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Comparison Of Sealing Methods For Polymer Electrolyte Membrane

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Abstract

The use of flat membrane humidifiers increases efficiency and extends the lifetime of fuel cells by humidifying the inlet airstream. The conditions under which the membranes mainly operate are determined by humidity, temperature, and pressure. The flat membrane humidifier uses the cathode-outflow of the flue cell to humidify the inlet airstream. Commonly available PFSA sandwich membranes are not necessarily designed to suit these operational conditions. Delamination of PFSA and the reinforcement layers may occur due to weak connection between the different layers. A delamination may lead to leakage, which could result in a bypass and pressure loss of the in- and outflow of the fuel cell. As a consequence, delamination of the PFSA membrane may cause failures of the flat membrane humidifier operation. To avoid delamination under such thermal and humidified conditions, it is necessary to strengthen the membrane during preparatory production steps against delamination. This paper examines different methods to strengthen the sandwich membrane against delamination due to water intake. It compares the effect of different sealing processes, focusing on increasing resistance against delamination. The investigated methods can also find application in PFSA membranes used under similar conditions, such as fuel cells. The technology selection process is focused on technologies enabling the flat membrane humidifier mass production for the automotive supplier MAHLE.

Keywords

Polymer Electrolyte Membrane (PEM) Fuel Cells; humidifier membrane; PFSA; technology screening; technology selection; flat membrane humidifiers; automotive industry

1. Introduction

Proton-exchange membrane fuel cells (PEMFC) have emerged as clean power sources with broad applications. In PEMFCs, chemical energy is converted to electrical energy through an electrochemical reaction, primarily utilizing hydrogen as fuel. Maintaining optimal humidity levels within the fuel cell is crucial to ensure efficient and stable performance.

In recent years, flat membrane humidifiers have gathered significant attention as effective solutions for humidifying reactant gases in fuel cells. Higher humidity levels in the fuel cell lead to increased efficiency and extended service life. The function of flat membrane humidifiers is to separate outgoing used and incoming fresh air and pass the humidity of the outgoing air to the incoming air. [1] Therefore, the flat membrane humidifier consists of various layers of alternating membranes and spacer, which need to be joined. [1] One of the most promising joining technologies for the layers of the membrane/spacer-stack seems to be adhesive bonding.

Experiences by the automotive supplier MAHLE have revealed weaknesses in the membrane used for flat membrane humidifiers, particularly related to delamination of the membrane layers when exposed to water.

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As operational conditions for flat humidifiers involve high water intake, optimizing the membrane's resistance against delamination becomes vital. Enhancing resistance to delamination, especially during water intake, appears to be beneficial in improving lifespan during an operation.

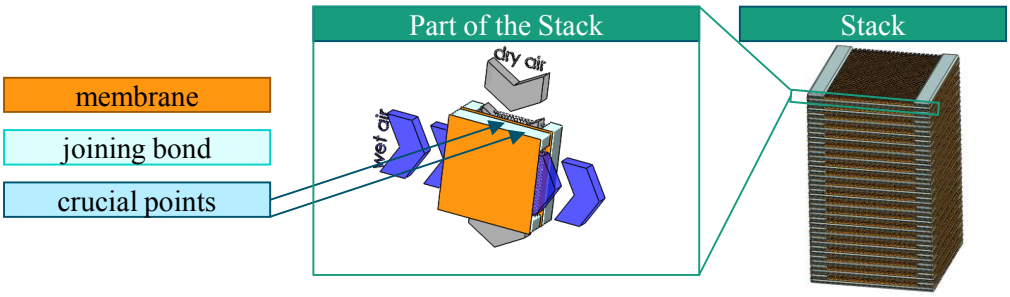

Figure 1: membrane stack for a flat membrane humidifier of a fuel cell system [1]

Delamination of the membrane of the flat membrane humidifier is critical, because it creates gaps and irregularities in the joining bond between the two membranes. Figure 1 shows these points as crucial points. When gaps or irregularities occur, dry and wet air can mix, leading to pressure loss and mixing air components This consequently results in a loss of functionality. A well-bonded membrane spacer stack is essential for the long-term durability of the humidifier. Delamination tendency of the membrane layers, ultimately reducing the membrane's lifespan and necessitating frequent replacements or maintenance.

