

Erosive wear of filled vinylester composites in water and acidic media at elevated temperature

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ABSTRACT

Due to their good corrosion properties, fibre reinforced polymer composites are often used instead of metals for example in hydrometallurgical processes. However, the erosion performance of polymer composites is rather poor when compared to metals. This study focused on the effect of mineral fillers on the erosion performance of vinylester composites. The erosion rates were tested both in water and in acidic environments at high temperature. To improve the erosion performance of the filled composites in these environments, to increase the filler particle hardness was an effective method. Within similar filler materials, better adhesion to the matrix improved the erosion performance, regardless if it was achieved by adhesion promoters or better mechanical interlocking. The hardness of the matrix was found to be disadvantageous for filled composites, although for pure vinylesters higher hardness decreased erosion rate. At the high service temperature, softer matrix accommodated more deformations and better absorption of energy of the impacting erosive particles. Consequently, improved adherence of the filler particles into the matrix and slower erosion rate was observed.

Keywords: erosion, vinylester, FRP, glass fibre, mineral fillers

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1. Introduction

At elevated temperatures and corrosive environments, fibre reinforced polymer composites (FRPs) are often used instead of metals. In hydrometallurgical processing, materials are constantly exposed to temperatures up to 95°C and to 5-15% sulphuric acid (H₂SO₄) solutions which makes corrosion resistant vinylester based FRPs a natural choice for structural parts. During service, there are also hard mineral particles with varying chemical composition in the H₂SO₄ solution, exposing the structural materials to erosion. Erosive acidic slurry removes material from the surface changing the mechanical response of the materials [1] which is further enhanced by the ageing of polymer matrix due to elevated temperature and the corrosive medium. Since the erosion resistance of polymers and their composites is in general poor compared to metals, a resin rich corrosion layer is used to protect the load bearing FRP layers from chemical and erosive attack in the hydrometallurgical process tanks [2].

In the literature, there are few studies on the erosive wear of vinylester based FRPs [3-7], and hardly any at elevated temperatures or in a slurry. Typically, the effects of the test material (e.g. filler or fibre type, fraction, orientation, and adhesion to the matrix) and the test parameters (e.g. temperature, particle velocity, impingement angle, and used abrasive material including its size and shape) have been studied

by an air jet erosion tester. In our earlier publications we have reported the slurry erosion performance of unfilled vinylester FRPs to study the effects of test parameters in aqueous [5] and acidic [6] high temperature environments.

Hard mineral particles are typically used as fillers to improve the wear resistance of polymers [8, 9]. Several mineral materials have been used in FRPs to improve the wear resistance of the material, such as Al₂O₃, SiC, SiO₂, TiO₂, ZnO, CaCO₃ and H₃BO₃ particles. Typically, the use of hard particles has led to improved erosion performance [10]. For example, Joshi et al. [11], Mahapatra et al. [12] and Patnaik et al. [13] have studied the effect of Al₂O₃ particles on the erosion performance of different matrices and have found significant improvement in the wear resistance. Moreover, the addition of Al₂O₃ particles has shown to be more effective than the application of SiC particles [12]. Although silica based fillers are the most used low cost fillers in vinyl ester linings [14], studies about their effect on the erosion resistance of vinylester FRPs has not been published. Singh et al. have studied the erosion resistance of TiO₂ and ZnO filled vinylesters and found that especially the TiO₂ led to improved performance, although they found a decreased tensile strength with increasing filler fraction [7].

The goal of this study was to further improve the slurry erosion behaviour of vinylester based FRPs by adding mineral particles into the composite structure. First, the erosive wear rates of pure commercial vinylester resins were measured. Second, the individual effects of SiO₂, SiC, and Al₂O₃ fillers and glass fibres on the erosion behaviour of vinylester resins were studied and finally the performance of filled FRP structures were compared. The erosion rates of the filled FRPs were tested both in aqueous and in acidic environments at a high temperature. The worn samples were characterized with a scanning electron microscope in order to evaluate the wear mechanisms in rather complicated, two- or three-component FRP structures.

2. Experimental details

2.1 Materials

In this study, the erosion performance of vinylester based polymers and their composites were examined. First, neat vinylester resin sheets (Derakane 411-350, Derakane 441-400, and Derakane 470-300 supplied by Ashland) were manufactured in an open mould. Resins were mixed with MEKP initiator and Co-nap6% accelerator. Air bubbles generated during mixing were removed from the resin using a vacuum. Manufactured sample sheets were cured for 24 h at room temperature and then post-cured for 6 hours at 80 °C. According to the manufacturer, these vinylester resins differ in their mechanical and thermal properties (Table 1): grade 470 obtains the highest modulus and heat distortion temperature (HDT) yet is more brittle than the other resins. It should be noticed that the service (test) temperature (95 °C) is close to the HDT of the 411 resin.

Table 1: Properties of the vinylester resins reported by the supplier.

Sample ID	Resin	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at yield (%)	HDT (°C)	T _g (°C)	Ref.
411	Derakane 411-350	86	3.2	5-6	105	120	[15]
441	Derakane 441-400	90	3.4	5-6	120	125	[16]
470	Derakane 470-300	90	3.6	3-4	145	165	[17]

To study the effect of a mineral filler on the erosion performance of the different vinylester resins, a silica filler (see SiO₂-2, Table 2) was mixed with all resin grades. Further, to study the effect of various

mineral fillers on the erosion performance of vinyl ester FRPs, resin 441 was mixed with different fillers (Table 2 and Fig. 1). The nominal volume fraction of all fillers was roughly the same in the matrix. The silica fillers, especially the SiO₂-2, were more difficult to mix with the resin than the other fillers. Therefore, the total filler content in SiO₂-2 samples remained low (17 wt%). The shape of all particles was rather irregular and sharp with an aspect ratio close to unity (Fig. 1). The particle size distribution was relatively large for the SiO₂ fillers (especially for the SiO₂-1) when compared with the other filler materials.

Table 2: The fillers and the filler properties reported by the supplier.

