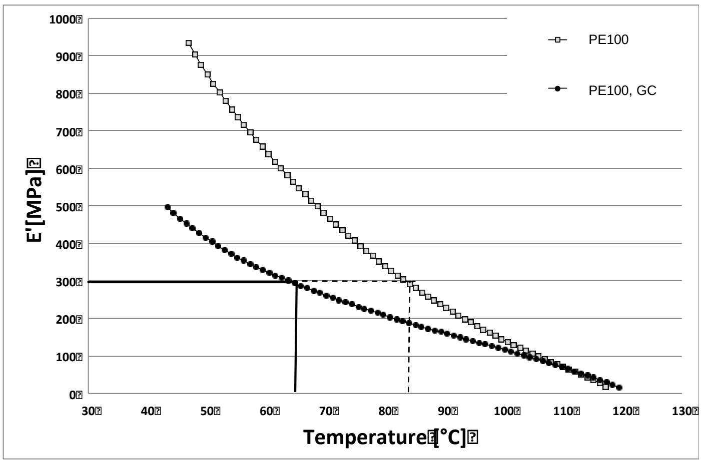

Figure 1. The dynamic secant modulus (E') of HDPE as a function of temperature in dry condition and saturated gas condensate.

At the maximum temperature rating of 65 ºC, immersed in gas condensate, E' = 300 MPa. This is the benchmark value of the modulus at elevated temperature.

The modulus of PE-RT polyethylene resins with "Raised Temperature" performance is depicted in figure 2.

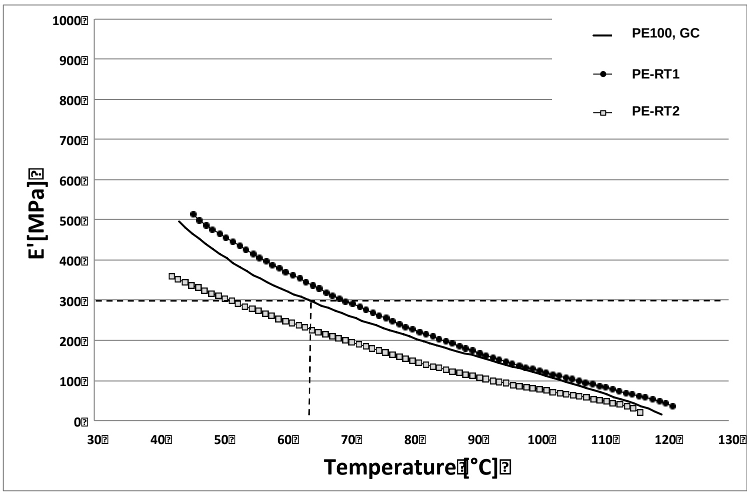

Figure 2. The dynamic mechanical secant modulus (E') of PE-RT grades as a function of temperature, saturated in gas condensate. HDPE is included for comparison.

In Figure 2 it can be seen that the relative improvement of the temperature performance of PE-RT types is very modest at best, up to about 5 ºC. PE-RT2 even shows significantly worse performance than HDPE.

The performance of cross-linked (PEX) materials is depicted in figure 3.

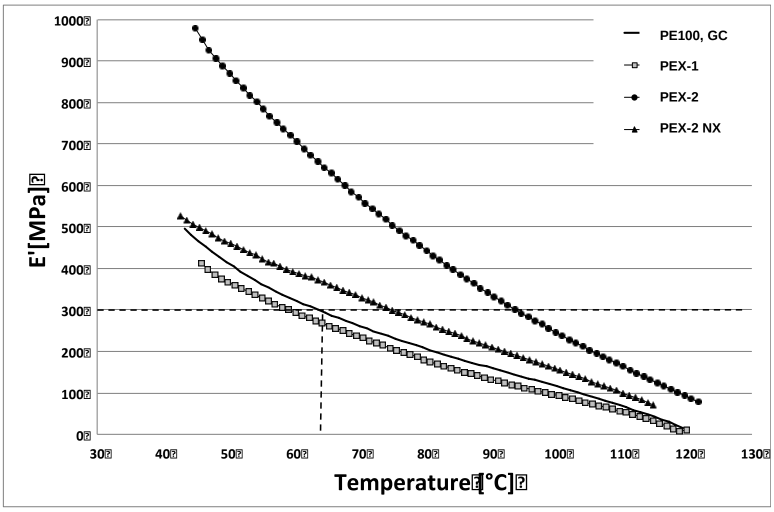

Figure 3. The dynamic mechanical secant modulus (E') of PEX grades as a function of temperature, saturated in gas condensate. HDPE is included for comparison.

