MODERN COATING MATERIALS FOR USE IN THE TECHNOLOGY OF BIOGAS PLANTS

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Abstract

At present, reinforced concrete or steel sheets with glass enamel are used for the construction of bioreactors, fermentation and storage tanks of biogas stations. To a lesser extent, corrosion-resistant steels are used and, in smaller dimensions, also plastics or fiberglass. Against leakage and corrosion due to biomass and biogas, reinforced concrete is mostly protected by bituminous coatings. Steel components are most often protected against corrosion by epoxy resins and cements. On the market there are modern plastic-based coating materials with high chemical and mechanical resistance, which can be applied to biogas stations to certain product dimensions. An initial study on the applicability of low-permeable ETFE ultra+ and PFA ultra+ hydrophobic anti-adhesion coatings of 700-1000 µm for steel components under anaerobic conditions exposed to corrosive effects of biomass and biogas was performed. Laboratory simulated conditions corresponding to the anaerobic bioreactor at 40 °C ± 1 °C included 2 months of incubation of the sample in biomass-based alkaline medium from the 1st fermentation stage of the agricultural biogas plant and then 3 months of incubation in acidic medium based on bio-waste mixture. While a structural steel samples lost a significant portion of their mass in the biomass contact area and also in the biogas contact area, the stainless steel samples exhibited intergranular corrosion under the microscope, and the ETFE and PFA coated samples did not change color or roughness, did not swell and no other change was visible. The tested coatings are found to be suitable for the protection of steel surfaces in contact with fresh acidic biomass entering the bioreactor, in contact with the alkaline slurry or sludge in the bioreactor and in contact with the raw biogas.

Keywords: Biogas plant, biomass, corrosion, coating, ETFE

1. INTRODUCTION

Biogas stations are biomass processing plants, a renewable energy sources producing biogas and a liquid or solid product - digestate. These facilities represent a stable, albeit still minority share in the Czech Republic's energy mix. The biogas production segment, whether it is on agricultural, industrial or municipal biogas stations, or on sewage treatment plants and municipal waste dumps, is slowly developing. Corrosion protection is an important aspect here because both raw biomass - bioreactor (fermentor) anaerobic sludge or digestate, and biogas are highly corrosive media.

Crude biomass of the type of cattle slurry, silage, food biowaste, municipal solid waste etc. is corrosive especially due to the presence of C_1-C_5 organic acids, a wide range of cations and anions, for example chlorides, sulphides, ammoniacal nitrogen. At entry to crushers and homogenization devices, the pH of the biomass is usually 3.0-8.0. For the upcoming hydrolysis and acidification of the prepared biomass mixtures in the pre-fermentors, the pH is most often in the range of 3.5-6.0. In methanisation fermenters at 37-43°C or 52-56°C, the pH is most often maintained within the range of 7.6-8.2. In the liquid digestate reservoirs the value even slightly exceeds the pH limit of 8.6.

Raw biogas as most often a mixture of 60% CH_4 with 37% CO_2 is highly corrosive due to the high moisture content (about 2.3% by volume at 20°C), hydrogen sulphide (<2000 ppm H_2S), ammonia (<1000 ppm NH_3) mercaptans (R-SH) and up to several thousand other minor substances.

At present, reinforced concrete or steel sheets with glass enamel are used for the construction of bioreactors, fermentation and storage tanks of biogas stations. To a lesser extent, corrosion-resistant steels are used and, in smaller dimensions, also plastics or fiberglass. Reinforced concrete is against corrosion due to biomass and biogas most often protected by epoxy or bituminous coatings [1]. Steel components are most often protected against corrosion by epoxy resins and cements. Modern plastic-based coatings with high chemical and mechanical resistance are available on the market and can be applied to biogas stations to certain product dimensions. Due to the high price, very little information is available on the use of ETFE or PFA coatings in the biogas plant sector to ensure steady long-term protection against bio-corrosion induced by SRB-bacteria and the like [2]. ECTFE coatings are applied to some elements such as valves and sliders. PFA coatings are applied primarily in heat exchangers, sampling tubes etc.

