TECHNOFORM

Optimization of corrosion protection in flue gas cleaning by the use of structural components made of chemical resistant plastics

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Tailored engineering plastics solutions

Foreword

At present, sewage sludge from municipal wastewater treatment plants in Germany is disposed of primarily by thermal treatment (incineration) and by recycling in agriculture and landscaping. With the increasing focus upon hygienization, soil protection and phosphorus recovery, energy recovery processes are growing in importance. In 2019, three-quarters of municipal sewage sludge was incinerated, and only one-quarter was recycled in agriculture, landscaping and other sectors [3].

With rising volumes of sewage sludge to be treated thermally, coupled with growing demands on the hygiene and sustainability of the processes, the demands made on the performance and design of thermal sewage sludge treatment plants are also changing. This particularly applies to plants for the treatment of flue gases produced during the incineration of sewage sludge. These plants must be capable of withstanding the increasing chemical, mechanical and thermal stresses in the flue gas. Corrosion protection continues to be a key challenge for engineers and operators.

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Optimization of corrosion protection in flue gas cleaning by structural components made of chemically resistant plastic

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We are available personally at all times to answer any questions you may have.

1. Corrosion in flue gas treatment

Corrosion damage is a serious issue for operators of industrial plants and power stations. Destructive chemical processes present a threat to steel structures and pipelines and can be costly. The World Corrosion Organization (WCO) estimates the damage caused by corrosion worldwide at US$ 2.5 trillion per year. This equates to 3 to 4% of the industrialized countries' GDP [6].
EN ISO 8044 defines corrosion as a "physicochemical interaction between a metallic material and its environment that results in changes in the properties of the metal, and that may lead to significant impairment of the function of the metal, the environment or the technical system, of which these form a part. This interaction is often of an electrochemical nature."
The causes of corrosion are numerous. Multiple factors are normally involved: chemical, mechanical and thermal influences may overlap and mutually reinforce each other. Corrosion is generally the cumulative or exponentiated effect of influencing variables which in isolation are often not critical.
What implications does this have for the selection of suitable materials for use in aggressive environments, such as those in thermal sewage sludge recycling plants?
To resist corrosion, construction elements must be geared to the application in question, i.e. a specific combination of influencing variables and stresses. These are by no means static and may vary widely during operation, as is the case in the multi-stage treatment of flue gases produced during sewage sludge incineration.

Two basic types of material system can be considered suitable for applications in aggressive environments. The first of these is solid high-grade materials that require no additional coating for protection against chemicals. Examples of such materials are high-grade nickel-based alloys, and plastics such as polyphenylene sulfide (PPS), a thermoplastic. The second material system comprises lower-grade materials. These require protection against chemical stresses, which takes the form of a high-grade coating. Thermosetting materials such as vinyl ester resins have been widely adopted for such coatings.
High-alloy metals have long been regarded as the material of choice for applications in aggressive environments. In applications involving high chemical and mechanical stresses, thermoplastics such as polyphenylene sulfide (PPS) are however in no way inferior to the usual metals, as has been demonstrated in comprehensive laboratory and field tests. PPS is shown in many applications to be a capable alternative to very high-grade metals and the most resistant thermosets.

2. Use of plastic as a corrosion-resistant construction material

The problem of corrosion is not limited to steel structures; plastics can also corrode under chemical stress in the sense of EN ISO 8044. In contrast to metals, however, plastics are often not dissolved by the corrosion. Instead, it causes swelling, discolouration, change in weight, blistering, embrittlement, cracking or a direct chemical reaction. In rare cases, depolymerisation and thus degradation of the plastic may occur.
In order to resist corrosion in aggressive environments, construction elements manufactured from plastic must withstand a specific combination of chemical, mechanical and thermal stresses.

The chemical stress depends largely upon the composition of the flue gas. Depending on the composition of the thermally treated sewage sludge, the flue gas comprises a mixture of different gases (CO, NOx, COx, SOx) and the acids derived from them and other gases present (H_2SO_4, HNO_3, HCl, HF). Particles present also cause continual abrasion of materials.

Parameter	Unit	Limit values (half hour/ daily average)	Mean operating value	Percentage of limit value (daily mean)
Sulphur oxides	mg/m³	200/50	3.8	7.7%
Nitrogen oxides	mg/m³	400/200	161	81%
Carbon monoxide	mg/m³	100/50	6.6	13%
Total carbon	mg/m³	20/10	0.60	6%
Dust	mg/m³	30/10	0.70	7%
Hydrochloric acid	mg/m³	60/10	0.78	7.8%
Ammonia	mg/m³	15/10	0.13	1.3%
Mercury	mg/m³	0.05/0.03	0.0019	6.3%
Dioxins/furans	ng TE/m³	0.1	0.0022	2.2%

Figure 1: Example of flue gas composition in energy recovery from sewage sludge (municipal wastewater utility, Frankfurt am Main) [2]

3. Selection of a thermoplastic material

The challenge is that of selecting a plastic suitable for the design of structural components in flue gas filter systems.
In practice, selection of a suitable material involves several steps. The first step is an expert shortlisting of potentially suitable thermoplastics. This entails selection firstly of the pure plastic, such as polyamide (PA), polybutylene terephthalate (PBT) or polyphenylene sulphide (PPS), and secondly of possible additives, for the application under consideration. High-grade glass fibres in particular have a crucial function where materials are used in load-bearing components.

The material is tested in the laboratory under extreme conditions to narrow down the selection further, or – ideally – to identify a suitable material. This is then tested for its suitability in a long-term test under real-case conditions.
PPS is known to be highly resistant to acids, bases and organic solvents. The following tests and analyses were therefore carried out on it, in pure form and in combination with glass fibres.

	Thermoplastics				Thermosets		Metals	
	PPS	PP	PEEK	PBT	Vinyl ester	Hastelloy	Stainless steel 316	Titanium
Corrosion resistance								
Hydrochloric acid 2%	+	+	+	0	+	+	0	+
Hydrochloric acid 37%	+	+	+	-	+	0	-	+
Sulfuric acid 2%	+	+	+	0	+	+	0	+
Sulfuric acid 70%	+	+	0	-	+	0/+	-	+
Phosphoric acid 10%	+	+	+	-	+	+	0	+
Phosphoric acid 85%	+	+	+	-	+	+	-	+
Hydrofluoric acid 40%	+	+	-	-	+	+	-	-
Cu/Fe/... chlorides (aq.)	+	+	+	0	+	0/-	-	+/0
Hydrogen sulfide (wet)	+	+	+	-	+	0/+	0	+
Sodium hydroxide 20%	+	+	+	0	+	+	+	-
Green death	+	+	+	-	+	0/+	-	0
Temperature resistance								
0–80 °C	+	0	+	+	+	+	+	+
80–120 °C	+	-	+	+	+	+	+	+
120–200 °C	+	-	+	-	-	+	+	+
Mechanical properties								
Relative strength	FFF	F	FFF	FFF	FFF	FFFF	FFFF	FFFF
Price level	€€	€	€€€€	€	€€€€	€€€€	€€	€€€€