Perfluorosulfonic acid (PFSA) membranes are considered the standard in PEMFC applications due to their superior thermal, mechanical, and chemical stability, as well as high proton conductivity. [2] This paper focuses on the production of a flat membrane humidifier by using a PFSA membrane as the active layer between the inlet and outlet airstreams. PFSA-based membranes are well-known for their exceptional water conduction properties. To enhance specific properties, such as mechanical strength and stability, the membrane is reinforced and built up as a "sandwich membrane".

The paper examines various approaches to preventing delamination in an existing PFSA sandwich membrane with non-woven reinforcement. The state of the art presents the properties of PFSA membranes. The methodology chapter investigates approaches to improve the mechanical properties of the PFSA membrane. At the end, the results are described and discussed. The paper concludes that conventional sealing methods are not helpful for increasing resistance against delamination during water intake.

2. State of the Art

The sandwich membrane of the flat membrane humidifier has two major functions, a structural/mechanical function (i.e., to serve as a chemically inert barrier to prevent bulk mixing of catholyte and anolyte solutions) and a chemical function (i.e., to selectively transport the specific ions from one solution to the other). [3]

To meet the requirements, PFSA polymers are used as membrane materials. The hydrophilic groups of the PFSA membrane act as proton-conducting pathways when hydrated and thus are responsible for the quality of proton conductivity. [4,5] The hydrophilic acid groups are agglomerated in clusters. Upon hydration, they take up water, which results in swelling of the clusters. Therefore, the clusters partially connect and build paths for hydrogen ions. [2]

Additional materials for PFSA membranes are non-woven materials. Non-woven materials are porous substrates that result in a higher membrane lifetime. [6] The membrane investigated in this paper is a sandwich membrane consisting of a non-woven reinforcement layer on the outside (Figure 2).

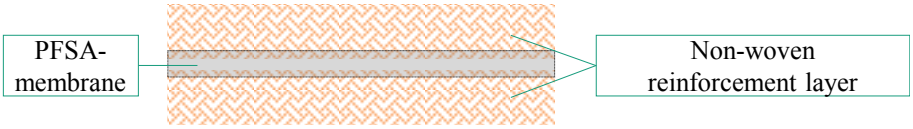

Figure 2: Schematic representation of the sandwich membrane

3. Methodology

Since delamination due to water intake was recognized through empirical experience in the usage test of the flat membrane humidifier, the behaviour of the membrane in humidified environments had to be analysed. Test conditions for humidified environments were achieved in a climatic chamber (95°C, 95 % rel. humidity). The conditions in the climatic chamber simulate the operating conditions during normal operation. Additionally, the samples were submerged in liquid water to model maximum water intake. The time out of water (ooW) before peel-off was defined as one of the main parameters.

The first step in this study was to inspect the structure of the sandwich membrane. An optical inspection of the sandwich membrane was done. Because of the fleece structure of the non-woven reinforcement, the bond between the reinforcement layer and the PFSA membrane is punctual (Figure 2). Different conventional sealing methods have been considered to improve the bonding quality between two layers.

Sealing technologies commonly used in the packaging industry are heat sealing (also called conduction sealing), high-frequency sealing, and ultrasonic (us) sealing [7]. Additionally, laser welding as a sealing technology has been considered. As laser welding resulted in smoke marks on the membrane, it is not described in the results. Since the membrane consists of non-metallic parts, high frequency sealing methods could not be applied. Additionally, adhesive bonding has demonstrated its potential as an effective joining technique, prompting investigation into its application for sealing purposes. The goal of the sealing technology was to improve the bonding strength of the layers of the sandwich membrane (non-woven layers and PFSA membrane), especially in humid environments.

In this paper, ultrasonic sealing, heat sealing and adhesive bonding experiments were carried out. Complementary, the authors applied a combination of heat sealing and adhesive bonding. Heat sealing and adhesive bonding, as the most promising sealing techniques, were tested under different stages of humidity.

4. Material, Machines, and Methods

The membrane is a sandwich membrane composed of a PFSA polymer and additional non-woven layers on the outside. A two-component polyurethane compound was used as an adhesive. Sealing experiments for ultrasonic sealing were carried out on the ultrasonic machine SonyTop from MS Ultrasonic Technology Group. The SonyTop machine uses a frequency of 20 kHz and 4 KW. The radius of the sonotrode is 2.5 mm, and the anvil has a radius of 1.5 mm. There are two linear sealing seams of ultrasonic sealing for each sample. Heat-sealing experiments were conducted using the laboratory-sealing device of SGPE HCT 320 Labormaster. The parameters that were used in the test are summarized in Table 1.

