RELATIONSHIP BETWEEN FIBER HUMIDITY AND FIBER PERMEABILITY IN PVDF-BASED MEMBRANES

Rafael Szabó*

Suez Water Technologies and Solutions, Blathy Otto utca 4, Oroszlany, Hungary, H-8360

*rafael.szabo@suez.com

Abstract

Fiber humidity and fiber permeability were measured in 678 samples of polyvinylidene-difluoride based fiber membranes, and then their relationship was investigated. We found that this can be described by a three-variable regression function. For 220 samples, we examined the effect of rewetting prior to permeability measurement. The result was that soaking for at least 12 hours was required for the membrane to reach maximum permeability.

Keywords: PVDF membrane; membrane drying; membrane permeability; membrane humidity

Összefoglalás

678 polivinilidén-difluorid alapú membránszálon mértük a szálnedvességtartalmat és a szálpermeabilitást, majd ezek kapcsolatát vizsgáltuk. Megállapítottuk, hogy az összefüggés leírható egy háromváltozós regressziós függvénnyel. 220 minta esetében kutattuk az

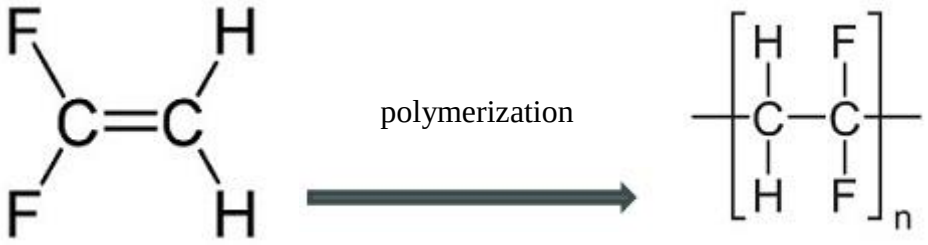
újranedvesítés hatását a szálpermeabilitás méréseket megelőzően és azt tapasztaltuk, hogy legalább 12 óra áztatás szükséges annak érdekében, hogy a membránszál elérje a maximális permeabilitását.

Kulcsszavak: PVDF membrán, membrán kiszáradás, membrán permeabilitás, membrán nedvességtartalom

Introduction

The use of membrane water treatment technology has been popular since the 1940s and continues up-to-now *(Pendergast and Hoek, 2011)*. At present, organic polymer-based membranes are used in almost all industrial sized applications and the most widely used of them is polyvinylidene-difluoride (PVDF) due to its outstanding properties *(Liu et al., 2011).* In this case PVDF ultrafiltration membranes were chosen for the research.

PVDF is a semi-crystalline substance composed of – (CH_2CF_2) – units (Fig. 1.). It has a high mechanical and chemical resistance, quite stable under higher temperatures and extremely resistant against ageing. Its use is not limited to micro- and ultrafiltration, but includes bioreactors, gas separation, and desalinating equipment, too *(Kang, et al., 2014).* All of these features make this material a superb raw material for sheet and fiber membranes, too *(Liu, et al., 2011).*



1,1-difluoroetilene PVDF

Fig. 1. Structure of 1,1-difluoretilene and PVDF (SpecialChem, 2020)

The main objective of the study is to validate or discard the need of rewetting before membrane fiber permeability measurements on fibers with different water content. From the obtained data, we would like to deduce whether the membrane drying is reversible and how the permeability of the membrane changes as a function of the rewetting time. I would like to find a reasonable rewetting time, what is enough to get a realistic picture of the expected operating filtration performance after the fiber permeability measurements. If such exists, I would like to describe the relationship between fiber humidity and fiber permeability

Materials and methods

Membrane type

Polyvinylidene-difluoride (PVDF) based wastewater treatment membranes were used in the study, with pore size between 0.02-0.04 μm, so this was in the ultrafiltration range (0.01-0.1 μm). This membrane is a tubular, supported type, what means that it has an inner polyethylene terephthalate (PET) yarn frame. To this shoelace-like skeleton comes the membrane layer during the production, what was thermally induced phase separation (TIPS). The final membrane fiber has approximately 2000 μm diameter (Fig. 2.). From water solutions this membrane can separate macro and micro particles, macro molecules, parasites, bacteria,

suspended solids, some viruses, proteins and colloids *(Morao et. al., 2001).* Practically it means that this is for cleaning of municipal and industrial wastewaters (*Szabó and Anda, 2018*).