Filler ID	SiO ₂ -1	SiO ₂ -2	SiC-1	SiC-2	Al ₂ O ₃
Trade name	Silbond W 12 MST	Silbond 600 VST	Sika ABR F240	C6 F240	Duralum White Microgrits WH F240
Manufacturer	HPF the Mineral Engineers	HPF the Mineral Engineers	Saint Gobain	Washington Mills	Washington Mills
Surface treatment	Methacrylsilane	Vinylsilane	Chemical treatment, details N.A.	N.A.	N.A.
Particle size [μm]	16	4	45	45	N.A.*
Density [g/cm ³]	2.65	2.65	3.21	3.21	3.95
Wt% in the resin	25	17	30	30	30
Calculated Vol% in the resin	12	8	13	13	10
Mohs hardness [-]	7	7	9-10	9-10	9
Datasheet	[18]	[18]	[19]	[20]	[21]

*Based on SEM micrographs: approximately 45 μm

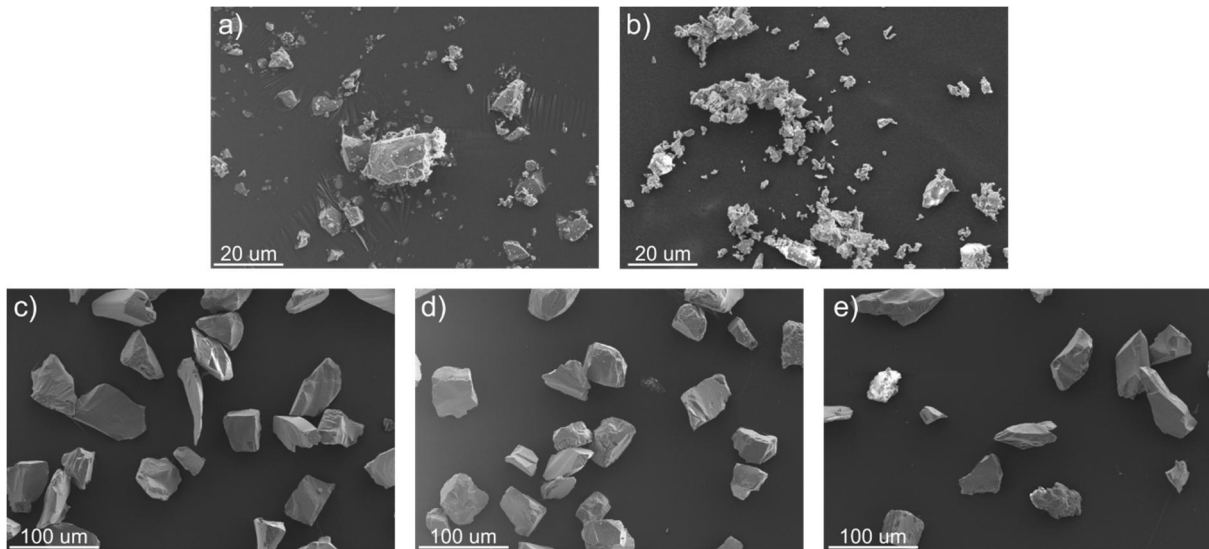


Figure 1: SEM micrographs of the fillers: a) SiO_2 -1, b) SiO_2 -2, c) SiC-1, d) SiC-2, e) Al_2O_3 . The difference between the scale bars of pictures a-b and c-e should be noticed.

Unfilled and filled glass fibre reinforced composite samples (referred as FRP samples) were manufactured by hand-lay up using the 441 resin. In addition, unfilled FRP samples were prepared from the 441 resin. The lay-up of the FRPs consisted of four layers of chopped E-glass strand mat (Owens Corning M723A, nominal weight 300 g/m^2) and one layer of ECR-glass surface veil on both surfaces (Owens Corning M524-ECR30S, 30 g/m^2). The lay-up of the FRP samples resembled the corrosion layer of hydrometallurgical process tanks. The thickness of the laminates was roughly 3.5 mm. The target glass fibre content in the laminates was 25 wt%. Curing of the samples was identical to the pure resin samples. All tested samples are listed in Table 3.

2.2 Sample characterization

Rectangular specimens for tensile (size 25 mm x 300 mm) and erosion (size 35 mm x 35 mm) tests were water jet cut from the laminates. Standard tensile tests were carried out according to the ISO 527. The samples were loaded at a crosshead rate of 2 mm/min using a tensile tester (Instron 5967) with a 30 kN load cell. The gauge length was 50 mm. The strain was measured using an extensometer (Instron 2630-112), but strain gauges were also glued on two samples prior testing in order to measure Young's modulus. From five to seven parallel samples were tested.

Slurry pot test is a commonly used test method in determining the erosion behaviour of different materials in laboratory scale. The erosion performance in slurry pot test is generally described by the weight loss of the specimens. Slurry pot devices can be used to rank materials based on their erosion resistance, examine the wear mechanisms present in the tests, and optimize the most suitable materials to a certain application. Slurry pot equipment consists of a horizontal impeller which is immersed into the slurry. The rotating impeller creates a particular fluid velocity. It is well established that a trailing vortex can be generated behind a moving impeller blade [22-26] causing turbulence that leads to extensive localized wear. On the other hand, the wear pattern on the pressure side is typically more uniform, which allows a simultaneous study of two different wear phenomena. The problem in the simple slurry pot devices is that the particle flow velocity and the impingement angle may be challenging to match with the real industrial reactors. Thus, the equipment used in laboratory scale should be designed to create as similar environment as possible compared with the real life processes.

Erosive wear tests were done with an in-house constructed erosion test apparatus (Fig. 2) that resembles real-life mineral leaching processes. The details of the erosion test equipment have been presented in our earlier papers [5, 6, 27-29]. The samples were attached to the agitator blades (fixed at 45° position) according to Fig. 2.b. In this study, the slurry erosive wear of FRP materials was studied in two different environments: water and 5% sulfuric acid (H₂SO₄) solution. The H₂SO₄ solution contained also ferrisulfate (Fe₂(SO₄)₃, 0.5 g/l) whose role was to act as corrosion inhibitor for the stainless steel parts tested simultaneously with the FRP samples.

Before the tests, the reactor tank was filled with 180 litres of fluid (tap water or H₂SO₄ solution) and 30 kg of quartz sand (Nilsjö quartz supplied by Sibelco Nordic Oy Ab). This roughly corresponds to the abrasive concentration of 15 wt%, which is typical for many hydrometallurgical processes. According to the manufacturer, the nominal particle size of the quartz was 50-200 µm. Detailed characterization of the used quartz abrasives can be found in our previous papers [5, 28]. The cut edges of the samples were sealed with vinylester resin (grade 441) in order to avoid excess water intake. From two to six parallel samples were tested. Before exposing samples to the erosive environment, all the samples were dried for 6 h at 80 °C and weighted. This was done to establish a fixed reference state.

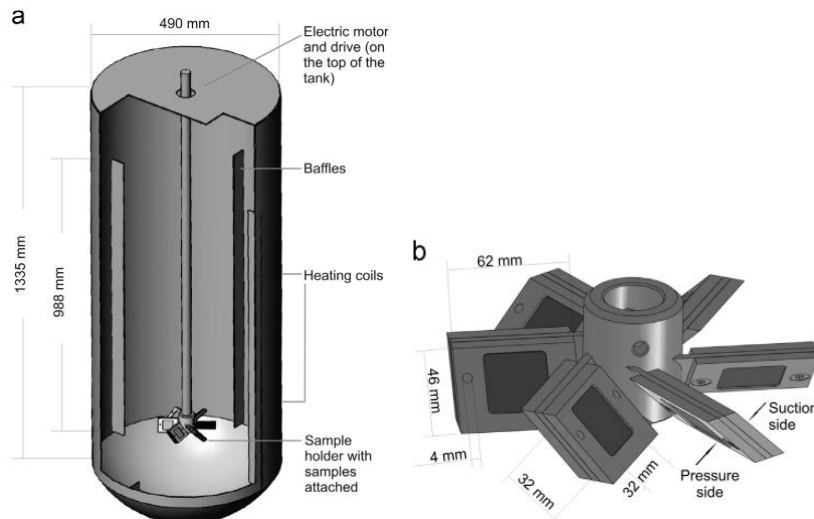


Figure 2: Schematic presentation of (a) the testing apparatus and (b) the impeller to which the samples were attached.