3.1. Chemical resistance

The test environment for assessing the chemical resistance is based on the composition of the flue gas. Many of the gases in such environments react in the presence of water to form acids. One example is the sulphurous/sulphuric acid produced by the oxidation of sulphur by means of oxygen and water.
The challenge is less that of determining the acids which arise, but rather of defining a test environment based on the prevailing temperature and the concentrations. This is not, of course, a substitute for a real-case test, but can aid in determining general suitability at an early stage. This saves time and reduces costs.
To reduce the duration of testing to a minimum, the concentration is usually set well above that anticipated under real-case conditions, and the temperature is often increased up to the boiling point. For plastic structural components of a sewage sludge incineration plant, concentrations of 60% – 70% and a temperature of 140 °C – 150 °C were set for the sulphuric acid tests in this actual case.
This test setup is intended to simulate the stress over several years at a lower acid concentration and lower temperature, such as that prevailing in wet flue gas scrubbing with an activated carbon system.

The resistance to hydrochloric acid and to mixtures of sulphuric acid, hydrofluoric acid and nitric acid was tested, as well as to sulphuric acid itself. The materials tested were in particular PPS in unreinforced raw material form, and PPS GF 40 with a 40% glass fibre content, which exhibits much greater mechanical stability.

Flexural strength and change in mass

The concentration and temperature are set in the test environments. The decisive assessment of the material's suitability for the specific application is attained by comparison of the resistance to mechanical stress before and after performance of the test. Testing was performed against EN ISO 178.
As can be seen from the diagram below, the modulus of elasticity of PPS remains almost constant over the six-month ageing period. Five samples per sampling campaign were studied. The slight increase in the results over time is due to progressive crystallization of the material, which increases the flexural strength and is typical of PPS.

Flexural strength of PPS

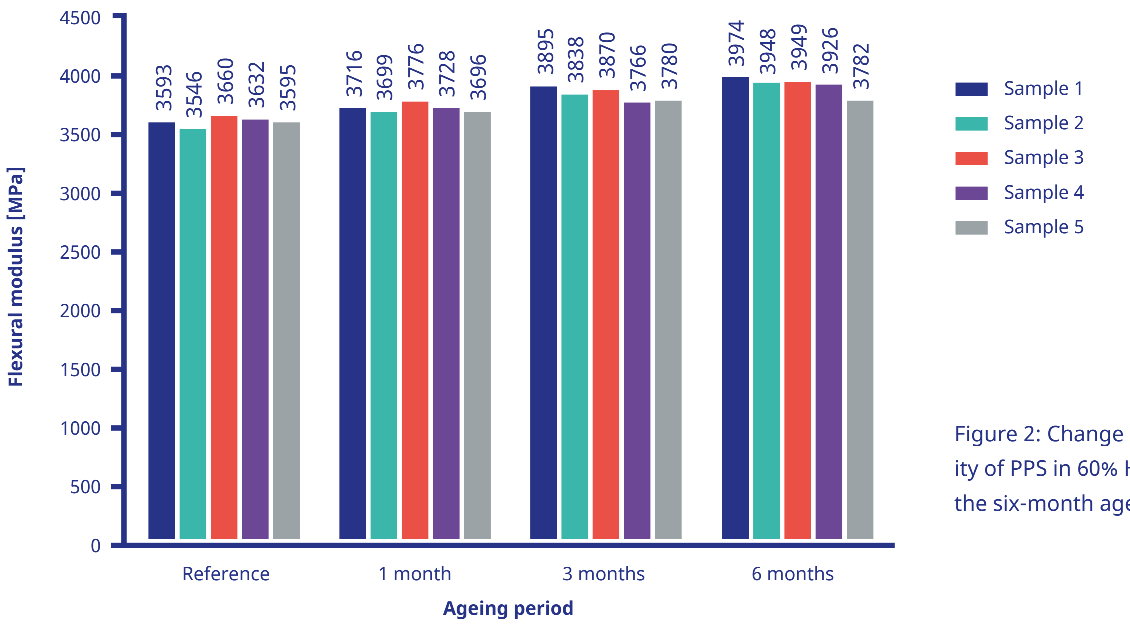


Figure 2: Change in the modulus of elasticity of PPS in 60% H_2SO_4 and at 140 °C over the six-month ageing period

The change in mass over a six-month ageing period was also observed. Here too, the average over five measurement samples reveals no significant increase.

Change in mass over the ageing period

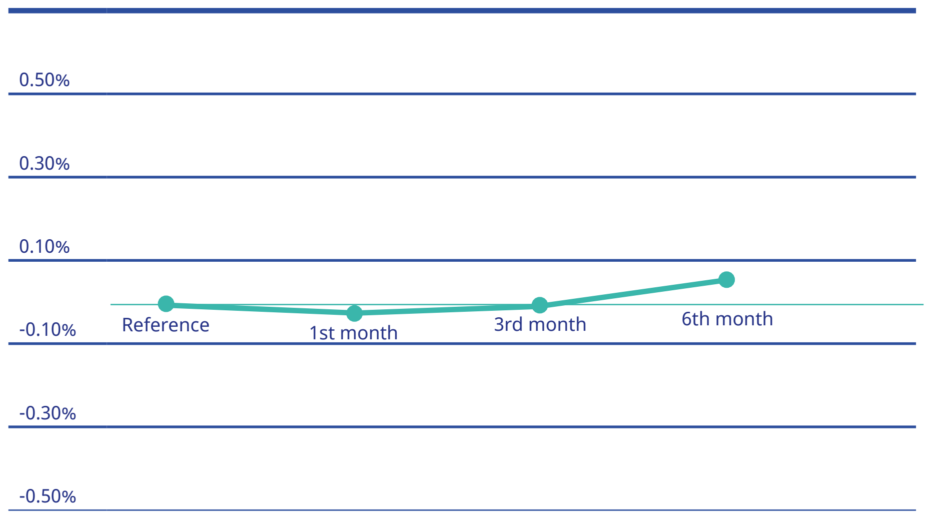


Figure 3: Change in mass of PPS in 60% H_2SO_4 at 140 °C over the six-month ageing period

In order to clarify the influence of the glass fibres on the modulus of elasticity and to test the durability of this reinforced material type, an additional short-term test of the GF 40 variant of PPS with 40% glass fibres was carried out at a sulphuric acid solution concentration of 70% and a temperature of 150 °C. Here too, no significant change in the flexural modulus was observed after two weeks' exposure to the acid solution. The mass increased by only 1%.