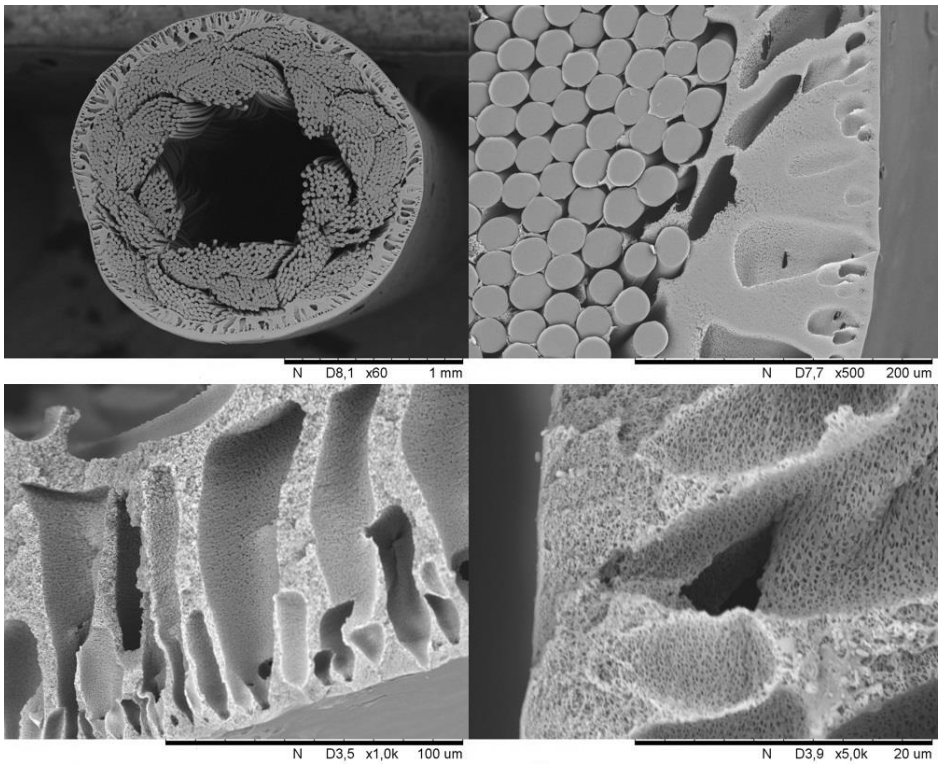


Fig. 2. SEM pictures of PVDF based supported membranes made with a Hitachi S-3000N microscope

Accelerated drying

During the experiments, the samples were dried in a temperature-adjustable VWR VENTI-Line oven at 60°C. The drying time varied depending on how low fiber humidity was to be prepared.

Fiber humidity measurement

The fiber humidity was measured with a Sartorius MA 35 moisture meter equipment (Fig. 3.). The device consists of a heating unit, a weight scale and a combined display and control panel. The humidity determination method is based on the thermogravimetric principle, the resolution of the device is 0.01%. In the first step of the measurement, the wet weight of the membrane fiber was measured, then the apparatus was heated to 110°C and the fiber was dried

for 5 minutes. During this time, the fiber dries to constant weight, so after another measurement, the dry mass can be obtained and thus the moisture content can be calculated in a simple division.

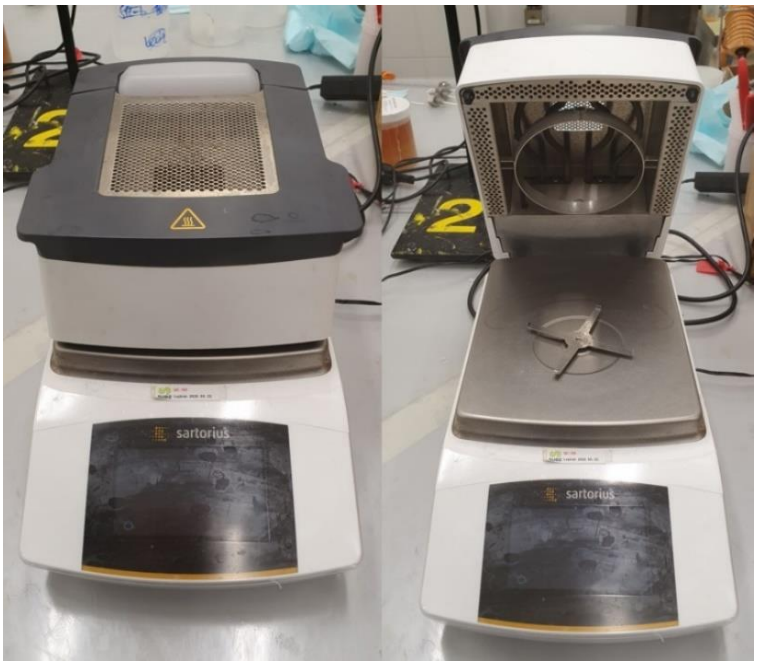


Fig. 3. Sartorius MA35 moisture meter equipment

Fiber permeability measurement

Fiber permeability was measured in low-ionic content water over a period of 5 min and at a pressure of 5 PSI using a custom-made equipment manufactured and calibrated by the manufacturer. The device consists of pipes that can be pressurized and filled with low-ionic water. During the measurement, the fiber must be placed in the machine in such a way that a piece of fiber of known length is located inside one of the tubes, surrounded by water. Based on the length and knowing the diameter of the fiber, the surface can be calculated. The two open ends of the membrane fiber stick out from the tube - this can be solved by first gluing them to a connector part - and after the pressure has been built up, the liquid entering the fiber flows through them. This is because water flows through the pores towards the lower pressure

space, i.e. to the lumen of the fiber. The effluent permeate can be collected in a vessel and the amount can be measured (Fig. 4.).