In the beginning of the tests, the slurry was heated to 95 °C using two heating coils situated in the lower portion of the reactor. The duration of the tests was 72 hours and the rotation speed 4.8 m/s (vinylester samples) or 7.2 m/s (FRP samples). After each test, the reactor was emptied and filled with fresh slurry. After the erosion test, the samples were washed in water and ultrasonically cleaned in order to remove the embedded erodent particles. Similar drying and weighting procedures were executed as prior testing. Selected wear surfaces were characterized with scanning electron microscope (SEM, model Zeiss ULTRAplus) using an accelerating voltage of 5 kV. Prior to SEM studies, the specimens were coated with a thin layer of gold to avoid charging.

The glass transition temperatures (T_g) of the manufactured materials were measured with a differential scanning calorimeter (DSC, model Netzsch DSC 204) under a nitrogen flow (20 ml/min) at a temperature range of 25–200 °C according to ISO 11357-1:2009 standard. Barcol hardness values were measured with Barber-Colman Impressor GYZJ-934-1 after sample drying. The densities of the components were defined by Sartorius Density Determination Kit and scale.

3. Results and discussion

3.1 Physical properties of the samples

The measured T_g values for the neat vinyl ester samples (Table 3) were close to the values given by the manufacturer indicating that the curing has succeeded well. Only the T_g of the grade 470 was 6% lower than the T_g given by the manufacturer. On the other hand, the densities of the neat vinyl esters were higher than the theoretical densities given by the manufacturer. Manufacturing conditions and the used curing system are assumed to cause the differences. The trend of the Barcol hardness values was similar to the T_g values being the lowest for the grade 411 and the highest for the grade 470.

Table 3: Measured physical properties for the samples.

Sample ID	Resin	T_g (°C)	Barcol hardness	Measured density (g/cm ³)	Theoretical density (g/cm ³)
411	Derakane 411-350	119	34 ± 3	1.12	1.05 [15]
441	Derakane 441-400	127	41 ± 1	1.17	1.07 [16]
470	Derakane 470-300	155	48 ± 2	1.19	1.08 [17]
411-SiO ₂ -2	Derakane 411-350	120	42 ± 1	1.28	1.45
441-SiO ₂ -2	Derakane 441-400	123	48 ± 1	1.32	1.47
470-SiO ₂ -2	Derakane 470-300	151	56 ± 1	1.34	1.47
FRP-441	Derakane 441-400	120	47 ± 1	1.31	1.44
FRP-SiO ₂ -1	Derakane 441-400	110	55 ± 1	1.45	1.62
FRP-SiO ₂ -2		113	52 ± 2	1.41	1.55
FRP-SiC-1		114	55 ± 2	1.51	1.76
FRP-SiC-2		117	53 ± 2	1.50	1.76
FRP-Al ₂ O ₃		117	50 ± 1	1.54	1.90

The addition of the fillers or the fibres decreased the T_g values of the samples slightly (10-15 °C). Fillers may lead to fewer cross-links in the resin matrix and thus affect the properties of the sample. However, the addition of fibres and fillers also influence the heat transfer during the measurement, which may cause the deviation. The densities of the FRP and filled FRP samples were lower than the calculated theoretical densities. This may be due to too low filler content or trapped air in the structure.

The tensile test results (Table 4) showed that the fillers increased the stiffness, but decreased the strength and the elongation at break of the composite. This result was expected since particles with low aspect ratio (e.g. spherical fillers) or particles that are randomly oriented in the matrix are not effective in bearing load of the composite. Instead, these particles can provide initiation states for fracture lowering the strength. For example, Patnaik et al. [13] have recorded a significant decrease in tensile strength values due to alumina particles. The samples that fractured close to the clamps were removed from the data set according to the standard apart from the FRP-Al₂O₃ samples, which all fractured close the clamps. Although this does not affect the modulus, there may be higher error in the strength values for Al₂O₃ samples.

Table 4: The tensile test results together with the standard deviation values for the unfilled and filled FRP samples based on the 441 resin.

	FRP	FRP-SiO ₂ -1	FRP-SiO ₂ -2	FRP-SiC-1	FRP-SiC-2	FRP-Al ₂ O ₃
Young's modulus (GPa)	6.5 ± 0.1	8.3 ± 0.6	8.3 ± 0.1	8.3 ± 0.5	8.1 ± 0.4	8.3 ± 0.2
Tensile strength (MPa)	76.0 ± 1.5	61.5 ± 2.9	60.4 ± 3.3	60.1 ± 1.6	57.4 ± 1.5	58.1 ± 2.1
Elongation at break (%)	1.7 ± 0.6	0.9 ± 0.1	0.9 ± 0.0	1.2 ± 0.1	1.1 ± 0.1	1.0 ± 0.1

3.2 The effect of vinylester grade on the erosion performance

The effect of different vinylester grades on the erosion performance was tested in water slurry at a blade tip rotation speed of 4.8 m/s. The results are shown in Fig. 3. As concluded also in our previous studies [5, 6], the wear was significantly higher in the suction side than in the pressure side of the samples. Also the surface wear patterns were different: a severe pit was seen on the suction side, whereas the pressure side was worn more evenly. The velocity and impingement angle variation at different locations of the blades is very complex [24, 30-32] and its detailed analysis is not in the scope of this publication. However, according to the differences between the suction and pressure side wear surfaces, we assume that at the pressure side the impact angle of the erosive particles is more constant than at the suction side where is the trailing vortex. Typically, the erosion rate of neat resins has a maximum at impact angles of 30-45° [10], although Singh et al. [7] have found a maximum erosion rate angle of 60° for neat vinylester. All in all, the results of the neat resins were more reliable and easier to interpret in the suction side due to higher weight losses when compared with the pressure side.