Flexural strength of PPS GF 40

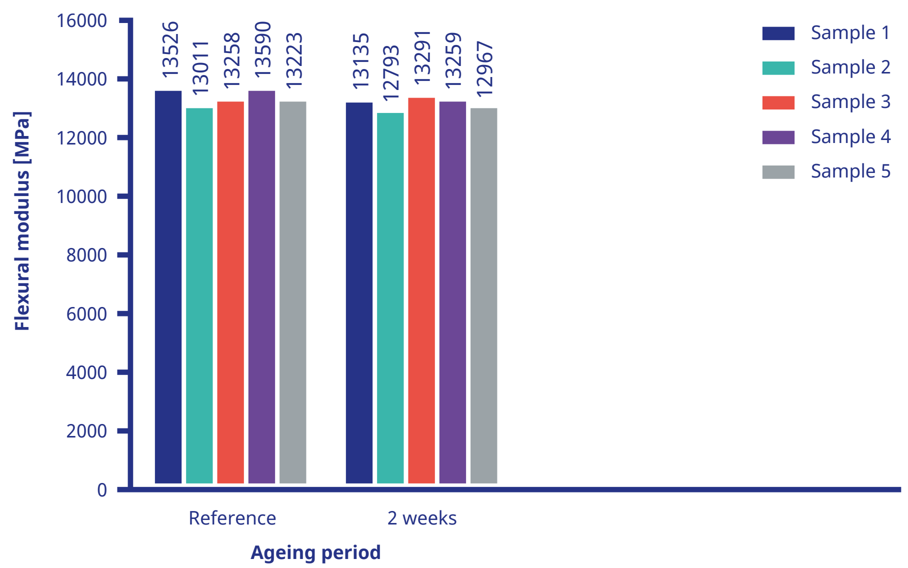


Figure 4: Change in the modulus of elasticity of PPS GF 40 in 70% H_2SO_4 and at 150 °C over the two-week ageing period

Besides the sulphuric acid tests described, ageing tests of the materials were carried out in hydrochloric acid and in a mixture of different acids. The concentration of hydrochloric acid solution was 36% and the temperature was set at 100 °C. The pure PPS exhibited an average decrease in flexural strength of approximately 5% following the test. The increase in mass was only 0.21%.

Flexural strength of PPS

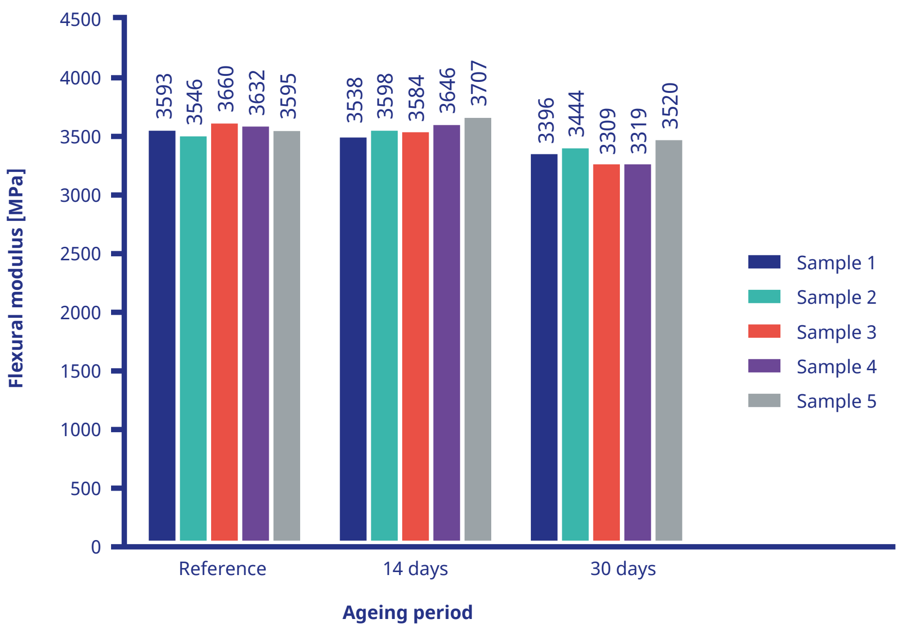


Figure 5: Change in modulus of elasticity of PPS in 36% HCl at 100 °C over a 30-day ageing period

Change in mass over the ageing period

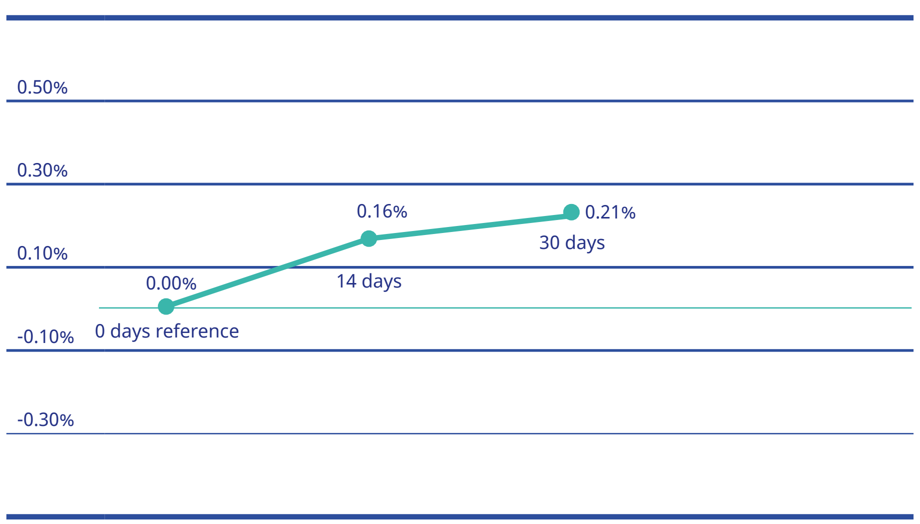


Figure 6: Change in mass of PPS in 36% HCl at 100 °C over the 30-day ageing period

Different individual gases are present simultaneously in a flue gas tract (see Figure 1). However, the tests described above were carried out with only one acid. They show the substance's influence on the material well, but do not reflect the conditions actually prevailing in terms of the gases' composition. Owing to synergy effects, mixtures of different acids in particular often exhibit a more aggressive effect on materials than their purely cumulative composition would suggest. For example, sulfuric acid and nitric acid act together as a nitrating reagent and attack some plastics. To investigate the influence of these mixtures, test environments comprising 15% H_2SO_4, 0.3% HNO_3, 0% HF and 15% H_2SO_4, 0.3% HNO_3, 0.5% HF at 65 °C were defined, and tests lasting 45 days were performed. PPS GF 40, PPS and abraded PPS GF 40 were the materials tested.