The tensile testing machine from ZwickRoell GmbH & Co. KG was used for testing. The tensile test was performed by delaminating a non-woven layer and clamping it onto the tensile testing machine. The tensile test was performed at 100 mm/min. All samples were conducted as strips with a width of 15 mm and a 10 mm wide sealing seam across the entire width for heat sealing and adhesive bonding, and two linear seams for ultrasonic sealing. Six samples of heat sealing and ultrasonic sealing and three samples of adhesive bonding were tested. The peel-off angle of the samples was at 180 degrees and the tests were conducted in a climate-controlled environment at 21.8°C and 64% relative humidity (r.h.).

For adhesive bonding experiments, the material was prepared in two different ways. First, the adhesive was applied to commercially available sandwich membranes, compressed to create a defined adhesive bead, and then dried for 24 hours at ambient temperature (Figure 3 left). Additionally, an adhesive was applied to the sealing bead of heat-sealed sandwich membranes (Figure 3 right).

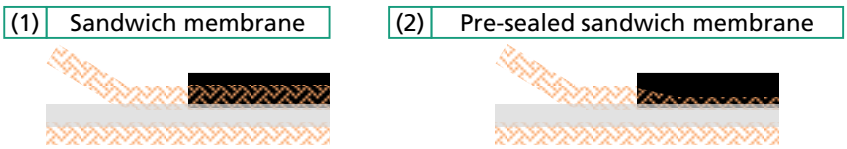

Figure 3: Schematic illustration of sample preparation

4.1 Optical inspection

The following chapter presents the results of the optical inspections, showing the actual structure of the membrane. To investigate the structure of the membrane, it was analysed under a scanning electron microscope (SEM). Additionally, the membrane was imbedded in resin and polished to examine the bond line with a light microscope (Figure 4).

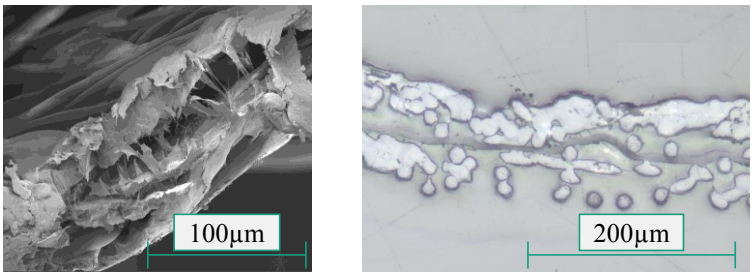

Figure 4: SEM (left) and micrographic inspection (right) of the sandwich membrane

As outlined in the state of the art, the sandwich-membrane consists of a continuous PFSA membrane, which is the active layer between two non-woven reinforcement layers. Due to the non-homogenous surface of the non-woven, the bond between PFSA and the non-woven layer only consists of single fibres enclosed with PFSA, as shown in Figure 4 on the right side. Consequently, adhesive forces between PFSA and the reinforcement layer cannot be as high as they would be if both materials had continuous surfaces. This results in decreased adhesion.

In further research, the process of delamination was examined optically. To this end, the different layers of the non-woven and the PFSA membrane were examined under the microscope and during delamination. It became apparent that one of the non-woven reinforcement layers can be peeled off more easily than the other one. Visually, this difference can not be explained.