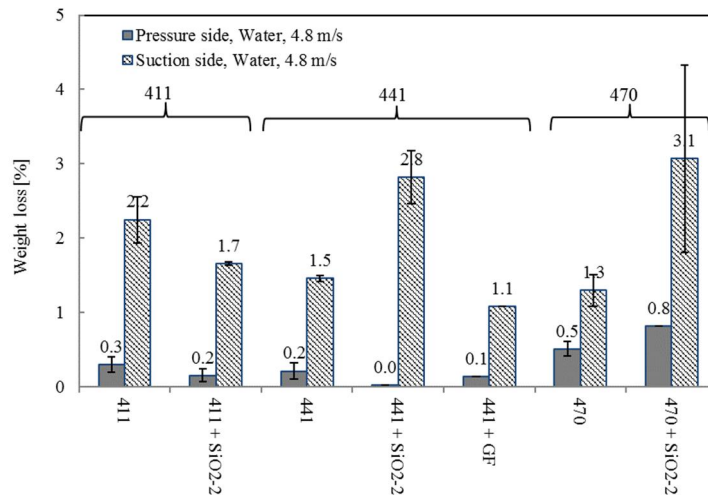


Figure 3: The weight losses and the standard deviation values for different unfilled and filled vinylesters.

In the suction side, the weight loss of the samples decreased as the hardness, T_g or the tensile modulus of the resin increased. For the resin 411, the weight loss was significantly higher than for the other resins. The hardness of the 411 resin was the lowest and as the test temperature (95°C) approached the HDT of the 411 resin (105°C) softening of the material could have occurred. Thus, the relatively soft resin combined with the localized wear led to poor erosion performance in the suction side. In the pressure side, where the wear was more uniform, the change in the weight losses were smaller and the trend was into opposite direction: the softer resins 411 and 441 were able to absorb the kinetic energy

of the erodent particles more effectively than the hard 470 resin. Therefore, higher hardness of the matrix seemed to have a positive effect on the resistance to localized erosion, but led to poor erosion performance in uniform wear conditions. However, the weight losses were so small at the pressure side that the reliability of these results is not sufficient for drawing definitive conclusions and the total weight loss (the sum of weight losses at suction and pressure sides) was dominated by the wear at the suction side.

3.3 The individual effects of filler and fibre on the erosion performance of vinylester

The individual effects of fillers and fibres were studied in water at a blade tip rotation speed of 4.8 m/s by adding either the SiO₂-2 filler or glass fibres in to the matrix (Fig. 3). The effect of fillers was studied with all matrices, but the effect of fibres only with the 441 matrix. The addition of the SiO₂-2 filler improved the erosion resistance of the 411 resin in both blade sides whereas for the 441 and 470 resins, the addition of the SiO₂-2 filler increased the weight loss which is a typical result for filled polymers reported in other studies [10].

The reason for the better performance of 411 resin in filled vinylester samples can be its softer nature. Due to the higher density of the filler particles, the removal of filler particles amplifies the weight loss when compared with the removal of pure matrix. Especially if the adhesion between the matrix and the fillers is poor, the weight loss may increase significantly. The energy dissipation of the soft 411 matrix is higher due to its better deformability when compared with the harder 441 and 470 resins. This will decrease the energy available for filler particle removal and so reduce the weight loss. Generally, a soft matrix combined with hard particles is considered to be advantageous for the wear performance. Better adhesion between the SiO₂-2 filler and vinylester would improve the erosion properties of the material [33, 34] which has also been concluded for fibre-matrix adhesion [35, 36].

The effects of the fillers and fibres were very different on the 441 matrix: the total weight loss of the filled 441 sample increased 65% whereas the weight loss of the fibre reinforced 441 sample decreased 29% when compared with the neat 441 resin. Considering the effect of higher density of the fillers and fibres when compared with the matrix, the adhesion of them to matrix plays a major role for the weight loss. In this case, the higher aspect ratio of the fibres improves the mechanical interlocking into the matrix whereas the roundish SiO₂-2 fillers are more easily removed from the matrix and this leads to increase in the weight loss in erosive environments. This is assumed to explain the differences between the weight losses of SiO₂-2 filled and glass fibre reinforced 441 matrices.

When comparing the weight loss of neat 441 matrix and glass fibre reinforced 441 matrix, the behaviour is opposite to the trend found for erosion performance of FRPs in air: Typically, increasing fibre volume has shown to increase the weight losses [10]. The main differences between air and slurry erosion are the phenomena introduced by the presence of water: cavitation and the ageing of the composite. The SEM studies revealed that the 441 based FRP tolerated cavitation well and it was not prone to the formation of micro-fractures that can lead to massive matrix removal during the erosion test [6]. In addition, considering the resin rich layer on the sample surfaces the increased hardness of the FRP has possibly improved the general erosion resistance of the composite when compared with the neat resin at small weight losses. However, this subject should be studied further to demonstrate the reasons for the differences in the general trends of erosion performance in air and in a slurry.

3.4 The effect of fillers on the erosion performance of FRP in water

The effect of different fillers on the erosion performance of 441 resin based FRPs in water was studied at a blade tip rotation speed of 7.2 m/s. The weight loss results are shown in Fig. 4. The increase of the

blade tip rotation speed from 4.8 m/s to 7.2 m/s led to a change in the wear behaviour: for higher rotation speed the weight loss in the pressure side was higher than in the suction side. This change has been reported and discussed elsewhere [5, 6]. The suction and pressure side results were very similar and visual inspection of the sampled showed similar wear patterns in both surfaces. Higher rotating speed seems to equalize the wear rate between blade sides. The weight loss results are shown in Fig. 4.

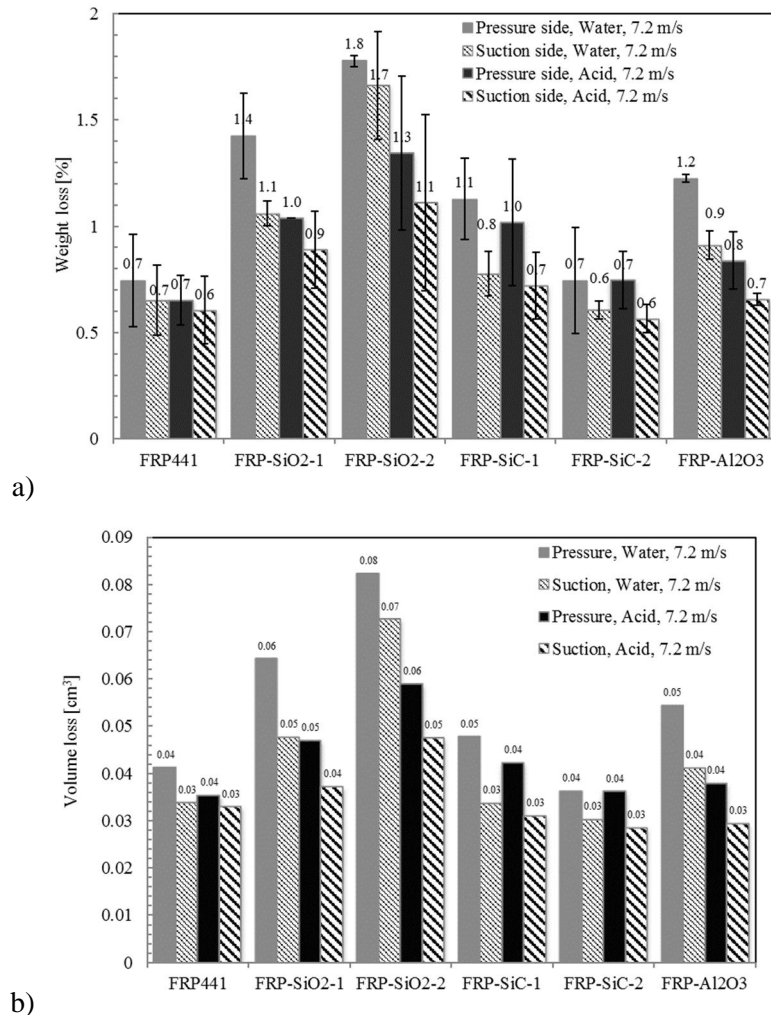


Figure 4: a) The measured weight losses together with the standard deviation values and b) the calculated volume losses for unfilled and filled vinylester FRP samples in water and H_2SO_4 solution environments.