Fig. 4. Membrane sample prepared for measurement, permeability measuring device and measuring cup for permeate water

Fiber permeability was calculated with the next formulas:

$$J = \frac{\delta V}{A \cdot \delta t} \qquad (1)$$

Where J is the flux measured through the membrane surface A, δV is the amount of permeate and δt is the flow time of the liquid.

$$\Phi = \frac{\frac{J}{\frac{\delta P}{\mu_1}}}{\mu_0} \qquad (2)$$

Where Φ is the permeability, J is the flux at δP pressure, μ_1 is the viscosity of water at the temperature of the measurement, and μ_0 is water viscosity at 20 °C. Flux was calculated by the next formula

Statistical methods

During the drying and rewetting experiments, it was necessary to determine the equality or difference of the data group means and for this we chose the one-way ANOVA method.

To use the ANOVA test, the examined data must meet two conditions, on one hand, they must be normally distributed, and on the other the variances of the examined groups must be homogenous. For the normality test, the Kolmogorov – Smirnoff test and the Anderson – Darling tests were performed. The Levene test was used for the homogeneity test.

We used a three-variable regression function to describe the relationship between fiber humidity and fiber permeability. The parameters of the regression function were found by an iteration method using the Gauss-Newton algorithm.

Minitab 18.1 statistical software was used to perform detailed statistical studies *(Minitab, 2017)*. The choice was made because it is widely used and contains a large selection of the necessary statistical methods.

Results and discussion

Relationship between fiber humidity and fiber permeability

After studying 678 samples, the relationship between fiber humidity and fiber permeability was evaluated. The following approximation function was used:

$$\varphi_i = \varphi_{max} - a_1 * e^{-a_2 * x} \qquad (3)$$

Where φ_i is the measured membrane permeability value, φ_{max} is the maximum permeability value of freshly manufactured membranes, a_1 and a_2 are the parameters of the regression function determined by Gauss-Newton iteration method and x is the fiber humidity of the measured membrane sample.

Determining the value of φ_{max} as a constant – in our case it was 65 gfd / psi – and identifying this with the empirical maximum value of the membrane fiber, we reduced the number of variables of the three-variable nonlinear functions to two. The maximum value was determined by taking the top 5% of the historical data and averaging it and then rounding it to the nearest whole number. In determining the values of the variables, we examined the stability and convergence of the iteration. The acceptance criterion was always the minimum of the calculated sum of squares errors (SSE) from the possible function forms.

The initial values of the iteration were determined by forming the natural logarithm of the differences of φ_{max} and φ_i and plotted against the corresponding fiber humidity values, i.e. x. A negative directional tangent was fitted to the points with the least squares method. From the obtained axis section and directional tangent, the searched parameters could be determined. A suitable range was determined around the initial values obtained and iteration was performed. From the obtained functions, the one with the smallest SSE of the regression was chosen as the best. This function is shown on Figure 5.

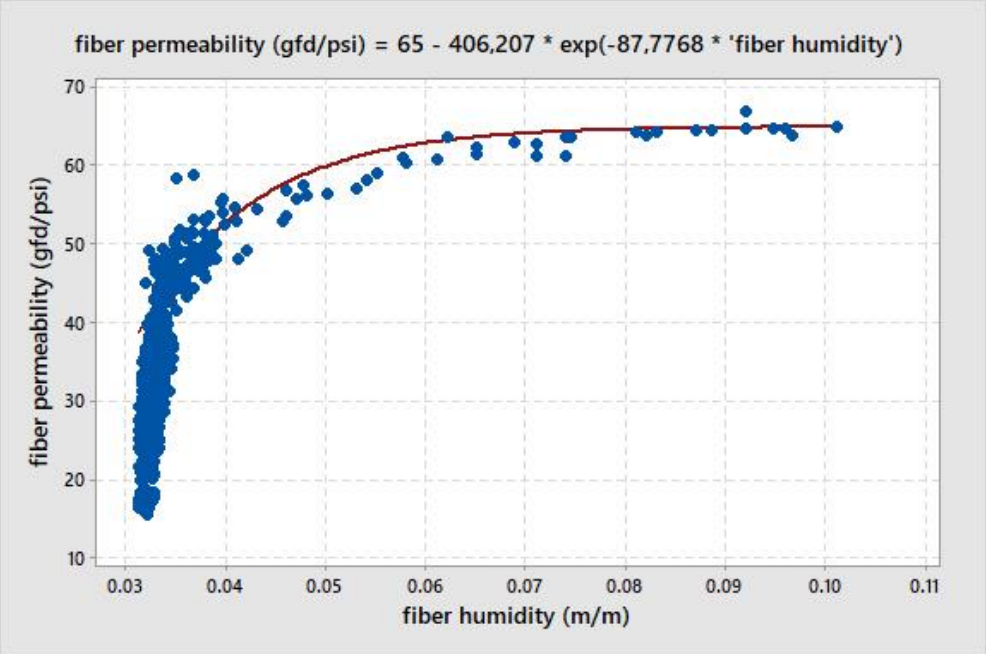


Figure 5. A function describing the relationship between fiber permeability and fiber humidity