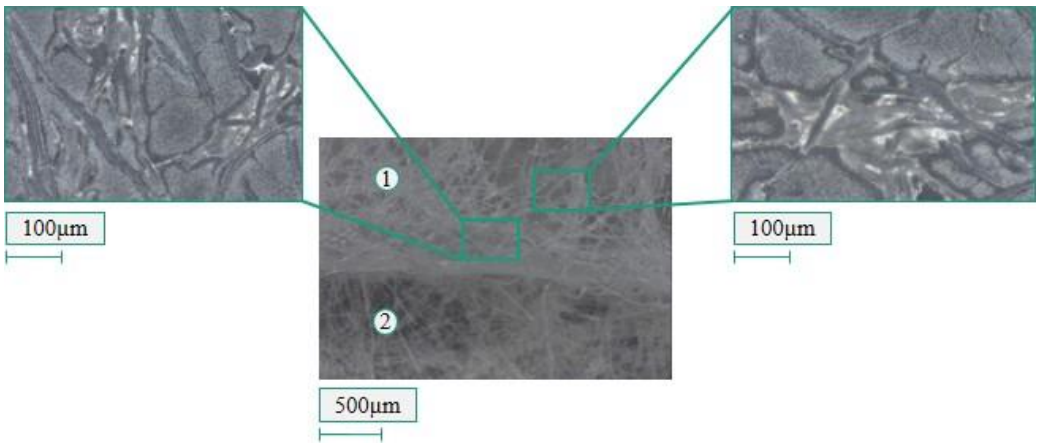

Figure 5: Microscopic image of the peel-off process (middle) and the peeled-off PFSA membrane (side))

Figure 5 shows the microscopic image of the sandwich membrane during the peel-off process. The middle figure illustrates the sandwich membrane. The area marked “2” depicts the peeled-off non-woven reinforcement layer. The upper part shows the remaining sandwich membrane consisting of PFSA membrane and a non-woven layer. The left and right images illustrate the PFSA membrane, once again in enlarged view. Peeled-off non-woven layers were also examined under the SEM. An EDX analysis was performed to obtain the type of material seen in the images.

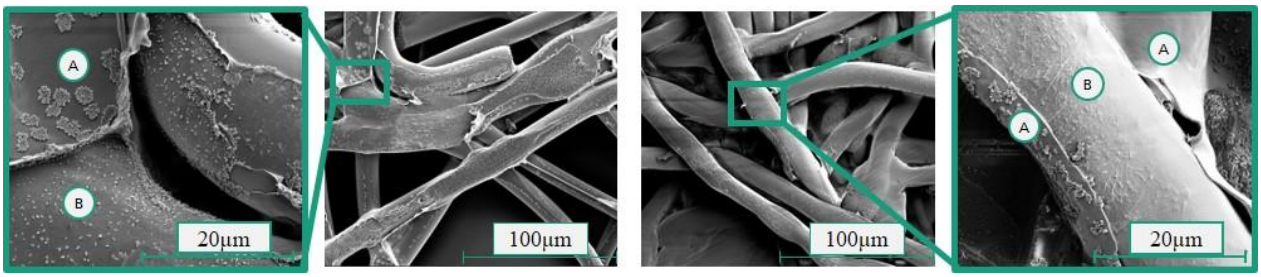

Figure 6: SEM of the dry (left) and wet (right) peeled-off non-woven membrane from the sandwich membrane

Figure 6 shows the peeled-off non-woven layer. In areas marked “A”, the EDX analysis detected mostly carbon and fluorine, leading to the assumption that those areas were PFSA. The SEM recognized carbon and oxygen only in areas marked “B”, mainly in the middle of the fibres. This indicates that those areas are non-woven fibres. There was no difference to be found between the dry peeled-off membrane (on the left side) and the wet peeled-off membrane (on the right side). The thickness of the layer of the PFSA around the fibres is smaller than 500 nm.

4.2 Results of Sealing Experiments

The following paragraph shows the results of the different sealing methods. Three sealing methods were investigated: Sealing by ultrasonic (us) sealing, sealing by heat sealing, and sealing by adhesive bonding. The results of ultrasonic sealing and heat sealing are shown in Figure 7