DMA test results following ageing in a mixed acid at 65 °C (0% HF)

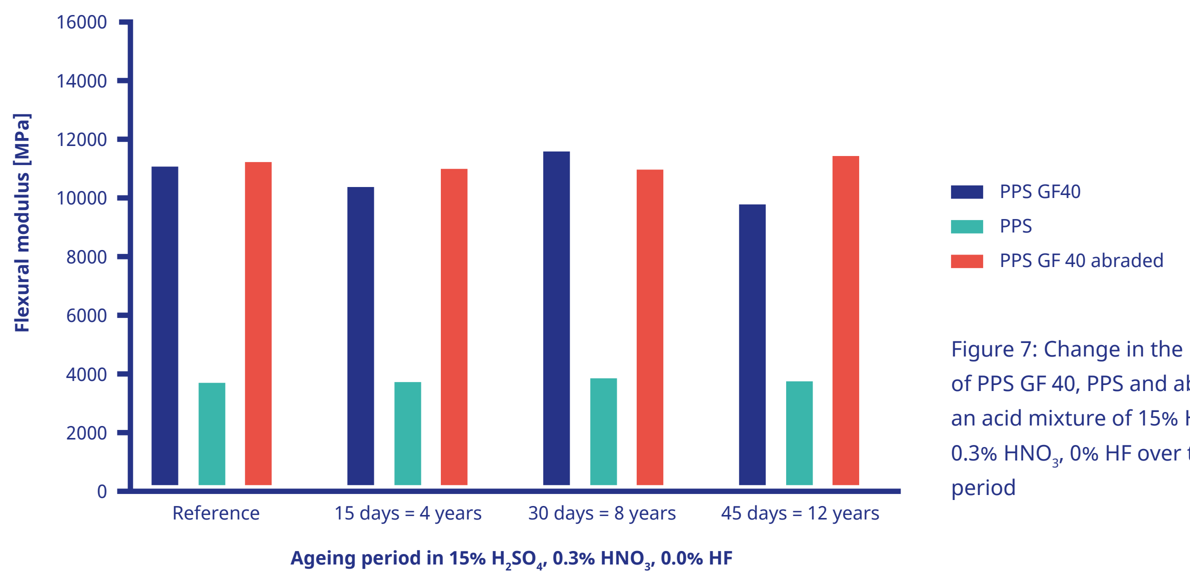


Figure 7: Change in the modulus of elasticity of PPS GF 40, PPS and abraded PPS GF 40 in an acid mixture of 15% H_2SO_4, 0.3% HNO_3, 0% HF over the 45-day ageing period

DMA test results following ageing in a mixed acid at 65 °C (0.5% HF)

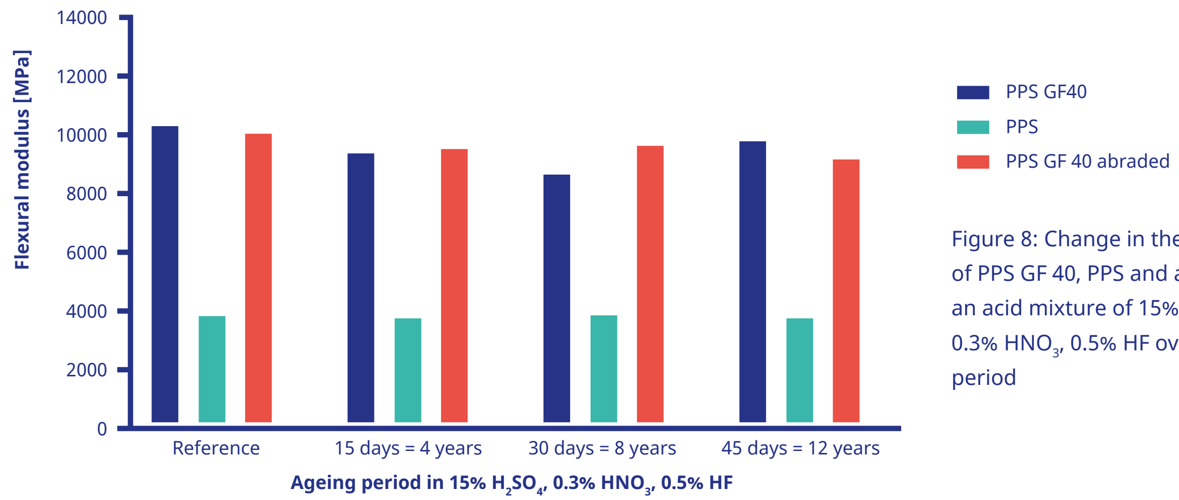


Figure 8: Change in the modulus of elasticity of PPS GF 40, PPS and abraded PPS GF 40 in an acid mixture of 15% H_2SO_4, 0.3% HNO_3, 0.5% HF over the 45-day ageing period

The two diagrams above show the flexural modulus after 45 days of ageing, determined by dynamic mechanical analysis (DMA). All materials exhibit practically no decrease in their mechanical stress resistance. By increasing the concentration by a factor of 100 over that of a field test, the objective was to simulate stress in the flue gas over a period of approximately 10 years. The fluctuations between the measured values can be attributed to variations in the material composition of the samples.

3.2 Further mechanical requirements to be met by the material

Besides chemical stresses capable of causing corrosion of the material used, mechanical stresses resulting from deformation and external influences are of particular relevance to selection of a suitable plastic. Structural components manufactured from plastic must not only be chemically resistant and thus resistant to corrosion, but also meet specific requirements for dimensional stability, strength and temperature resistance. Thermoplastics suitable for a specific application can be selected by comparison of common thermoplastics in the literature.

3.2.1. Creep behaviour

Creep refers to the plastic deformation of materials under stress (tension) as a function of time and temperature. A parameter of creep is the creep modulus. Since thermoplastics consist of large entangled molecular chains, they slide and disentangle under exposure to external stress, resulting in elongation. This deformation must be taken into account in the design of plastic components. Polyphenylene sulfide (PPS) is characterized by a very high creep modulus compared to other plastics.

Plastic	cc	Plastic	cc
PE-HD	0.45	PPA	0.88
PE-LD	0.60	PPS	0.93
PE-UHMW	0.50	PPSU	0.85
PP	0.50	PSU	0.90
PA6	0.73	LCP	0.80
PA66	0.75	ABS	0.68
PA666	0.75	ASA	0.68
PA612	0.70	PMMA	0.80
PA6/6T	0.85	PS	0.80
PA6/6I	0.90	SAN	0.80
PA11	0.58	SB	0.70
PA12	0.70	TPA	0.70
PA46	0.70	TPC	0.75
PBT	0.75	TPU	0.83
PET	0.75	(ASA+PC)	0.80
POM homopolymer	0.60	(PBT+ASA)	0.87
POM copolymer	0.65	(PBT+PET)	0.85
PC	0.88	(PC+ABS)	0.72
PESU	0.80	(POM+PUR)	0.70

Figure 9: Comparison of creep behaviour of plastics [1]

3.2.2. Tensile strength

Depending on the function and design of structural components manufactured from plastic, for example for use in a flue gas filter, the tensile strength of the material – including at high temperatures – is of key importance for the performance and service life of the components. In this context, a high-performance plastic such as PPS performs significantly better than an engineering plastic such as polyamide PA66, even when the latter is glass-fibre-reinforced.