Figure 3 shows that an increase of performance can be expected by using high density PEX. Medium density PEX shows comparable performance to standard HDPE. The difference between PEX-2 and PEX-2 NX shows the importance of cross-linking for good performance. PEX-2 , immersed in gas condensate, has the same modulus as HDPE at 95ºC, an improvement of 30ºC.

Figure 4 shows the temperature dependence of the modulus of a recently developed PE100 with nanoparticles based compound, HDPE-F.

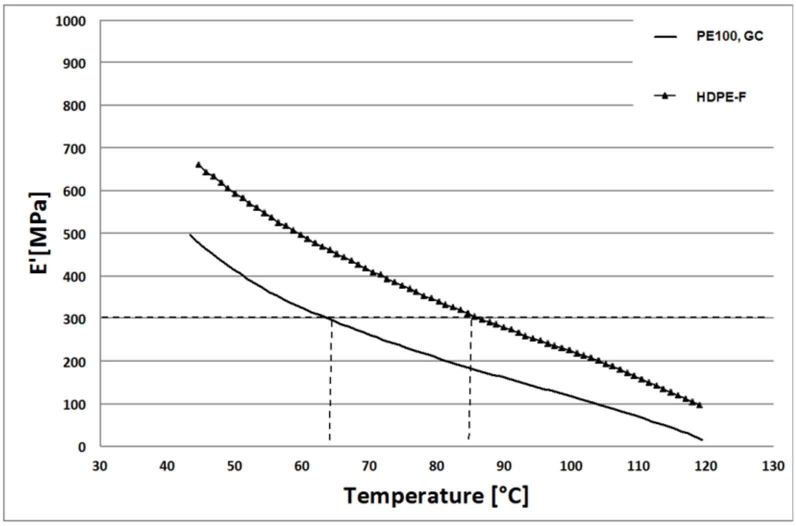

Figure 4. The dynamic mechanical secant modulus (E') of HDPE-Fas a function of temperature, saturated in gas condensate. HDPE is included for comparison.

At 85ºC HDPE-F shows the same modulus as HDPE at 65ºC, which is an improvement of 20 ºC. Considering the fact that, although PEX solutions show a higher modulus than the HDPE-F, PEX liners are quite difficult to install in comparison to the HDPE liners, it was decided to continue testing with the HDPE-F modification.

Hydrocarbon permeation

The permeation of hydrocarbons through HDPE and nanoparticle filled HDPE (HDPE-F) have been compared, using hydrocarbon test fluids of different affinity to the materials:

- n-pentane (100 %), an aliphatic hydrocarbon
- toluene (100 %), an aromatic hydrocarbon
- 50vol% / 50vol% n-pentane and toluene mixture

The mixture has a Hildebrandt solubility parameter [2] which closely matches the solubility parameter of HDPE, and is expected to show the highest solubility and permeability, and thus serves as a “worst case scenario”.

The permeability coefficients have been determined experimentally at 23 ºC and 65 ºC, respectively, according to the method in paragraph 7.2.9 of EN 14125:2004.

The results are presented in Table 2. As expected, the small amount of nanoparticles in the HDPE-F compound hardly influences the permeability of hydrocarbons.

Table 2. Coefficients for permeation of different pipe systems at 23 ºC and 65 ºC.

Pipe material	Solution	Permeation coefficient [g.mm/m^2.day] at 23 ± 2 ºC	[g.mm/m^2.day] at 65 ± 2 ºC
HDPE	**Pentane**	32,1	394,0
	Toluene	31,5	308,0
	50-50 vol%	38,8	310,1
HDPE-F	**Pentane**	31,8	281,5
	Toluene	32,2	278,8
	50-50 vol%	50,8	359,7

Strain Hardening

To gain the strain hardening modules (<Gp>), the Strain Hardening test method as described in ISO 18488 [6] is followed. The strain hardening modulus (<Gp>) is related to the resistance against slow crack growth. The higher the <Gp>, the better the resistance against slow crack growth.