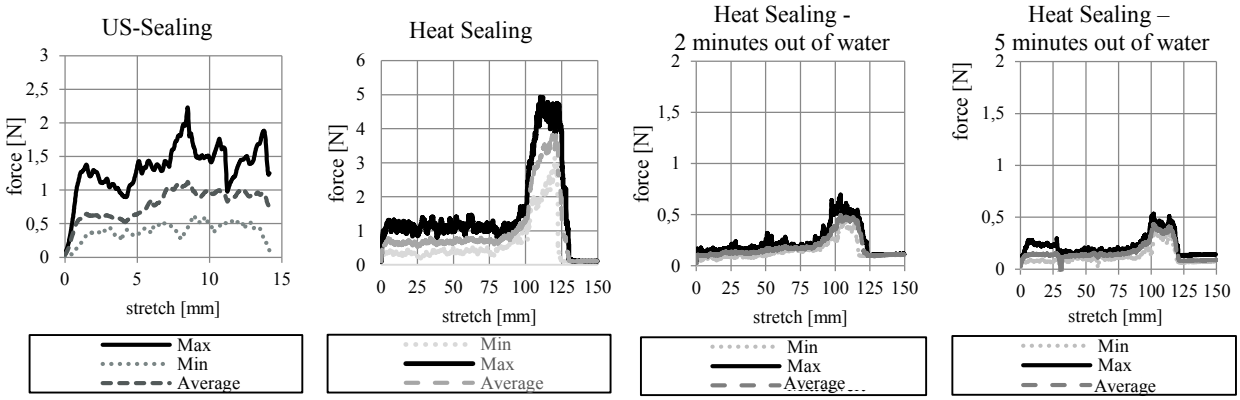

Figure 7: Comparison of tensile tests of ultrasonic sealing and heat sealing, and after water intake

Figure 7 shows that dry ultrasonic-sealed membranes reach a maximum peel strength of 2.23 N, which is significantly lower than the maximum peel strength of heat-sealed membranes (4.93 N). It also shows the difference between non-sealed and sealed areas. Thus, it can be concluded that sealing does in fact have an impact on the peel-off strength of dry membranes. Since heat sealing provided better results, it was chosen for the upcoming experiments. All results are summarized in Table 2.

With wet, heat-sealed membranes (after 2 or 5 minutes out of water), the resistance against delamination is drastically lower than in a dry state. It shows that the maximum peel-off strength of heat-sealed membranes that had been out of water for only 2 minutes is approximately the same as for the reference membrane (non-sealed). Measuring the peel-off strength every 15 minutes demonstrated that resistance against delamination

rises with time out of water until it is back at the level of dry heat-sealed membranes. Figure 8 shows the peel-off strength of the sandwich membrane after the climatic chamber and after 30 minutes out of water.

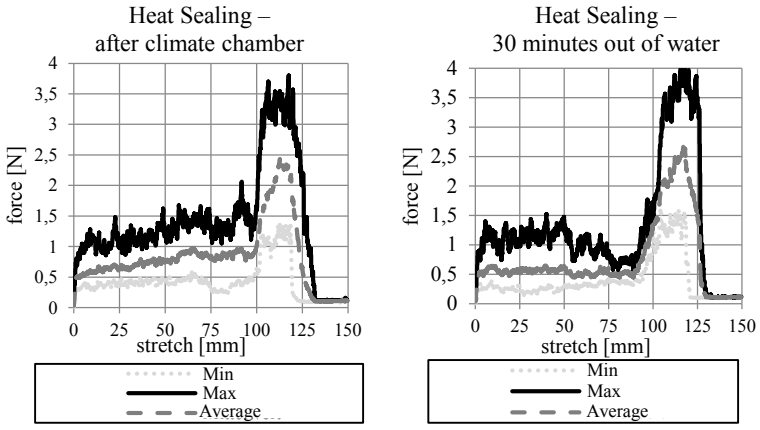

Figure 8: Tensile stress after climatic chamber and after drying process

Figure 8 shows that, after 30 minutes out of water, the resistance against delamination again reaches the level of dry, heat-sealed sandwich membranes. Likewise, the sandwich membrane outside of the climatic chamber is almost in no time at the level of a dry, heat-sealed sandwich-membrane.

To examine an additional non-conventional sealing process, adhesive bonding was investigated as a means to prevent delamination. The investigation assessed whether pre-sealing before adhesive bonding would improve resistance against delamination in the sandwich-membrane samples. The samples were pre-sealed using heat sealing before applying adhesive on the sealing seam. Figure 9 illustrates the results of these experiments.