Comparison of PPS high-performance plastic and PA engineering plastic

Plastic	PPS GF 40	PA66 GF 40
Modulus of elasticity, standard test specimen [GPa]	14.7	8.5
Tensile strength, standard test specimen [MPa]	195	145
Continuous operating temperature [°C]	-200 to 240	-40 to 150
Short-term operating temperature [°C]	260	240

Figure 10: Strength of PPS GF 40 compared to PA66 GF 40 [4]

3.3. Conclusion from laboratory tests and the literature

Polyphenylene sulfide (PPS), a high-performance thermoplastic, has proved its chemical resistance in tests involving a range of acids and concentrations corresponding to typical stresses occurring over several years in flue gas treatment in sewage sludge incineration plants. PPS is also resistant to mixed acids, which are particularly aggressive owing to their high oxidation potential and multi-stage chemical reactions. Glass fibres in the GF 40 PPS variant improve the mechanical properties without impairing the chemical resistance under the conditions tested. In contrast to coated materials such as high-alloy metals, abrasion of their surfaces does not lead to degradation of the material caused by corrosion.
Based on these convincing results, our next step was to test PPS GF 40 over a period of two years directly in the operation of a sewage sludge incineration plant.

4. Field tests in a sewage sludge incineration plant

With the support of a sludge dewatering and incineration plant operator, long-term testing was performed of several materials and material combinations that are particularly suitable for aggressive environments and offer high chemical, thermal and mechanical resistance. These materials were PPS GF 40, PESU GF 30, PPS Graphite and PK GF 30.
Three different test environments were selected for the practical test: one in the lower area of the plant (area of acid condensate accumulation), one in the upper area (gas inlet area, subject to temperature fluctuations) and one in the middle area (varying conditions). Test specimens of different materials were placed in these locations and abraded selectively for test purposes.
After six months of operation, the first check was performed to determine whether any changes in the material could be detected. The total test duration exceeded two years, reflecting the regular inspection interval for the plant.

4.1. Chemical resistance

The long-term test in the flue gas of the sewage sludge incineration plant demonstrates that PPS GF 40 retains its chemical resistance almost entirely. This is demonstrated both by tests of several samples in the raw gas over six months, and by the test in the activated carbon bed over two years: the deformation under stress after two years in the flue gas hardly differs at all from that of untreated PPS GF 40 not exposed to the flue gas at the beginning of the test.

Flexural strength of PPS GF 40 after ageing in raw gas

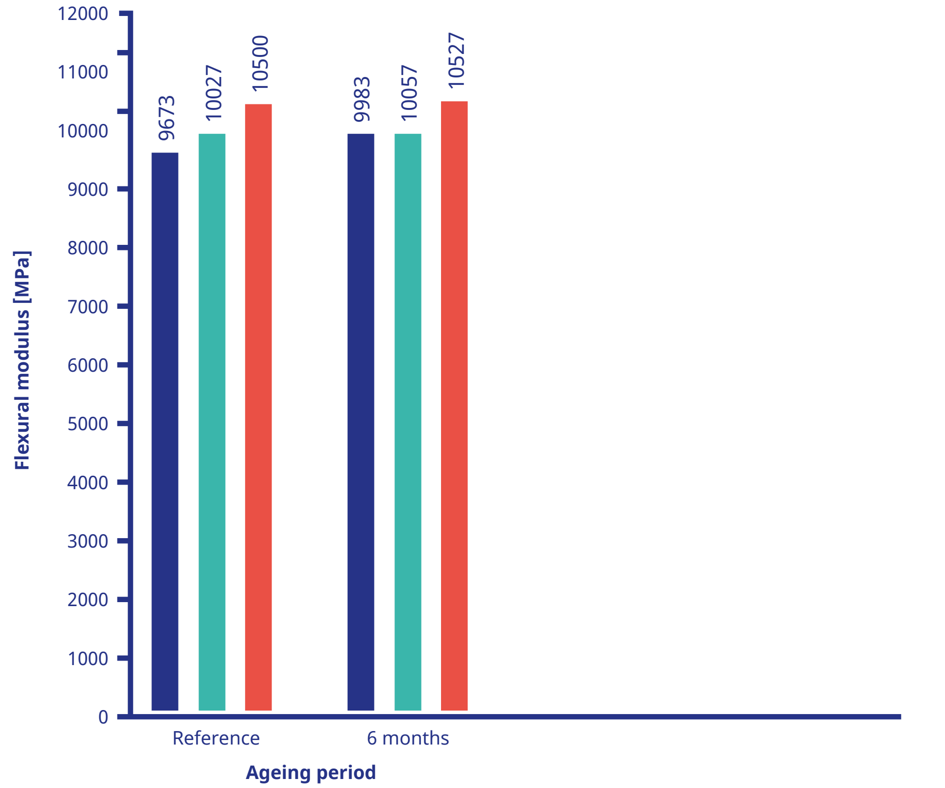


Figure 11: Change in the modulus of elasticity of three PPS GF 40 samples in raw gas over a six-month ageing period

2-year long-term test in flue gas

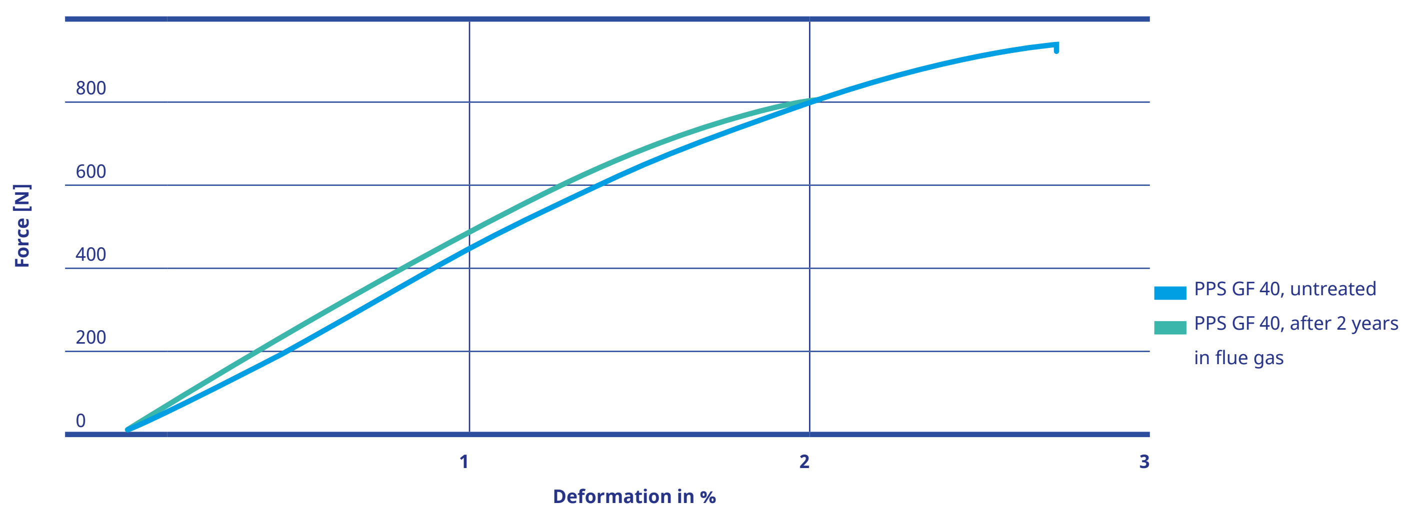


Figure 12: Deformation of PPS GF 40, untreated vs. under stress after two years in a filter plant with sulphur-doped activated carbon

4.2. Surface properties

Besides the deformation behaviour under exposure to chemical and mechanical stress, the stability of the surface properties of PPS GF 40 was also tested. Microscopic close-ups in a thin section of the peripheral layer reveal no significant differences between the reference material at the beginning of the test and the material after six months' ageing in the raw gas of the flue gas treatment plant.