Membrane rewetting measurements

During the experiment, 220 samples were dried, fiber humidity was measured, then the membranes were rewetted, and permeability was measured. The oven-dried samples with a given moisture content were rewetted by soaking in low-ionic water for 2, 12, 24 and 48 hours and then their permeability was measured. As a starting point, non-soaking fibers were also measured, which were subjected to permeability measurement immediately after drying.

Permeability values of the membrane samples after different rewetting times are shown on Figure 6.

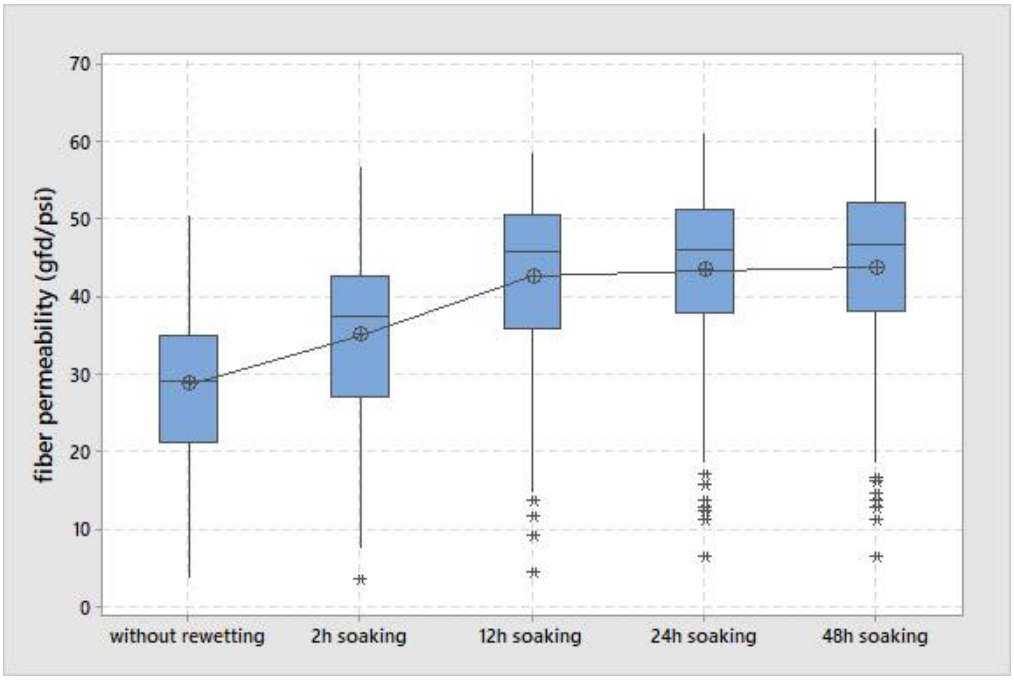


Fig. 6. Comparison of permeabilities of membranes with different rewetting times

Analysis of variance (ANOVA) was performed to determine if the average permeability of samples for a given soaking period varied as a function of rewetting time. Before performing ANOVA, we verified its applicability. Normality was examined in all cases, and since they showed a normal distribution and the standard deviations could be considered identical, there was no theoretical obstacle to performing the analysis of variance. For the former, ANOVA was considered valid for the entire population. We can state that the individual groups cannot

be considered the same - since the value of p (x) became 0.00, which is lower than the value of p = 0.05 at the 95% significance level - and thus the alternative hypothesis is true, i.e. there is a difference between the averages.

The previously described 3-parameter functions, together with the equations, fitted to the points showing the fiber humidity – fiber permeability relationship measured on the membranes, together with the equations, are presented below. Figure 7. shows the fibers without soaking, Figure 8. shows the values measured on the membranes after 2 hours, Figure 9. after 12 hours, Figure 10. after 24 hours and Figure 11. the values measured on the membranes after 48 hours.