In the framework of an anaerobic bioreactor development project, poly (ethene-co-tetrafluoroethene) coatings, ETFE abbreviations, and poly (perfluoroalkoxy alkane), abbreviated as PFA, were obtained. ETFE is a recyclable copolymer with high chemical resistance, excellent strength, toughness and durability over a wide temperature range (-100°C to + 150°C). In particular, its toughness at low temperatures is excellent. It has a very high melting temperature and excellent resistance to chemical, electrical and high-energy radiation. Compared with glass, ETFE has only 1% of its weight, it delivers more light (up to 95%), and even the health-promoting component A of ultraviolet radiation. It is used, for example, for the roofing of airport halls. ETFE installation is considerably cheaper than glass, since it does not require a massive load-bearing structure due to its weight. It is also more flexible and more tough than glass, can carry up to 400 times its weight. ETFE has very good anti-adhesive properties. Thanks to the non-stick surface it has self-cleaning ability. The disadvantage is the ease of cutting the foil. Layers up to 7mm can be created. ETFE is most often injected at temperatures of 300-340°C. It is essential that all parts in contact with the melt are made of anticorrosive materials [3]. PFA (tetrafluoroethene - perfluoroalkyl vinyl ether) is a copolymer with high stability of parameters and resistance to aggressive chemicals in the temperature range (-200°C to +260°C). It is a copolymer of tetrafluoroethene (C_2F_4) and perfluoroethers ($C_2F_3OR^f$, where R^f is a per fluorinated group such as trifluoromethyl (CF_3). The properties are similar to polytetrafluorethene (PTFE) but the alkoxy group allows processing in the melt at 170-430°C. Again there must be all aids from corrosion resistant materials. Due to excellent bending strength and excellent anti-adhesive properties, it is used for the production of non-combustible pipes, heat exchangers, gas purifiers, etc. [4]. PFA is UV stable and weldable [5]. Manufacturer of coatings RUDOLF GUTBROD GMBH (Dettingen/Erms, Germany) provided ETFE ultra$^+$ [6] and PFA ultra$^+$ [7] test specimens. These coatings can be applied to metal components only under controlled conditions directly at the manufacturer. The maximum dimensions of the components are: 7x5x5 m or 9x2.5x2.5 m to the maximum weight of 7 tons.

2. METHODOLOGY

2.1. Samples

For the testing of corrosion resistance against biomass and biogas, simple incubation methods were used, see below. At first, samples of structural steel of the 11 343 (S235JRG1; Gr.36) type, marked „K“, stainless steel 17249 (X2CrNi10; AISI 304 L) type, marked „N“, structural steel with ETFE ultra$^+$ coating, marked „E“ and structural steel with PFA ultra$^+$ coating, marked „P“ were prepared. K and N samples were ring (50/30/3 mm in size) and E and P samples were rings (70/46/12 mm in size). Always three samples of the same type were tested. Subsequently, ETFE ultra$^+$ and PFA ultra$^+$ flat samples were obtained from the coating manufacturer. The samples were 150x100x7 mm in size and in one corner they were equipped with a Ø 11 mm hole with a R3 radius to increase the tension of the coating and to verify its long-term adhesion on the edge.

2.2. Coating thickness measurement

First, the initial thickness of the coating (see below) was measured for ring samples E and P. After incubation in corrosive biomass and biogas, the measurement was repeated. Elcometer 456 Coating Thickness Gauge, 1600 µm range (± 1% accuracy, calibrated to 1000 µm) was used for the measurement. Each of the ring and flat coated samples was marked with the front and the top. Each sample was measured at several points (front side, back side, inside, outside). Each point was measured 4 times and the average value is shown. No base coat was applied to any sample.

2.3. Weight measurement

The initial mass of all ring samples was measured by analytical weights. The initial mass of the flat samples was measured by conventional laboratory weights. After incubation in corrosive biomass and biogas, the measurement was repeated. Weight changes were expressed as a percentage (see **Table 2**).