Close-up of the peripheral layer, reference (left) and after six months' ageing in the raw gas (right)

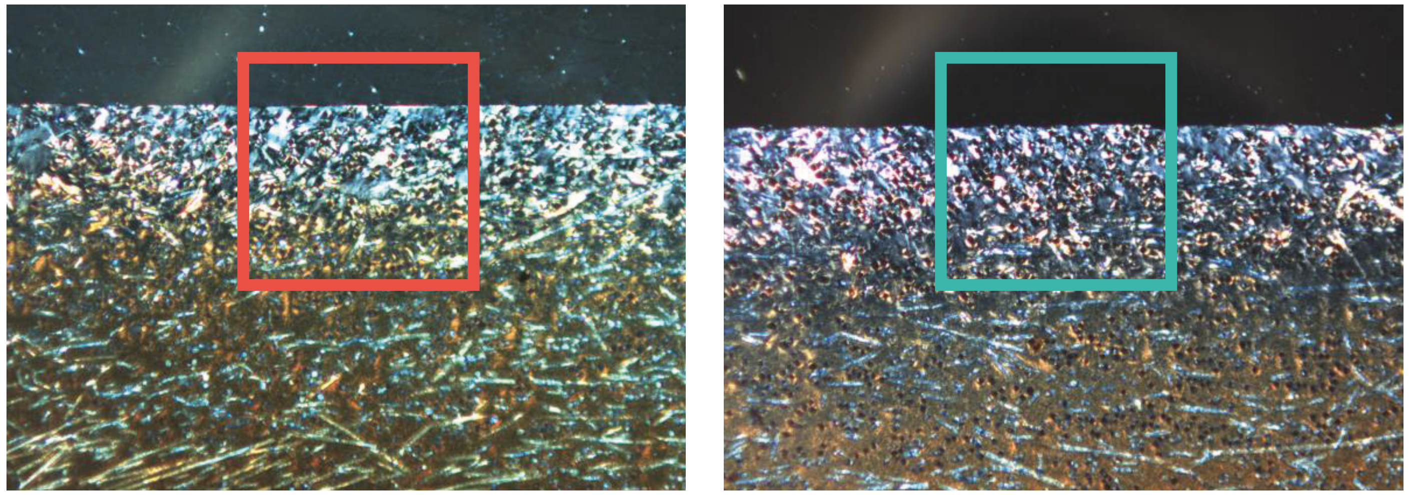


Figure 13: Thin section with view of periphery. Left: reference; right: after 6 months

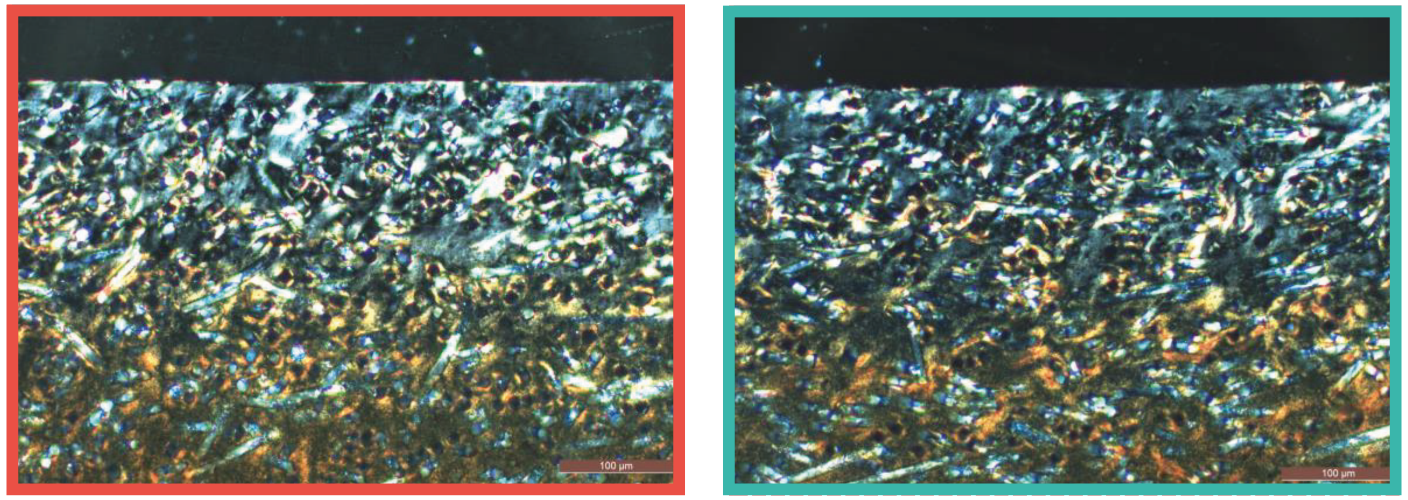


Figure 14: Close-up from Figure 13, no significant differences

4.3. Chemical properties

Examination by means of differential scanning calorimetry (DSC) revealed no degradation of the polymer caused by chemical attack. Broadening of the melting peak or a shift to lower temperatures would be characteristic here owing to a shorter chain length.