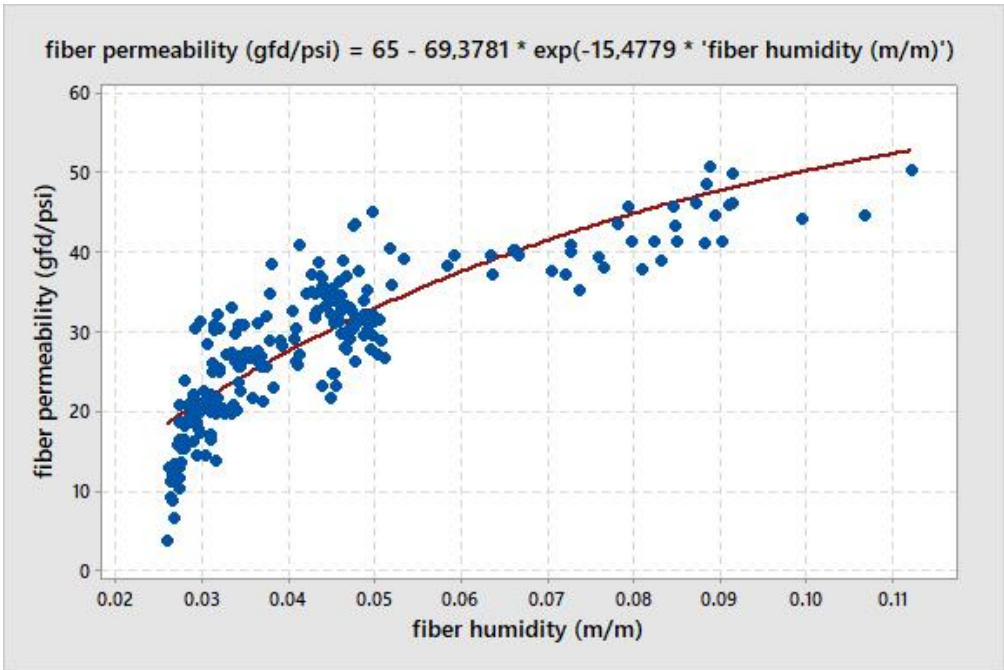


Fig. 7. Relationship between fiber permeability and fiber humidity without rewetting

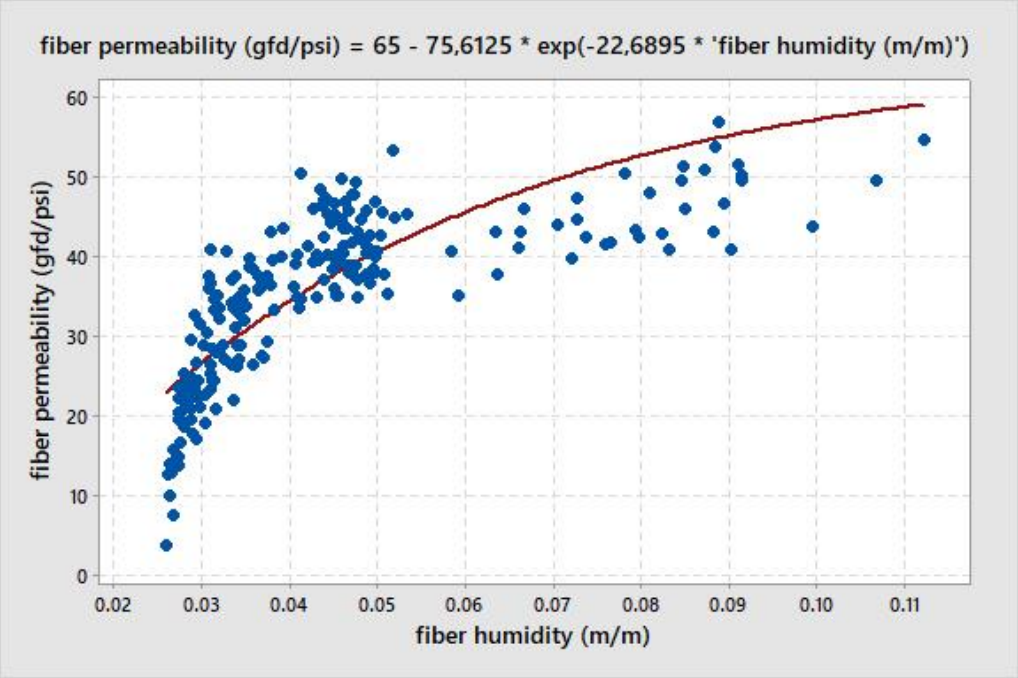


Fig. 8. Relationship between fiber permeability and fiber humidity after 2h soaking