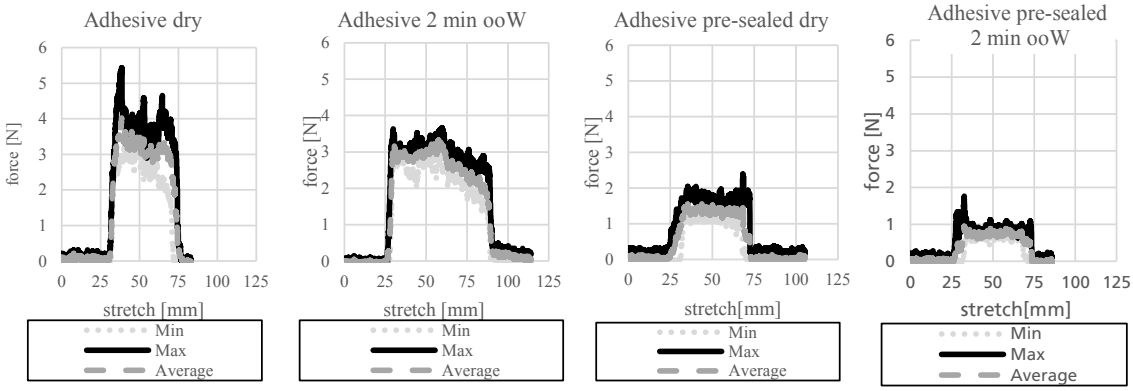

Figure 9: Comparison of tensile test of adhesive bonding as sealing with and without pre-sealing

The resistance against delamination of the dry adhesively bonded membranes is nearly equivalent to that of the heat-sealed membranes (5.43 N adhesive | 4.93 N heat-sealing). Even though the resistance against delamination decreases when submerged in water, the decrease is less pronounced compared to the heat-sealed membranes (3.60 N adhesive | 0.69 N heat-sealing | 2 min ooW). In general, non-pre-sealed membranes are able to sustain higher peel-off forces than pre-sealed membranes. When pre-sealed membranes are exposed to water, the decrease in peel-off strength is more substantial compared to non-pre-sealed membranes. Nevertheless, resistance is still higher than that achieved only by heat sealing. The results are summarized in Table 3.

5. Discussion

5.1 Optical investigations

Figure 5 presents the membrane after the peel-off process. The structure remaining on the PFSA membrane is cratered, resembling a negative imprint of the non-woven fibres. The SEM image in Figure 6 indicates that, typically, the PFSA is present around the fibres and subsequently torn off during the peel-off process. Consequently, the effect of wet delamination is not due to a lack of adhesion but due to lower cohesive forces within the PFSA. A decrease in mechanical strength of PFSA while humidified has been observed in past research [4,8,2] .

Additionally, it was found that one non-woven layer is easier to peel off than the other. This circumstance might be due to the manufacturing process of the sandwich-membranes. Due to the roll-to-roll manufacturing process, the non-woven layers may be applied at different points in time or at different stages in the process.

5.2 Sealing processes

Figure 7 and Figure 8 demonstrate that heat sealing and ultrasonic sealing enhance the pull-off force. This observation points to an adhesive effect. During sealing, the contact area between PFSA membrane and non-woven layers increases, increasing adhesive strength in those areas. Combined with mechanical interlocking, the overall strength of the bonding between PFSA membrane and non-woven layers increases.

Notably, heat sealing proves to be more effective than ultrasonic sealing, which could be expected since ultrasonic sealing uses only a small line contact for sealing. This effect seems to result from two impacts: the non-continuous nature of the non-woven results in pores within the layer. In those areas, melting material is less available (compared to solid materials), potentially leading to lower adherence between non-woven layer and PFSA. Heat sealing allows for sealing a more extensive area, so the probability of melting areas with more fibres is higher. Additionally, the intermittent contact between the non-woven layer and PFSA membrane in the line contact area can result in a non-continuous seam for ultrasonic sealing. Fibres may not be present in some areas along this line of contact. Consequently, ultrasonic sealing exhibits lower durability than heat sealing. In contrast, the seal seam of the heat-sealing process is broader, and by taking more time and pressure, ensures more material in the contact area.

In both cases, water intake weakens the strength of the seal seams. It can be attributed to a two-fold effect. Firstly, the difference in swelling due to water intake for PFSA and a non-woven layer could reduce the adherence between these two materials. [9] Secondly, the mechanical strength of PFSA decreases under humid conditions. [8] This effect is underpinned by the sandwich membrane exhibiting greater resistance against delamination when dry compared to when wet.

Noteworthy is that the effect of decreasing resistance against delamination seems to be reversible. As the membrane gradually dries, the resistance increases once again. Another notable observation is the marked disparity in the effect between the experiments conducted in humid air in the climate chamber and the membranes exposed to pure water. The effect appears to be significantly stronger when PFSA is exposed to pure water rather than humid air. Since water intake of PFSA is drastically higher when exposed to liquid water instead of saturated water vapour [10], it can be assumed that delamination is directly related to water intake of PFSA membranes. This suggests that heat sealing could provide a durable sealing seam during flat humidifier operations when the membrane is not exposed to liquid water.