2.4. Incubation in biomass and biogas

Ring samples were subjected to two consecutive incubations. For the first incubation, three different media representing the environment of the anaerobic biogas plant fermenter were selected: 1 - neutral cattle slurry from the dairy farm ZEMSPOL Studénka a.s., Pustějov, Moravian-Silesian Region; 2 - slightly alkaline reacting biomass from the 1st fermentor of the agricultural biogas station Pustějov; 3 - a slightly acidic mixture containing 90% of the Pustějov biomass, 7% of the food residues from the VŠB - Technical university of Ostrava canteen and 3% of the bio-waste from the production of lanolin. Food residues were chosen as a quick source of C_1-C_5 organic acids. Lanolin was chosen as a fast H_2S source. Each of the K, N, E and P ring samples was suspended in its own glass bottle and from one half was immersed into 2.0 kg of biomass suspension. The other half of the sample was exposed to biogas, see **Figure 1**. The bottles were closed with a nitrile glove and placed in a MEMMETR IF450 incubator at 40 ° C ± 0.5 ° C, see **Figure 2**.

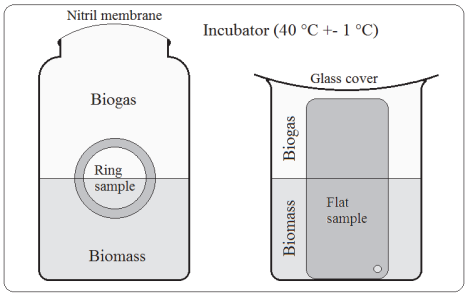

Figure 1 Sample incubation scheme

Figure 2 Ring samples incubation in the 1st and 2nd corrosive media

After 1 month and 2 months, the samples were removed from the biomass, washed, dried, and the changes in weight, coating thickness and biomass pH-value were measured. Subsequently, the circular samples were uniformly subjected to the 2nd incubation in the corrosive medium. For the 2nd incubation, three different media representing a very acidic biomass mixture were selected: 1 - Acidic food residues; 2 - A mixture of 88% food residue and 12% of sugar sorghum; 3 - A mixture of 88% food residue and 12% of milled dry pastry. Such acid biomasses are common in homogenization reservoirs, acidification fermenters, some mixing devices, pumps, etc. The amount of biomass was once again 2.0 kg, the immersion again was ½ and the temperature was again set to 40 ° C ± 0.5 ° C. After 3 months, the samples were removed, cleaned, and the weight and thickness of the coating were measured. The surface of the circular samples was examined under a microscope at 100x magnification.

Flat samples were incubated for 3 months at 40 ° C in strongly acidified biomass (mixture of media 2 after incubation of ring samples), see **Figure 3**.

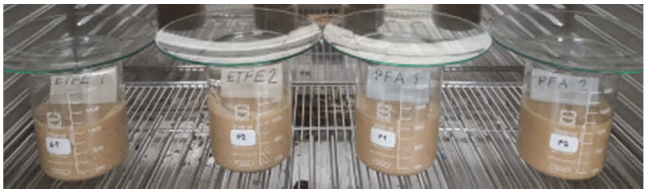

Figure 3 Flat samples incubation

Figure 4 Ring samples after all tests

3. EXPERIMENTAL

The pH values of media for the incubation of ring and flat samples are shown in **Table 1**. Changes in sample weight are given in **Table 2**. The thicknesses of the E and P coatings are given in **Table 3**. Ring samples after all tests are shown in **Figure 4**.

4. RESULTS AND DISCUSSION

4.1. pH value change

For ring samples in the case of the 1st set of media, the pH of the originally neutral or slightly acidic or alkaline biomass, due to the ongoing anaerobic digestion process, gradually increased to a value corresponding to the $NH4^+$ - NH_3 equilibrium. In the case of the 2nd set of media, the pH of the originally strongly acidic biomass slightly decreased by the continuing activity of acidifying and acetogenic microorganisms. When the flat samples were incubated, the pH of the acid medium was stable.