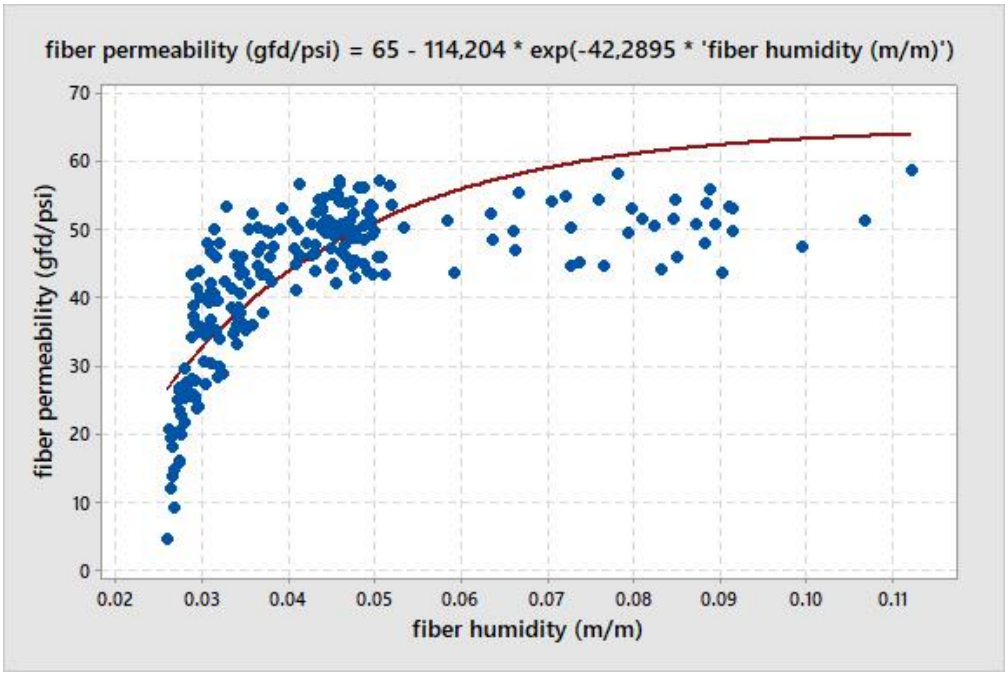


Fig. 9. Relationship between fiber permeability and fiber humidity after 12h soaking

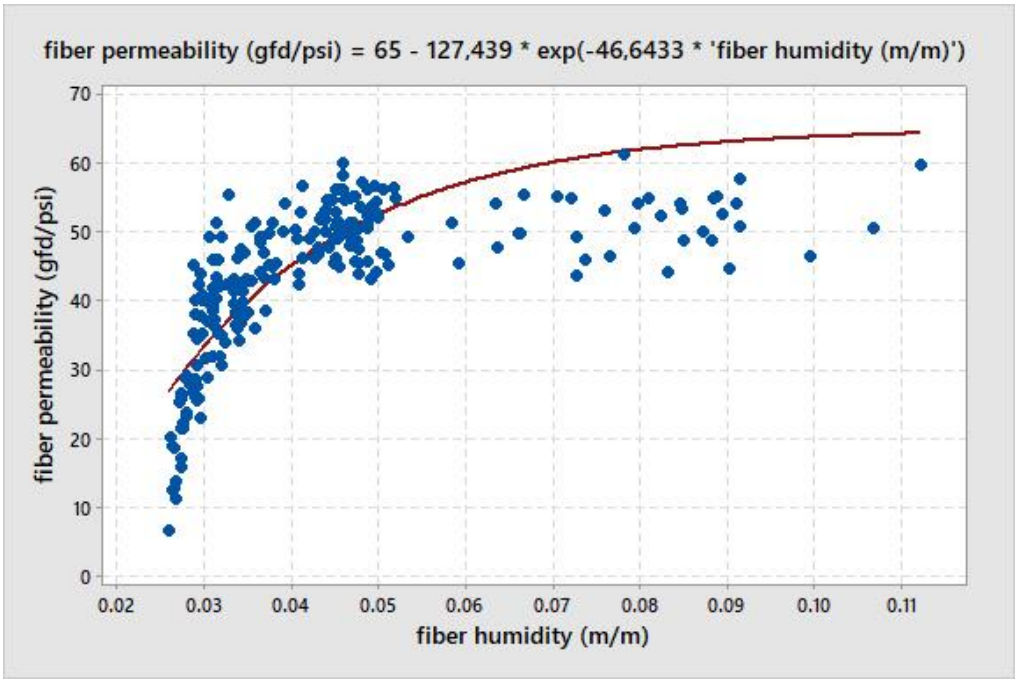


Fig. 10. Relationship between fiber permeability and fiber humidity after 24h soaking