As a measure of wear, volume loss is typically the most interesting indicator. However, due to practical reasons, mass loss is most often used. The volume losses for the FRP samples were evaluated with the aid of the densities of the filled FRP samples (Table 3) assuming an even wear of matrix and fillers (Fig. 4.b). However, the trends measured for the mass losses were the same as evaluated for the volume losses. The similarity of the weight and volume loss results indicated that weight loss was a reliable way to compare the studied materials in this case.

When comparing the effect of different fillers, the SiC filled FRPs showed the best erosion behavior, the Al_2O_3 filled the medium ones and the SiO_2 filled the poorest. These results are in line with the Mohs hardness values of the fillers implying that the hardness gives a rough tool to predict the erosion performance of filled FRPs. However, there was a clear difference between the two SiO_2 filled samples.

The SEM micrographs (Fig. 5) showed that the SiO₂-2 particles were detached more extensively from the matrix surface than the SiO₂-1 particles which explains the high weight loss of FRP-SiO₂-2 samples. Also, the interface between the SiO₂-1 particles and the matrix was continuous whereas the faults around the SiO₂-2 particles were observed more often. Evidently the vinylsilane surface treatment of SiO₂-2 was not as effective as the methacrylsilane treatment in vinyl ester resins used in aqueous environments. However, since the tensile test results of the FRP-SiO₂-1 and FRP-SiO₂-2 specimens were similar, it is assumed that the initial adhesion between the SiO₂ particles and the matrix was sufficient in both cases and the problems arose first in the presence of water.

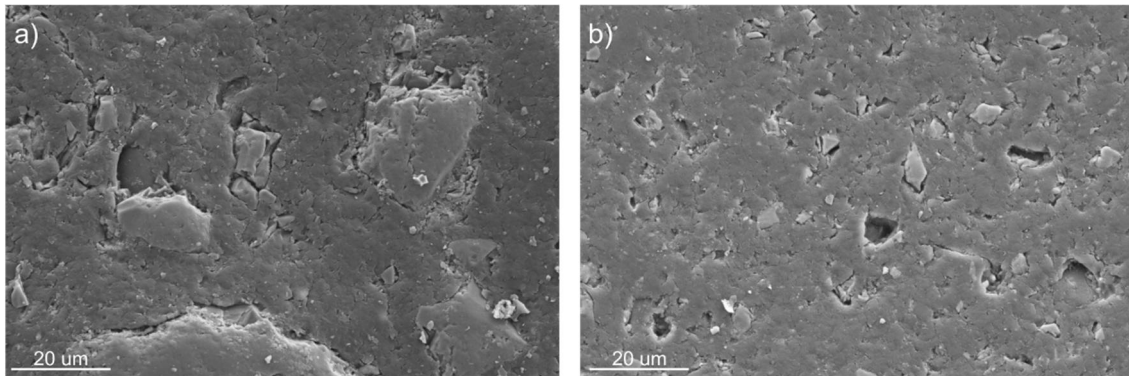


Figure 5: Micrographs of a) the FRP-SiO₂-1 and b) the FRP-SiO₂-2 specimens from the suction side.

When comparing the effects of the filler hardness and the filler particle-matrix adhesion on the erosion performance, it can be concluded that both factors are significant. When comparing different filler materials, there is a clear trend between the filler hardness and the erosion (Fig. 6). On the other hand, within one filler material, the particle-matrix adhesion has a clear effect as well. However, due to the qualitative nature of the particle-matrix adhesion strength data within this study, it cannot be concluded which factor has greater effect on the erosion performance.

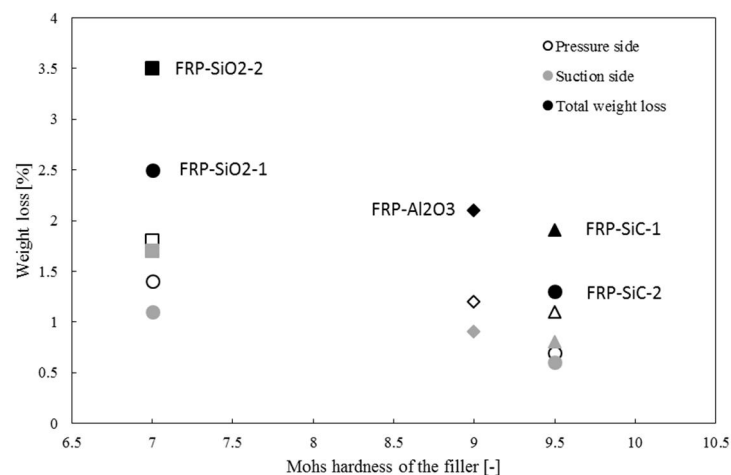


Figure 6: The effect of the filler Mohs hardness on the weight loss of the filled FRP samples. Tested in water environments at a blade tip rotation speed of 7.2 m/s. A Mohs hardness value of 9.5 is used for the SiC particles, since it is reported to be 9-10 (Table 2).

3.5 The effect of fillers on the erosion performance of FRP in H₂SO₄ solution

Similar to water environment, the effect of different fillers on the erosion performance of 441 resin based FRPs in acid solution was studied at a blade tip rotation speed of 7.2 m/s. The results are shown

together with the water environment results in Fig. 4. The acidic slurry caused smaller weight losses than the water environment. Possible reasons are the decreased effects of hydrolysis, swelling and cavitation. The diffusion of sulphuric acid solution is slower into the matrix when compared to water [37], which protects from the degradation of mechanical properties due to swelling and hydrolysis and thus decreases the weight loss. On the other hand, the boiling temperature of 5% sulphuric acid is few degrees higher than the boiling point of water. Consequently, less gas bubbles may be generated to the acidic slurry decreasing the effect of cavitation erosion. However, the changes in the cavitation behaviour are supposed to be minor.