The results of strain hardening testing of HDPE-F (nano-filler reinforced HDPE) are compared to the results of standard PE100, type HDPE grade in Table 3.

Table 3. Average Strain Hardening Moduli <Gp> and the standard deviation of the two materials.

Pipe material	Average <Gp> (MPa)	Stand. dev. (MPa)	Cv (%)
HDPE	74.56	1.03	1.39
HDPE-F	52.95	3.07	5.80

The graph below (figure 5) places the strain hardening modulus of HDPE-F in perspective of the strain hardening modulus of other pipe grade HDPE materials.

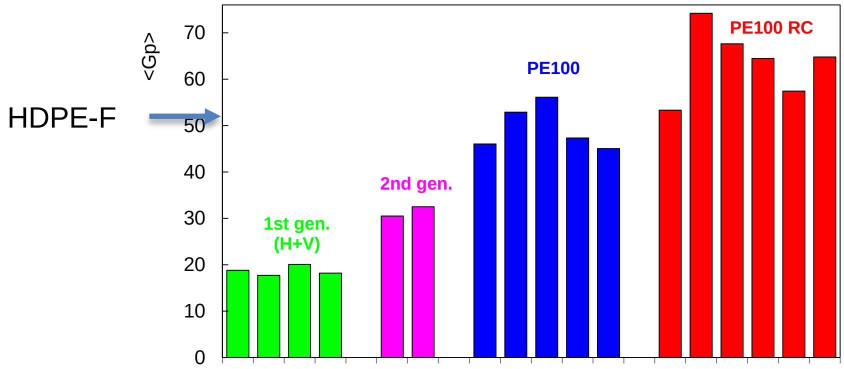

Figure 5. The strain hardening modulus of different pipe-grade HDPE materials of the first and second generation, PE100 and PE100 with improved slow crack resistance (PE100 RC) [5].

HDPE-F shows a comparable strain hardening modulus as most PE100 resin grades, and somewhat lower than RC high crack growth resistant grades. The strain hardening modulus of HDPE-F is significantly better than PE pipe grades of the first (PE 63) and second (PE 80) generation.

DISCUSSION & CONCLUSIONS

By compounding a standard HDPE pipe grade resin with a nano-filler material, the modulus, while saturated with a 50 % aromatic light hydrocarbon mixture, can be increased to a level at which, at 85 ºC, the filled material has a similar modulus as the un-filled and hydrocarbon soaked resin at 65 ºC.

HDPE materials are generally used up to about 65 ºC as an inner-liner material in steel pipe and reinforced thermoplastic pipe for hydrocarbon and gas applications. This suggests, a nano-filled HDPE material can be used for these applications up to 85 ºC, ensuring the same level of external hydrostatic collapse resistance and mechanical integrity. This is comparable to the temperature rating of polyamide 11 and polyamide 12 inner-liner materials.

PE-RT materials, which have been originally developed for stand-alone domestic hot water pipe applications, do not offer any significant improvement compared to PE100 with regard to the use as an inner-liner material for hydrocarbon and gas piping. Cross-linked HDPE (PEX) may offer a significant improvement compared to HDPE, but these materials are still difficult to process into large diameter thick-walled pipe, which is required for oil and gas production and transport piping. Unfortunately, PEX is therefore not yet always an economically and technically viable alternative for these applications.

Nanoparticle filled HDPE shows a very comparable resistance to slow crack growth as standard HDPE pipe material, suggesting that there is no extra risk of crack formation involved when used as an inner-liner material.

Nano-filled PE100 (HDPE-F) shows a very similar permeation rate towards aliphatic and aromatic light hydrocarbons as the HDPE base resin. In those applications where hydrocarbon permeation is not an issue, both HDPE-F and HDPE can be utilized. If the permeation rate of HDPE is unacceptably high, other low permeation resins, like PA11 or PA12 could be used, or a multilayer pipe construction, with a permeation barrier layer is an option.

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