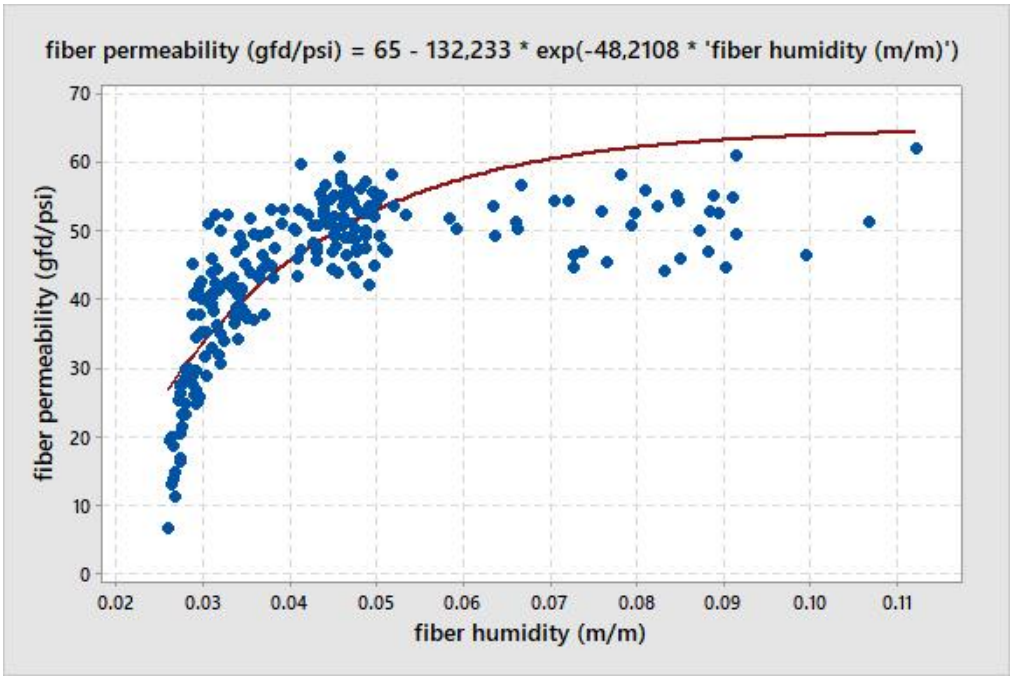


Fig. 11. Relationship between fiber permeability and fiber humidity after 48h soaking

The patterns shown in the figures confirmed the results of ANOVA, i.e. the permeability measured on membranes without soaking was lower than where the measurements were preceded by rewetting, i.e. drying is reversible.

We compared the two extreme groups of the experiment, i.e., the samples without soaking, with those that had spent 48h in low-ionic water prior to the permeability measurement. The aim was to prove our hypothesis that rewetting plays a role in the increase of permeability.

Comparing the two graphs in Figure 12., the difference in the distribution of permeability values can be clearly seen. After 48 hours of soaking, the permeability definitely increased compared to the values without soaking, which can be attributed to the fact that the membrane pores became more permeable under the influence of water. This is explained by the fact that the glycerol remaining in them absorbs water due to its hygroscopicity, even though the hydrophobic membrane makes this difficult.

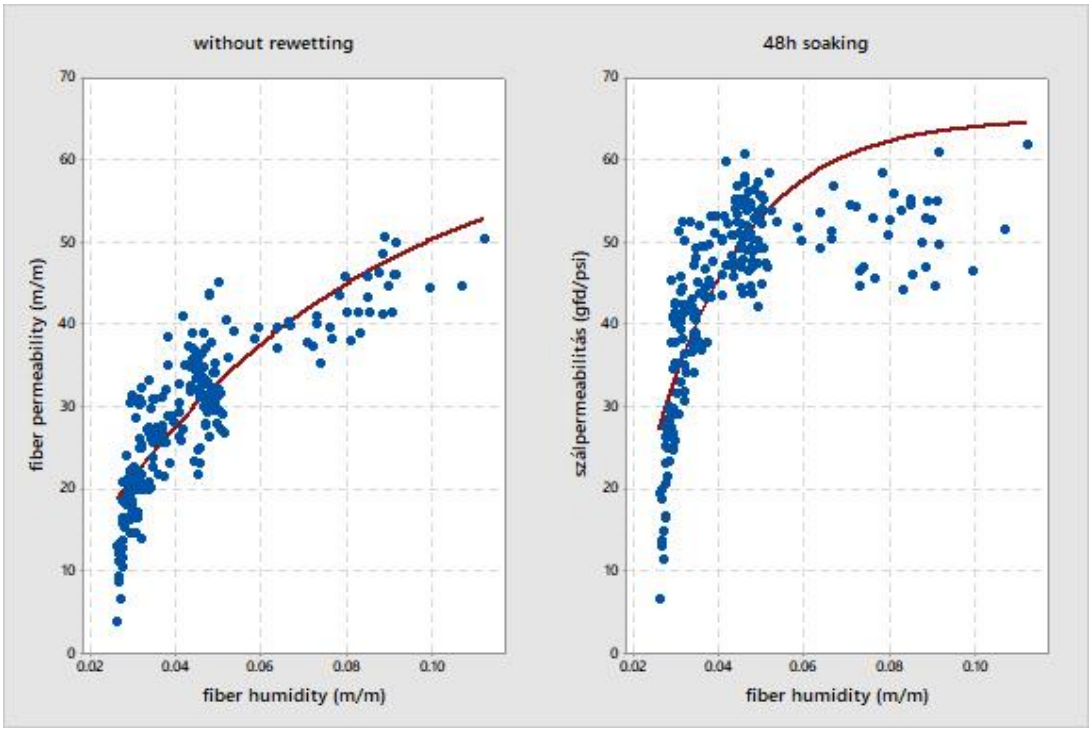


Fig. 12. Comparison of samples measured without rewetting and after 48h soaking

The change in permeability can be seen even more clearly on Figure 13., where the values without rewetting were subtracted from the permeability values measured after 48 hours of soaking. The differences obtained were plotted as an increase in permeability as a function of fiber humidity. It can be seen that after 48 hours of soaking, the permeability of samples with initially lower fiber humidity increased to a greater extent. This can be explained by the fact that the pore diameter decreased due to the evaporating water, more evaporation resulted in smaller pores and lower fiber moisture content, and the measurements showed lower permeability. The glycerin remaining in the pores of the membranes with lower fiber humidity absorbed water during wetting, the higher the glycerin concentration, the more absorbed water, thereby increasing the pore size to the greatest extent, resulting in the highest increase in permeability.