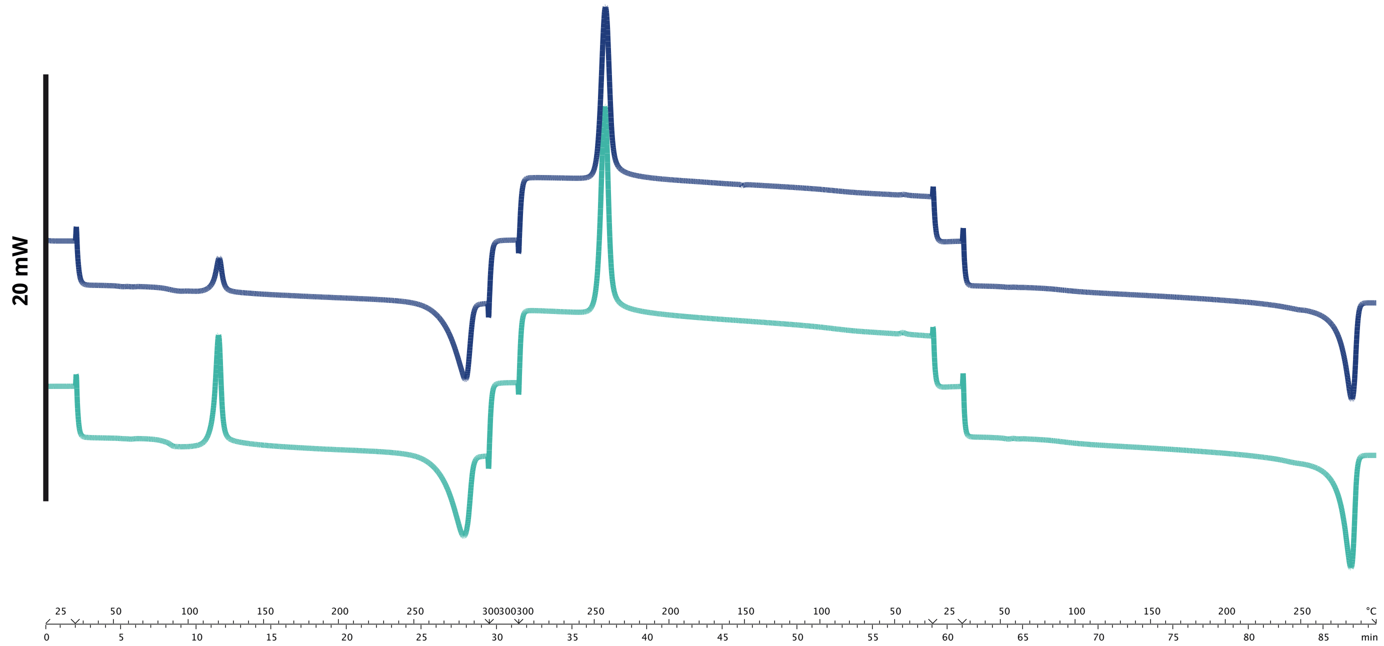


Figure 15: DSC examinations on the component

DSC PPSGF40 SEF sample, 6 months

DSC PPSGF40 SEF, reference

4.4. Conclusion from the field test

Of the four materials tested, two were not able to satisfy the mechanical requirements in the long-term test: PPS graphite proved to be too brittle, and PK GF 30 exhibited deformation. These two materials were consequently excluded from subsequent testing of the chemical resistance.
Two glass-fibre-reinforced materials were shortlisted: PPS GF 40 with a glass fibre content of 40%, and PESU GF 30 with a glass fibre content of 30% (not shown here). These materials were notable for both their high mechanical and high chemical and thermal resistance.
In practice, it is the cost-effectiveness of the material used, particularly the price of the material and its suitability for efficient manufacturing, that is ultimately decisive. PPS GF 40 proves to be the material of choice in this case.

5. From field test to plastic solution

In laboratory tests and field tests conducted in the flue gas treatment systems of sewage sludge incineration plants, we were able to demonstrate that PPS GF 40 is very well suited as a material for structural components in extreme environments. This makes this thermoplastic a high-performance alternative to thermosets and alloyed metals in many applications. To demonstrate this material's resistance to stress, mechanical tests were carried out on the finished profiles. One purpose of the tests is to model the stress arising during installation or caused by stacking in the application. Transport involving torsion and impact was also simulated. A small sample of these tests is shown below.

5.1. Example of a mercury filter, W. L. Gore & Associates

The GORE® Mercury Control System (GMCS) [5] is a fixed sorbent system for capturing elemental and oxidized gas phase mercury from industrial flue gases. The system is based on stackable modules that are installed within the flue gas cleaning system as required.
For structural engineering reasons and owing to the aggressive ambient conditions, the frame of the modules, composed of profiles and corner couplings, was for a long time manufactured from a nickel-molybdenum alloy. A development project conducted by W. L. Gore & Associates and Technoform enables load-bearing profiles and fasteners manufactured from PPS GF 40 to be used in the future.

Figure 16: Frame structure of the GORE® Mercury Control System manufactured from thermoplastic material

5.2. PPS profiles

For production of the frame system, the load-bearing and supporting corner profiles were extruded from PPS GF 40 in the form of an L-shaped hollow chamber profile. The fasteners at the ends of the profiles were injection-moulded from the same material.

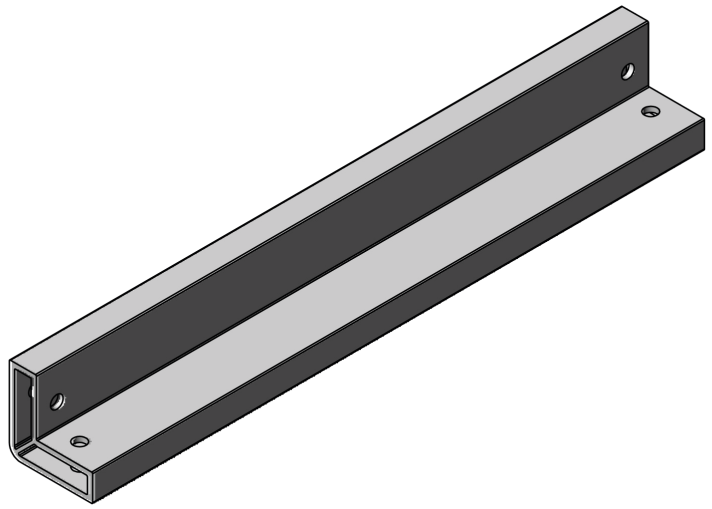
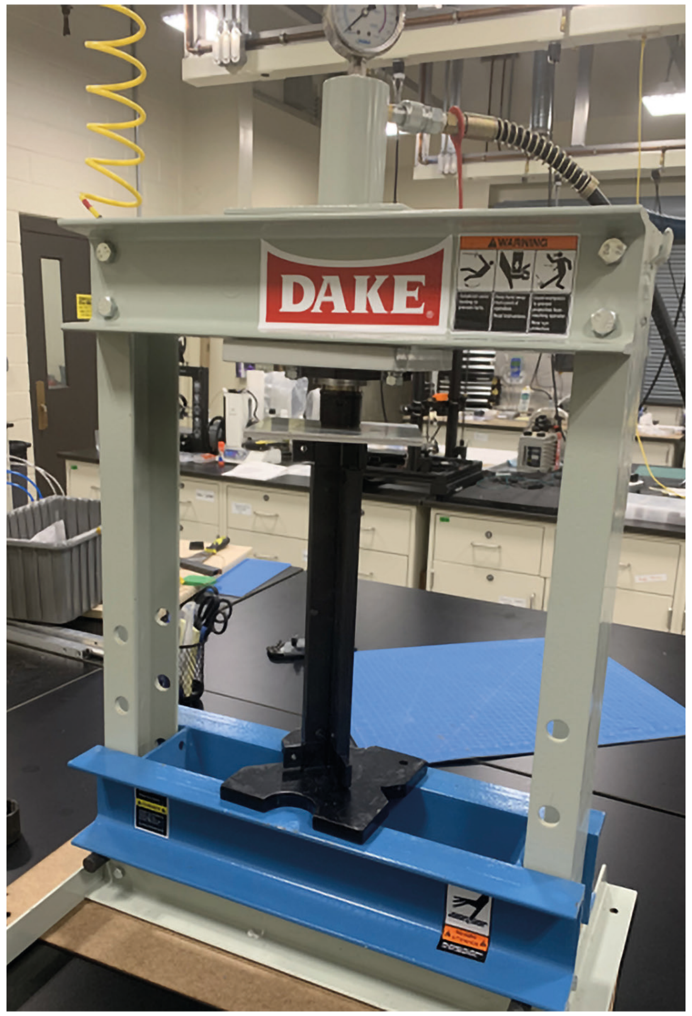