Table 1 Incubation of ring and flat samples in corrosive biomass - pH value change

Base material / Coating	Ring sample	pH value [-], 40°C ± 1°C						
		1st set of corrosive media	Initial	After 1 month	After 2 months	2nd set of corrosive media	Initial	After 3 months
Structural steel / None	1K	Neutral cattle slurry	7.06	8.17	8.48	Acidic food leftovers	4,58	3.88
	2K	Slightly alkaline biom.	7.71	8.46	9.06	Acidic food, sorghum	4.35	3.90
	3K	Slightly acidic biomass	5.09	8.45	9.04	Acidic food, pastry	4.62	3.95
Stainless steel / None	1N	Neutral cattle slurry	7.06	7.93	8.41	Acidic food leftovers	4.58	3.76
	2N	Slightly alkaline biom.	7.71	8.50	8.56	Acidic food, sorghum	4.35	3.97
	3N	Slightly acidic biomass	5.09	8.44	8.62	Acidic food, pastry	4.62	3.87
Structural steel / ETFE	1E	Neutral cattle slurry	7.06	7.90	8.12	Acidic food leftovers	4.58	3.72
	2E	Slightly alkaline biom.	7.71	8.13	8.70	Acidic food, sorghum	4.35	3.74
	3E	Slightly acidic biomass	5.09	8.45	8.69	Acidic food, pastry	4.62	3.86
Structural steel / PFA	1P	Neutral cattle slurry	7.06	7.88	7.90	Acidic food leftovers	4.58	3.81
	2P	Slightly alkaline biom.	7.71	8.43	8.86	Acidic food, sorghum	4.35	3.73
	3P	Slightly acidic biomass	5.09	8.46	8.47	Acidic food, pastry	4.62	3.82
	Flat sample	Corrosive medium						
Structural s. / ETFE	ETFE1	Mixture of strongly acidified biomass from the end of the ring samples incubation					3.77	3.95
	ETFE2							3.97
Structural s. / PFA	PFA1							3.94
	PFA2							3.99

4.2. Weight change

In the case of the 1st set of media, the decrease in mass of the structural steel samples after two months of incubation was approximately three times the decrease in the stainless steel samples. Initially, the slightly acidic biomass was the most corrosive. For samples with E and P coatings, a slight increase in weight was recorded. The reason is obviously the deposition of the pores of the coatings with biomass particles and imperfect drying before weighing, or even a very slight swelling of the coating. In the case of the 2nd set of media, most masses (on average 10.7%) lost structural steel samples. The weight loss of stainless steel was one order lower. The composition of very acidic medium did not play a bigger role. For E-coated samples, weight loss averaged 1%. Explanation is not clear, dissolution of the coating appears to be unlikely. For samples with P coatings the weight increased on average by 0.75%, which was probably due to pollution or slight swelling. During the incubation of flat samples in very acidic biomass the sample weight did not change.

Table 2 Incubation of ring and flat samples in corrosive biomass - weight change

Base material / Coating	Ring sample	1st set of corrosive media	Initial (g)	After 2 months (g)	Weight change (%)	2nd set of corrosive media	Initial (g)	After 3 months (g)	Weight change (%)
Structural steel / None	1K	See Table 2	30.8842	30.6241	-0.84	See Table 2	30.6241	27.2862	-10.90
	2K		30.4705	30.1914	-0.92		30.1914	27.4511	-9.08
	3K		30.6045	30.3138	-0.95		30.3138	26.6687	-12.02
Stainless steel / None	1N		28.9905	28.9006	-0.31		28.9006	28.4381	-1.60
	2N		28.8135	28.7199	-0.32		28.7199	28.5148	-0.71
	3N		28.8843	28.7874	-0.34		28.7874	28.4932	-1.02
Structural steel / ETFE	1E		123.7264	123.7595	0.03		123.7447	121.9829	-1.42
	2E		123.5606	123.8110	0.20		123.8110	121.8456	-1.59
	3E		117.9614	118.2148	0.21		118.2148	117.9736	-0.20
Structural steel / PFA	1P		121.8324	122.0497	0.18		122.0497	123.5716	1.25
	2P		122.9204	123.1738	0.21		123.1738	123.7369	0.46
	3P		121.9690	122.2291	0.21		122.2291	122.9363	0.58
	Flat sample								
Structural s. / ETFE	ETFE1	-				See Table 2	629.33	629.36	0
	ETFE2						623.21	623.29	0
Structural s. / PFA	PFA1						641.24	641.27	0
	PFA2						635.96	636.02	0