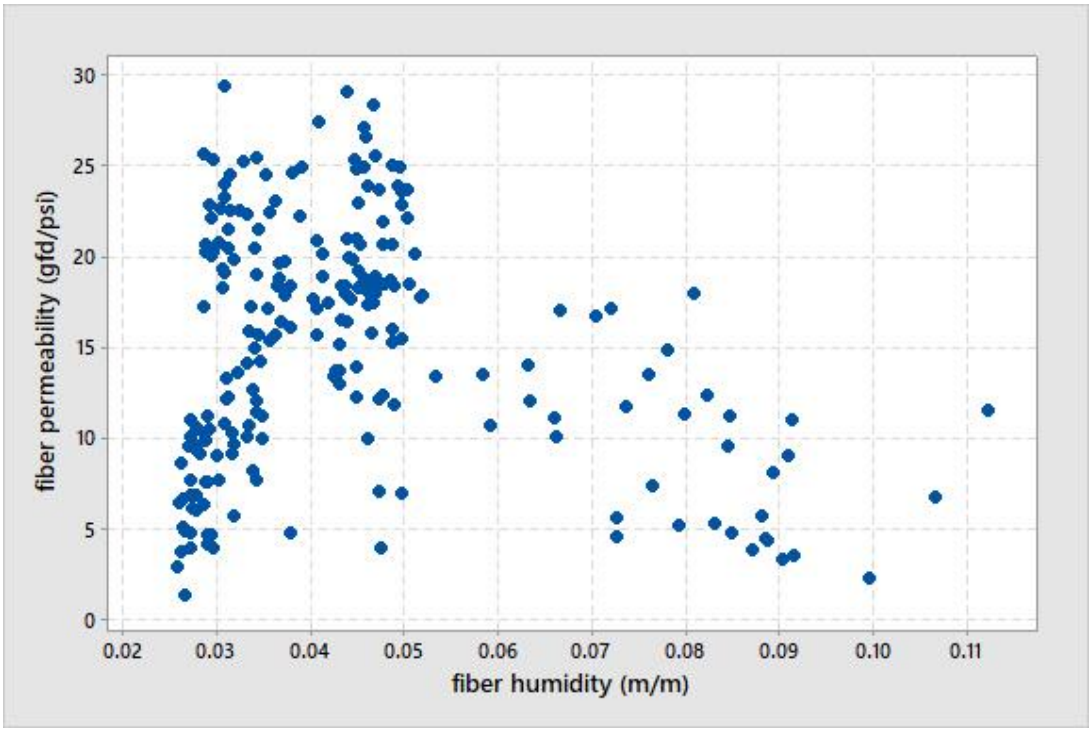


Fig. 13. Difference in permeability of membranes without rewetting and soaking for 48 hours as a function of membrane moisture

Conclusions

We described the relationship between fiber permeability and fiber humidity with an approximate equation that can be written as follows:

$$\varphi_i = \varphi_{max} - a_1 * e^{-a_2 * x}$$

The significance of the determination of the equation comes from the fact that with its help it is possible to approximate the fiber permeability only by performing in-situ fiber humidity measurements, from which we can deduce the expected operating performance, i.e. permeability.

We found that soaking prior to permeability measurements had an important role in the values obtained. After our tests we consider it necessary to soak for at least 12 hours, so we recommend this as a minimum rewetting time before measurement.

References

Kang, G. D., Y. M. Cao. 2014. Application and Modification of poly(vinylidene fluoride) (PVDF) membranes – A review, *Journal of Membrane Science* **463**. 145–165.

Liu, F., N. A. Hashim, Y. T. Liu, M.R.M. Abed, K. Li. 2011. Progress in the production and modification of PVDF membranes, *Journal of Membrane Science* **375**. 1–27.

Minitab 18.1, Minitab LLC. 2017. State College, Pennsylvania, U.S.A.

Morão, A., Brites Alves, A. M., Cardoso, J. P. 2001. Ultrafiltration of demethylchlortetracycline industrial fermentation broths, *Separation and Purification Technology* **22–23.** 459–466.

Pendergast, M. M., Hoek, E. M. V. 2011. A review of water treatment membrane nanotechnologies, *Energy & Environmental Science* **4**. 1946–1971.

SpecialChem. 2020. Polyvinylidene Fluoride (PVDF): Complete Guide, https://omnexus.specialchem.com/selection-guide/polyvinylidene-fluoride-pvdf-plastic#content

Szabó, R., Anda, A. 2018. Drying of water treatment membranes, *Filtration and Separation* **55**. 22-27.