5.3 Adhesive bonding as sealing

The resistance against delamination for dry adhesively bonded membranes is slightly higher than for heat-sealed membranes. This suggests that the adherence between PFSA membrane and adhesive is slightly stronger than the bonding between heat-sealed non-woven and PFSA membrane. The adhesive effectively

fills the pores of the non-woven layer and adheres to PFSA. As a result, the contact area between PFSA and non-woven/adhesive increases, enhancing delamination resistance.

The adhesive bonding experiments did not point to significant differences in peel strength between the wet and dry state. Several explanations could account for this effect. Since the adhesive has an elongation at break of 210 %, it might compensate for the difference in swelling caused by water intake in non-woven fibres and PFSA. Thereby, the adhesive force is maintained. Another possibility is that the adhesive limits the absorption of water of PFSA, resulting in less swelling of PFSA.

When examining the pre-sealed adhesively bonded samples, the resistance against delamination is not equally strong. Pre-sealing the membranes melts the non-woven fibres and therefore closes the pores of the non-woven. Consequently, the adhesive cannot flow through the pores sufficiently and adhere to the PFSA. Hence, the positive effect of adhesive bonding is reduced when dealing with pre-sealed membranes.

6. Conclusion

The goal of this paper was to explore methods to enhance the resistance against delamination in humidified conditions for sandwich membranes during the operation of a flat membrane humidifier. Firstly, the structure of the PFSA membrane was optically analysed. Subsequently, different sealing methods, including ultrasonic sealing, heat sealing, sealing by adhesive bonding support, and sealing by adhesive bonding support with additional pre-sealing were investigated under both dry and wet conditions.

It was observed that conventional sealing technologies did not exhibit a strong positive effect against delamination in wet conditions. However, adhesive bonding support showed promising results, significantly increasing the resistance against delamination in both wet and dry conditions. Surprisingly, the combination of pre-sealing and adhesive bonding did not yield a positive effect. In the end, adhesive bonding as a support against delamination emerged as the most promising approach in this study.

Acknowledgements

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Appendix

Table 1: Parameter of sealing techniques used (4. Material, Machines, and Methods)

Process	Force	Power	Sealing time	Amplitude
Ultrasonic sealing	500 N	200 W	0.3 s	0.04 mm
Process	Pressure	Temperature	Sealing time	-
Heat sealing	2 MPa	220°C	2 s	-

Table 2: Results of the sealing techniques (4.2. Results of Sealing Experiments)

Process	F_{max}	F_{min}	$F_{Ø}$	SD	SD/ $F_{Ø}$	sample width
Ultrasonic sealing	2.23	0.,96	1.42	0.47	0.33	15 mm
HS - dry	4.93	3.19	4.32	0.61	0.14	15 mm
HS – 2 min ooW	0.69	0.49	0.59	0.07	0.12	15 mm
HS – 5 min ooW	0.8	0.32	0.74	0.05	0.07	15 mm
HS – 10 min ooW	2.81	1.21	1.60	0.61	0.38	15 mm
HS – 20 min ooW	5.16	2.14	4.11	1.03	0.25	15 mm
HS – 30 min ooW	4.18	2.05	3.01	0.92	0.31	15 mm
HS – CC	3.8	1.55	3.25	0.43	0.13	15 mm
reference membrane	0.63	0.54	0.59	0.02	0.03	15 mm

Table 3: Results of sealing techniques (4.2. Results of Sealing Experiments)

Process	F_{max}	F_{min}	$F_{Ø}$	SD	SD/ $F_{Ø}$	sample width
Adhesive dry	5.43 N	3.60 N	4.56 N	0.75	0.16	15 mm
Adhesive 2 min ooW	3.67 N	3.60 N	3.63 N	0.03	0.01	15 mm
Adhesive pre-sealed dry	2.68 N	2.01 N	2.35 N	0.27	0.12	15 mm
Adhesive pre-sealed 2 min ooW	1.91 N	1.41 N	1.62 N	0.21	0.13	15 mm

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Biography

Gregor Müller (*1992) is a research associate at the Fraunhofer Institute for Manufacturing Engineering and Automation IPA which he joined in 2021. He was working in the mechanical construction department at Siempelkamp Maschinen- und Anlagenbau GmbH. He studied production engineering at the RWTH Aachen University and is an Alumnus focusing on mechanical engineering and automation

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