In our previous study, we have shown that sulphuric acid is very detrimental to the glass fibres not protected by the matrix [38]. From the SEM micrographs (Fig. 7) it was observed that in sulphuric acid the glass fibres revealed from the matrix were more often fractured than in the samples tested in water, which exhibited often worn glass fibre surfaces. This can be due to the decreased mechanical properties of the glass fibre. Also, the micrographs showed continuous fibre-matrix interfaces at the wear surfaces in acidic environment. This could imply that the fibre-matrix adhesion withstands better the acidic than the neutral slurry. No remarkable differences were found in the matrix after erosion in water or in sulphuric acid solution.

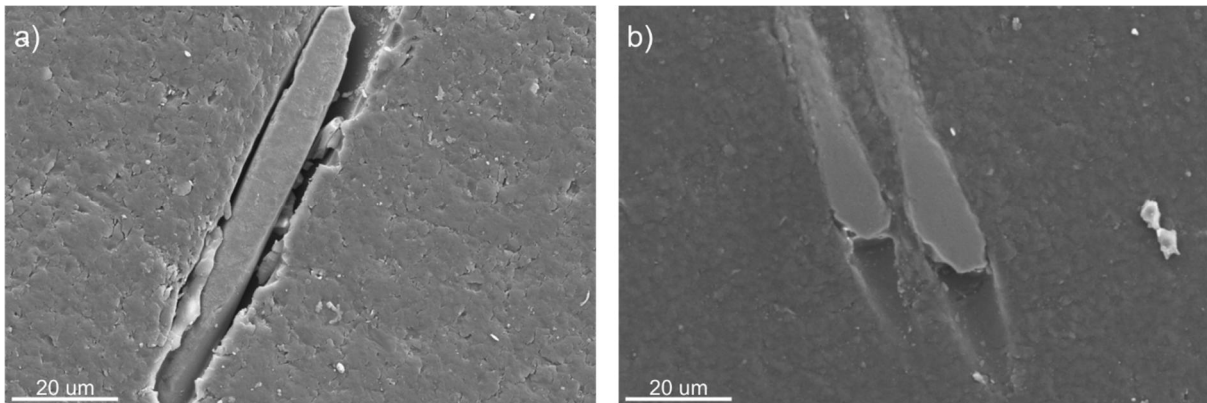


Figure 7: Exposed glass fibres at the suction side of FRP-441 samples tested in a) water and b) acidic environment.

Similar to the water environment results, the weight loss of the FRP-SiC-2 samples was the smallest within the filled FRP samples, the FRP-SiC-1 and FRP-Al₂O₃ results were at the same level and the SiO₂ filled FRPs had highest weight losses. Again, these results are in line with the Mohs hardness values of the fillers. However, in H₂SO₄ solution the differences between the samples were smaller than in water and the total weight loss for the FRP-SiC-2 was the same in both test environments.

Surprisingly, the SEM studies revealed that the interface between SiC particles and the matrix was not very good (Fig. 8). A fault between the filler particles and the matrix was often observed and some of the fillers were detached from the matrix. However, most of the filler particles were still attached to the matrix and the matrix was worn around the hard SiC particles, as indicated with arrows in Fig. 8. Presumably the combination of the physical and mechanical adhesion between the irregularly shaped, rather large SiC particles was enough to hinder the detachment of the particles during erosion. No difference was observed between the appearances of the two SiC filled FRP samples from the SEM micrographs.

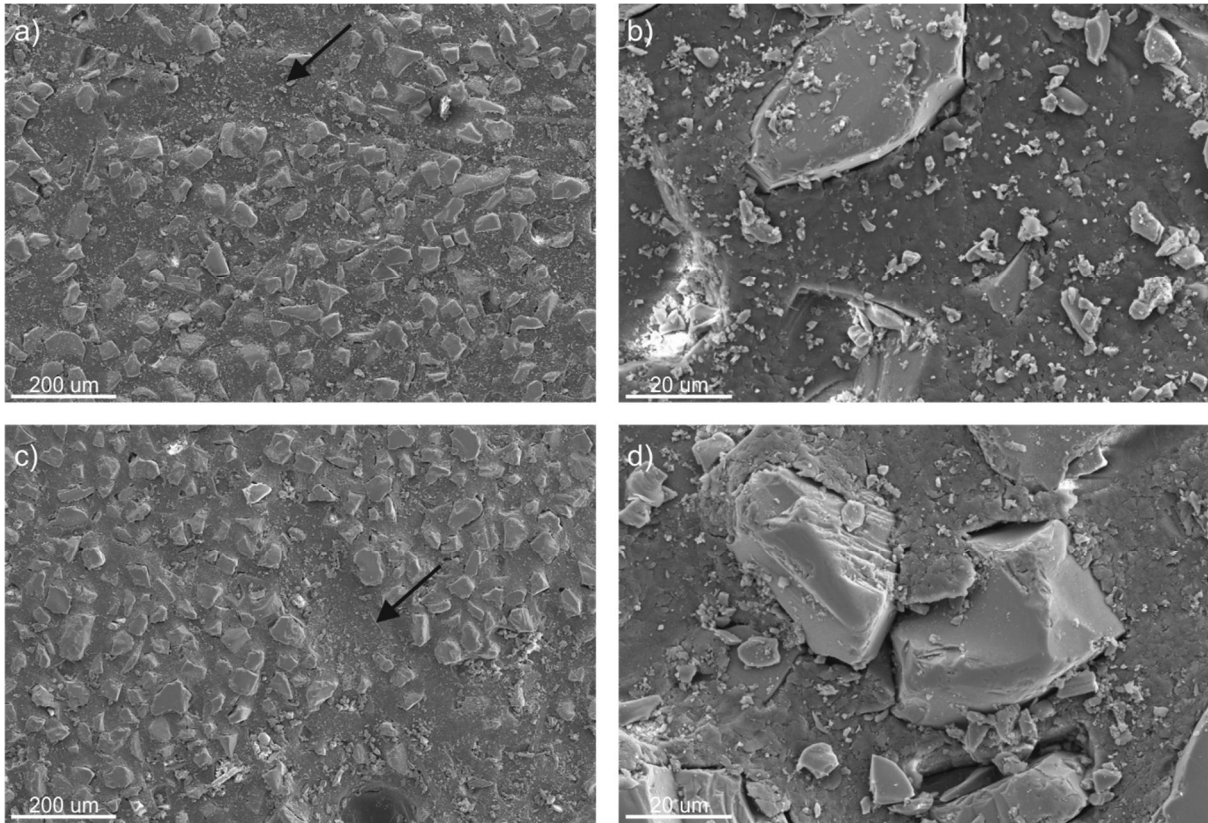


Figure 8: The suction side wear surfaces of a-b) the FRP-SiC-1 and c-d) the FRP-SiC-2 samples tested in acidic environment. The arrows indicate the heavily worn matrix areas between the filler particles.