4.3. Coating thickness change

The coating manufacturer mentioned a coating thickness of 800 µm for ETFE and PFA ring samples. Initial measured coating thicknesses were 690 µm (-47, + 63 µm) for ETFE coating and 1129 µm (-164, + 214 µm) for PFA coating.

After incubation of ring samples in the 1st set of media, no significant change in the thickness of E and P coatings was found. After the incubation of the ring samples in the 2nd set of media (strongly acidic biomass), a slight decrease in the thickness of the E coatings was detected. This corresponds to a slight weight loss. Either the ETFE coating has actually been etched, or it is the inaccuracy given by the measurement at different

sample points. For P coatings, a slight increase in thickness was observed, but again the measurement imprecision could have occurred. The coatings thicknesses of the flats samples, which were easier to measure at the same points, did not change after incubation in strongly acidic biomass. Perhaps etching or swelling of ETFE and PFA is unlikely to occur.

Table 3 Incubation of ring samples in corrosive biomass - coating thickness change

Base mat. / Coating	Ring sample	Point position	Coating thickness [µm], 20°C						
			1st set of corrosive media	Initial	After 1 month	After 2 months	2nd set of cor. media	Initial	After 3 months
Structural steel / ETFE	1E	1	See Table 2	1494	1516	1491	See Table 2	1491	1311
		2		1575	>1600	>1600		>1600	1268
		3		>1600	>1600	1581		1581	1460
		4		>1600	>1600	1554		1554	1321
	2E	1		1397	1460	1380		1380	1311
		2		1229	1260	1346		1346	1355
		3		1315	1405	1360		1360	1325
		4		1288	1377	1232		1232	1156
	3E	1		1026	1025	1017		1017	1215
		2		1271	1176	1068		1068	1054
		3		1089	1158	1061		1061	1076
		4		1253	1257	1242		1242	1326
Structural steel / PFA	1P	1		1146	1139	1102		1102	1221
		2		1089	1110	1109		1109	1368
		3		1020	1123	1006		1006	1298
		4		1248	1214	1088		1088	1360
	2P	1		1106	1225	1168		1168	>1600
		2		1124	1273	1240		1240	1524
		3		1059	1213	1127		1127	>1600
		4		1241	1426	1373		1373	>1600
	3P	1		1227	1122	1123		1123	1167
		2		1376	1161	1239		1239	1225
		3		1129	1071	1075		1075	1121
		4		1381	1289	1287		1287	1317

5. CONCLUSION

Corrosion resistance tests of ETFE Ultra+ and PFA ultra+ low-permeability anti-adhesive hydrophobic coatings were performed. The thickness of the coating applied to structural steel was 700-1300 µm. After comparison with structural steel and stainless steel samples, it is possible to say that the coatings resist under anaerobic conditions the corrosive effects of the highly acidic to moderately basic biomass typical of mesophilic biogas plants. The coatings also resist the corrosive effects of crude acidic biogas. The coatings prevent high weight losses of structural steel and intergranular corrosion of stainless steel. The PFA coating is mechanically more

durable. Due to the possibility to apply coatings only at the coating factory, on the surfaces of components of limited dimensions, and due to the high price, real application is only expected for key technology components and small volume fermenters.

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