Figure 17: Corner profiles manufactured from PPS. Length: 294 mm; wall thickness: 2.5 mm



It was demonstrated in a hydraulic press that the profiles with a wall thickness of only 2.5 mm including corner coupling are capable of withstanding a load of up to 2.5 tons. The frame structure is thus safely able to withstand the mechanical loads, even when several filter modules are stacked and additional man loads applied during installation and maintenance.

Figure 18: Corner profile in the load test
(Source: W.L. GORE ASSOCIATES)

The filter modules are stacked during installation in the plant. Different loads act on each individual module depending on the number of modules. These loads were tested in a further test arrangement. A 320 kg load acting centrally on the frame structure (profiles and rivets) corresponds to four times the man load potentially acting on a module during installation.

Figure 19: Corner profile in the load test
(Source: W.L. GORE ASSOCIATES)

5.3. Fasteners

Several forms of coupling between supporting corner profiles and load-bearing profiles may be considered. One of these is a positive coupling in which friction welding (EN ISO 4063: process 42) or ultrasonic riveting is used to join the profiles. Mechanical connections and adhesive bonding are further options.
For the GORE® Mercury Control System constructed from thermoplastic materials, a riveting process employing positive coupling was chosen in which injection-moulded pins are heated and pressed into place. This process has the advantage of exerting very low stress upon the glass fibres in the plastic and permitting fast and reproducible implementation. A further advantage is that the same material is used for all construction elements, thereby obviating the need for further material tests.

Riveting can also be carried out quickly and reproducibly even on complex profile geometries with poorly accessible corners. The frame of the GORE® Mercury Control System is designed such that no shear forces act on the plastic pins under normal load. Rivet tests have nevertheless been carried out to determine the load capacity of heated and non-heated rivets. The unchanged load capacity of the pins before and after riveting shows that the forming process causes no damage to the material or the fibres. In quantitative terms, the load capacity is approximately three times (with safety factor) the target value.

Rivet shear test with non-riveted and riveted pins manufactured from PPS GF 40

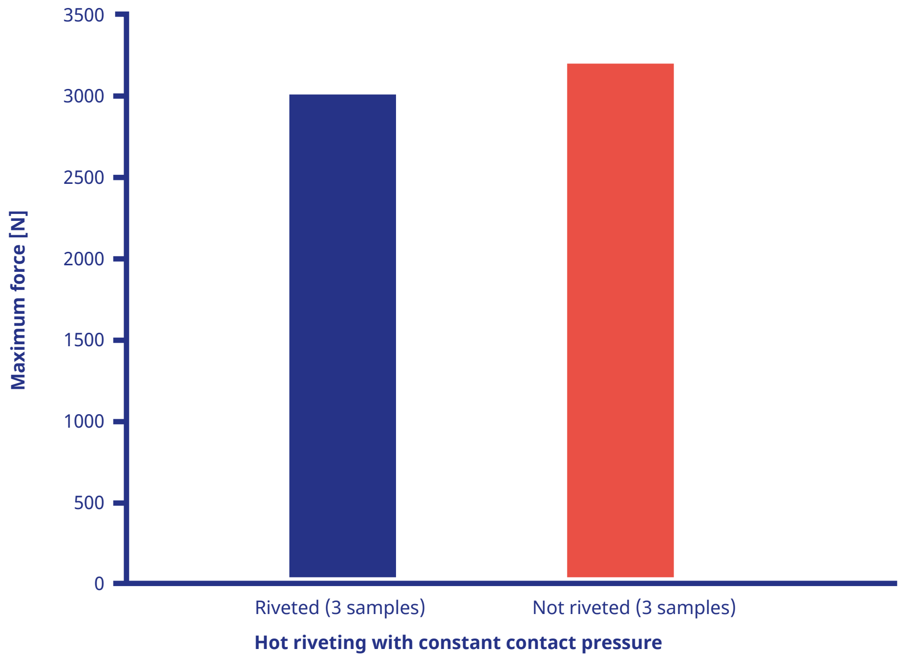


Figure 20: Rivet shear test with non-riveted and riveted pins manufactured from PPS GF 40

6. Summary

Corrosion protection is a key challenge for engineers and operators of flue gas cleaning plants in thermal sewage sludge treatment. Structural components manufactured from chemically resistant solid plastic can improve corrosion protection in many applications, and serve as a substitute for common composite materials such as thermosets and high-alloy metals. In laboratory and field tests, we were able to demonstrate the chemical and mechanical resistance, particularly of PPS with a 40% glass fibre content (GF 40), both for load-bearing and supporting profiles and for fasteners such as plastic rivets. As a result, PPS GF 40 is already being used successfully in flue gas treatment and will gain in importance in this area.

7. References

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- Automotive
- Aviation
- Chemicals
- Building industry
- Electrical engineering
- Insulating glass
- Lighting
- Mechanical engineering
- Oil and gas industry
- Power generation
- Railway vehicles
- Seawater desalination
- Shipping
- Airhandling units
- Windows, doors, facades

8. Technoform – tailored engineering plastics solutions

Technoform offers a wide range of custom solutions and standard plastic applications – worldwide and for a variety of industries.
For applications in aggressive environments such as those found in industrial flue gas treatment, we rely primarily on PPS as a material. PPS is characterised by its very high chemical resistance in combination with outstanding mechanical properties. We use this material to develop complex construction elements that combine multiple manufacturing processes and joining technologies, and offer them as a complete solution from a single source.

Technoform is a family-owned company with over 45 production and sales sites worldwide. We are a manufacturer of plastic profiles with a global presence and over 1,600 employees.
Our numerous sites mean that we are on hand wherever you need our expertise. At the same time, we can build on a flexible and worldwide network in which we share our knowledge and many years of experience in the processing of engineering and high-performance plastics. This enables us to offer custom solutions.

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