Considering the similar Mohs hardness and weight loss of the Al_2O_3 filled samples when compared with the SiC based samples, it was expected that the appearance of the Al_2O_3 and SiC filled samples were similar. The only difference found was that in the FRP- Al_2O_3 samples, the matrix and fillers were worn more evenly leaving a smoother surface (Fig. 9) than in the FRP-SiC samples. The higher erosion of the fillers explains the higher weight losses of the Al_2O_3 filled samples when compared with the SiC filled samples.

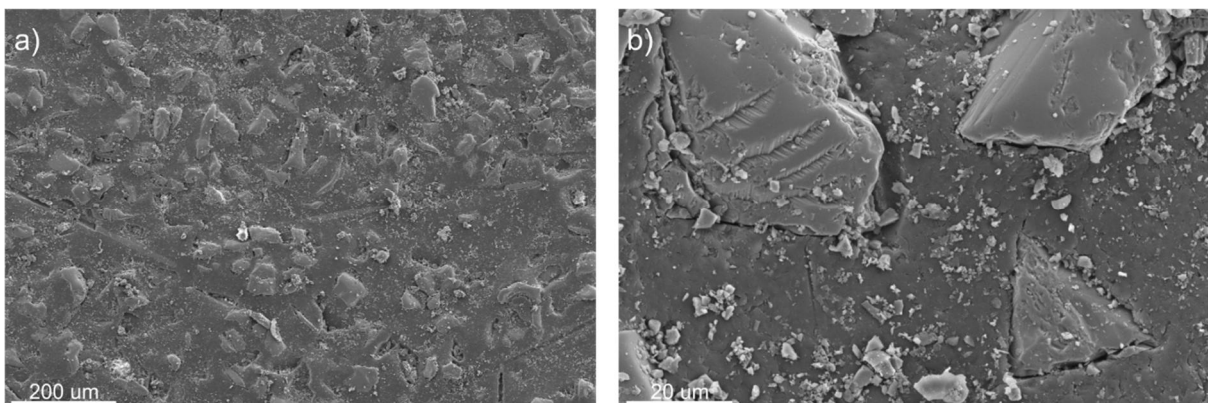


Figure 9: The suction side wear surfaces of the FRP- Al_2O_3 samples tested in acidic environment.

The main difference between the SiO_2 -1 filled samples when compared to other samples was, that the particle-matrix interface was mainly continuous without faults (Fig. 10.a). There was even some cracks

in the matrix close to the particles (insert in Fig. 10.a), indicating very good compatibility between methacrylsilane treated SiO₂-1 filler and vinylester. The FRP-SiO₂-2 samples, having the largest weight losses of all the samples, had lost a high amount of filler particles from the matrix (Fig. 10.b). So, the methacrylsilane surface treatment of SiO₂-1 seems to be better than vinylsilane treatment of FRP-SiO₂-2 for vinylesters also in the acidic environments. When comparing the effects of filler hardness and filler particle-matrix adhesion on the erosion performance of FRPs in the H₂SO₄ solution, a similar trend can be found as in the water environment (Fig. 6).

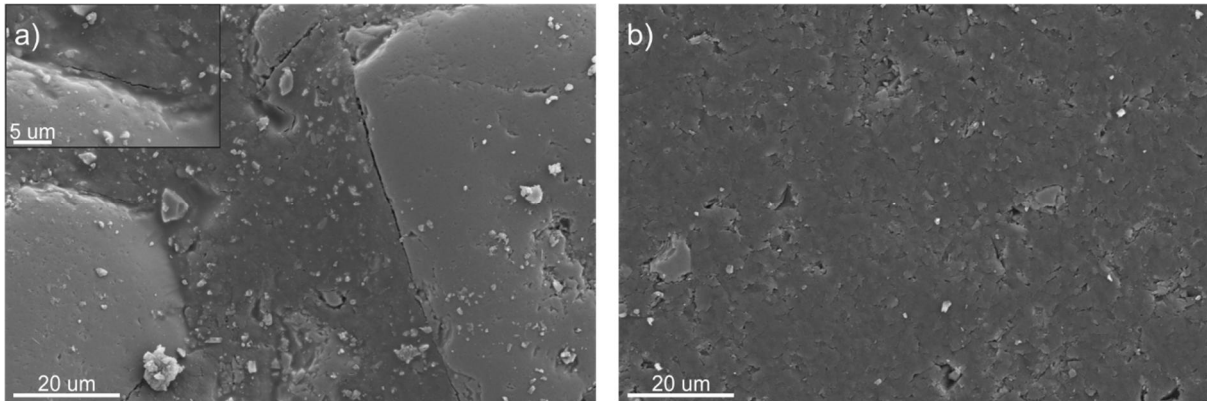


Figure 10: The suction side wear surfaces of a) FRP- SiO₂-1 and b) FRP- SiO₂-2 samples tested in acidic environment.

4. Conclusions

The goal of this study was to study the effect of fillers on vinylester matrices and glass fibre reinforced vinylester composites. Slurry erosion tests were performed to measure the wear rates of SiO₂, SiC, and Al₂O₃ filled vinylester composites and compared with samples without fillers. The erosion rates of the filled FRPs were tested both in aqueous and in acidic environments at high temperature.

For different vinylester grades it was found that high hardness had a positive effect on the erosion resistance of the pure matrix. However, if fillers were used soft matrix led to best performance. This was related to the higher deformability of the softer matrix and consequently to higher energy dissipation which decreases the energy available for filler particle detachment.

The hardness of the fillers had a strong effect on the wear rate of the filled samples. Thus, the SiC filled FRPs showed the best erosion resistance, the Al₂O₃ filled showed moderate erosion resistance and the SiO₂ filled showed the poorest resistance. Within different filler materials, the effect of filler-matrix adhesion was masked by the effect of hardness. Presumably the combination of the physical and mechanical adhesion between the irregularly shaped filler particles was enough to hinder excessive detachment of the particles during erosion.

When comparing similar filler materials, improved adhesion decreased the erosion rate. Especially, methacrylsilane surface treatment for SiO₂ was found to be more effective than vinylsilane treatment in water and in acidic environments despite the equally good initial adhesion. In addition, the filler aspect ratio had a clear effect on the wear rate: the higher aspect ratio of the fibres improves the mechanical interlocking into the matrix whereas the roundish fillers are detached more easily from the matrix causing effectively high mass loss.

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References

- [1]: J.E. Miller, Slurry Erosion in Friction, Lubrication, and Wear Technology, Vol 18, ASM Handbook, ASM International, 1992, p. 233–235.
- [2]: D. Rispono and T. Johnson, Proven Solutions for Phosphoric and Sulfuric Acid Service, Ashland Inc.
- [3]: S. Kumar, B.K. Satapathy, A. Patnaik, Thermo-mechanical correlations to erosion performance of short carbon fibre reinforced vinyl ester resin composites, *Mater. Design* 32 (2011) 2260–2268.
- [4]: S. Kumar, B.K. Satapathy, A. Patnaik, Thermo-mechanical correlations to erosion performance of short glass/carbon fiber reinforced vinyl ester resin hybrid composites, *Comp. Mater. Sci.* 60 (2012) 250–260.
- [5]: E. Sarlin, M. Lindgren, R. Suihkonen, S. Siljander, M. Kakkonen, J. Vuorinen, High-temperature slurry erosion of vinylester matrix composites – The effect of test parameters, *Wear* 328–329 (2015) 488–497.
- [6]: R. Suihkonen, M. Lindgren, S. Siljander, E. Sarlin, J. Vuorinen, Erosion wear of vinylester matrix composites in aqueous and acidic environments at elevated temperatures, *Wear* 358–359 (2016) 7–16.
- [7]: A. K. Singh, Siddhartha, P. Gupta, P. K. Singh, Evaluation of Mechanical and Erosive wear Characteristics of TiO₂ and ZnO Filled Bi-Directional E-glass Fiber Based Vinyl Ester Composites, *Silicon* (2016) 1–19.
- [8]: B. T. Åström, Manufacturing of polymer composites, Chapman & Hall, 1997, pp. 91–92.
- [9]: W. Brostow, H. E. Hagg Lobland, N. Hnatchuk, J. M. Perez, Improvement of Scratch and Wear Resistance of Polymers by Fillers Including Nanofillers, *Nanomaterials* 7(3) (2017) 66.
- [10]: N. Miyazaki, Solid particle erosion of composite materials: A critical review, *J. Comp. Mater.* (2016) 3175–3217
- [11]: A.G. Joshi, M.P. Kumar, S. Basavarajappa, Influence of Al₂O₃ Filler in Slurry Erosion Behaviour of Glass/Epoxy composites, *Procedia Mater. Sci.* 5 (2014) 863–872.
- [12]: S.S. Mahapatra, Amar Patnaik, Study on mechanical and erosion wear behavior of hybrid composites using Taguchi experimental design, *Mater. Design* 30 (2009) 2791–2801.
- [13]: Patnaik A, Satapathy A and Mahapatra SS. Study on erosion response of hybrid composites using Taguchi experimental design, *J. Eng. Mater. Technol.* 131: Paper No. 031011 (2009).
- [14]: W.R. Slama, Polyester and Vinyl Ester Coatings, JPCL (1996) 88–109.
- [15]: Technical datasheet of Derakane 411–350 Epoxy Vinyl Ester Resin, Ashland Inc, 2011.
- [16]: Technical datasheet of Derakane 441–400 Epoxy Vinyl Ester Resin, Ashland Inc, 2011.
- [17]: Technical datasheet of Derakane 470–300 Epoxy Vinyl Ester Resin, Ashland Inc, 2011.
- [18]: Datasheet Silbond Quartz Flours, The Mineral Engineers.
- [19]: Datasheet SIKA ABR III silicon carbide, Saint-Gobain.
- [20]: Datasheet Carborex silicon carbide, Washington Mills, 2017.
- [21]: Datasheet Duralum White, Washington Mills, 2017.
- [22]: J. Wu, L.J.W. Graham, D. Lester, C.Y. Young, T. Kilpatrick, S. Smith, B. Nguyen, An effective modeling tool for studying erosion, *Wear* 270 (2011) 598–605.
- [23]: Z. Doulgerakis, M. Yianneskis, A. Ducci, On the interaction of trailing and macro-instability vortices in a stirred vessel-enhanced energy levels and improved mixing potential, *Chem. Eng. Res. Des.* 87 (2009) 412–420.

- [24]: S. Roy, S. Acharya, M.D. Cloeter, Flow structure and the effect of macro- instabilities in a pitched-blade stirred tank, *Chem. Eng. Sci.* 65 (2010) 3009–3024.
- [25]: R. Escudié, D. Bouyer, A. Liné, Characterization of trailing vortices generated by a Rushton turbine, *AIChE J.* 50 (2004) 75–86.
- [26]: M. Schäfer, M. Yianneskis, P. Wächter, F. Durst, Trailing vortices around a 45° pitched-blade impeller, *AIChE J.* 44 (1998) 1233–1246.
- [27]: S. Siljander, M. Kiviniemi, E. Sarlin, M. Lindgren, R. Suihkonen, J. Vuorinen, Erosion testing of filled and/or reinforced vinyl ester composites in water medium at elevated temperature, *Proceedings of the 20th International Conference on Composite Materials, Copenhagen, 19-24th July 2015*
- [28]: M. Lindgren, R. Suihkonen, J. Vuorinen, Erosive wear of various stainless steel grades used as impeller blade materials in high temperature aqueous slurry, *Wear* 328-329 (2015) 391–400
- [29]: M. Lindgren, S. Siljander, R. Suihkonen, P. Pohjanne, J. Vuorinen, Erosion-corrosion resistance of various stainless steel grades in high-temperature sulfuric acid solution, *Wear* 364-365 (2016) 10–21.
- [30]: Z. Doulgerakis, M. Yianneskis, A. Ducci, On the interaction of trailing and macro-instability vortices in a stirred vessel-enhanced energy levels and improved mixing potential, *Chem. Eng. Res. Des.* 87 (2009) 412–420.
- [31]: K.C. Kee, C.D. Rielly, Measurement of particle impact frequencies and velocities on impeller blades in a mixing tank, *Chem. Eng. Res. Des.* 82 (2004) 1237–1249.
- [32]: T. Kumaresan, J.B. Joshi, Effect of impeller design on the flow pattern and mixing in stirred tanks, *Chem. Eng. J.* 115 (2006) 173–193.
- [33]: AH. Saputra, A. Hasrin, M Kubouchi, Effect of surface treatment on sand erosion behavior of glass beads-filled epoxy resin. *Compos. Interface* 6 (1999) 531–541.
- [34]: AP. Harsha, US Tewari, B. Venkatraman, Solid particle erosion behavior of various polyaryletherketone composites, *Wear* 254 (2003) 693–712.
- [35]: N. Miyazaki, N. Takeda, Solid particle erosion erosion of fiber reinforced plastics, *J. Compos. Mater.* 27 (1993) 21-31.
- [36]: N. Miyazaki, T. Hamao, Effect of interfacial strength on erosion behavior of FRPs, *J. Compos. Mater.* 30 (1996) 35-50.
- [37]: E. Sarlin, R. Sironen, T. Pärnänen, M. Lindgren, M. Kanerva, J. Vuorinen, The effect of matrix type on ageing of thick vinyl ester glass-fibre-reinforced laminates, *Comp. Struct.* Volume 168 (2017) 840-850
- [38]: E. Sarlin, M. von Essen, S. Palola, M. Lindgren, P. Kallio, J. Vuorinen. Determination of environmental degradation of matrix and fibre materials with a novel, statistically reliable micro-robotic approach. *Proceedings of the 17th European Conference on Composite Materials, Munich, Germany, 26th – 30th June 2016.*