Activation of PVDF flat sheet membrane through facile hydroxylation of polymeric dope

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Abstract

Poly(vinylidene fluoride) (PVDF) membranes are very important in several applications due to their chemical and physical properties. Tuning the properties of this material enables a sharp selectivity for the target application. One of the direct methods to achieve this goal is the selective functionalization with labile groups like OH. In this study, an effective method of PVDF functionalization was developed toward the fabrication of functionalized PVDF flat sheet membrane. A modified two-step alkali/acid treatment was developed. The advantage of this method is the application of short time-duration of modification under mild stress of alkali media (5% KOH). Extensive physicochemical (CA, SFE, W_{adh} , γ_{cr}), material (mean flow pores, bubble point) and surface (roughness, S, F_{adh}) characterization were performed on the prepared membranes, applying goniometric, microscopic, surface and spectroscopic methods. Moreover, the deep wetting characterization analysis was done by determining the mechanism of wetting (dynamic measurements), critical surface tension, and spreading pressure. Strong influence of roughness on the hydrophobicity level was observed and hence the modified membranes possessed higher contact angle values ($> 120^\circ$). The efficiency of the alkali treatment was determined by TGA-MS, ATR-FTIR, and Raman spectroscopy.

Keywords: PVDF, modification, dehydrofluorination

1. Introduction

Membrane technology possesses a huge potential to be utilized in different industrial applications including petrochemicals and pharmaceutical industries, water and wastewater treatment, and food and beverages industries. One of the widely used membrane materials is poly(vinylidene fluoride) (PVDF). PVDF is a highly inert and pure thermoplastic fluoropolymer made by the polymerization of vinylidene difluoride. It possesses high thermal and mechanical stability, and excellent chemical and UV resistance ¹⁻⁵. Therefore, it is commonly utilized in various applications such as microfiltration and ultrafiltration processes, membrane distillation (MD), and membrane contactor ⁶⁻¹². Furthermore PVDF has good thermodynamic affinity with various polymers such as hexafluoropropylene (HFP) ¹³⁻¹⁴, chlorotrifluoroethylene (CTFE) ¹⁵, and methyl methacrylate (MMA) ^{1, 16-17}. It is also an appropriate candidate in bio-separation and biomedical applications, due to the low level of extractables present in it ^{18-20,21}. It has found applications in cell encapsulation, drug delivery, water softening, electronic devices, and sensors ²²⁻²³.

In some applications, inherent hydrophobic characteristics of the PVDF membrane poses some limitations. For example, its hydrophobicity causes low water permeability and rapid fouling in micro/ultrafiltration membranes. It also causes attenuation in the water transport mechanism and/or non-compatibility of hydrophilic additives during membranes fabrication process such as phase separation¹. The aforementioned disadvantages are significant when membranes are used for treating aqueous solutions containing natural colloidal and organic matters as they are prone to adsorb and deposit on the membrane surfaces ⁴⁶. These challenges increase the need to overcome the limitations of PVDF by various modifications.

Physical and/or chemical modifications are employed in order to fine-tune the target-specific membrane properties. Physical modification usually involves the introduction of various nanomaterials such as carbon nanotubes ³⁴⁻³⁵, titanium dioxide ^{6, 36-38}, aluminum oxide ³⁹, and metal organic frameworks ⁴⁰⁻⁴¹ into the polymeric membrane matrix. On the other hand, chemical methods involve adsorption ^{18, 26}, coating ²⁷⁻²⁹, graft polymerization, and alteration of membrane materials ^{2, 24-25}. Due to its inert nature, most of the chemical modification methods require the initial activation of PVDF membrane surface. One such approach is the hydroxylation of PVDF surface so as to utilize the resulting hydroxyl groups as the anchorage points for the covalent immobilization of chemical moieties. Plasma irradiation ^{38, 43-44}, gamma and X-ray irradiation ⁴⁷⁻⁴⁸, electron beam radiation⁴², and ozone method ⁵⁰⁻⁵¹ were studied for the hydroxyl generation followed by modification of PVDF membranes. However, the above-mentioned methods were not efficient in the generation of OH groups ^{1, 45}. Chemical treatment of PVDF with acidic or basic treatment were reported to enhance their hydrophilicity/wettability. However, it requires long acid/alkali treatments (~12-48 hours) under severe conditions. There are reports indicating that PVDF polymer suffer from degradation by treatment with strong base like sodium hydroxide (NaOH) (ref). Generally, during the PVDF alkali-treatment, high concentration of alkali medium was used (up to 12M) ^{4, 25, 53-54}. Moreover, the modification was maintained at longer exposure time (up to 48h), otherwise, phase transfer catalyst was essential to complete the reaction ^{4, 25, 53-54}. The higher concentration of NaOH and the elevated temperature promotes the degradation process. Furthermore, intensive treatment with alkali followed by sulfuric acid, degrades the non-woven support of the flat sheet membrane. Therefore, it is crucial to achieve a suitable experimental protocol for membrane modification using alkaline media. There is a dearth of literature on the PVDF membranes treatment under mild condition (short treatment period and low concentrations of alkaline solution) taking into consideration of the impact of such

treatment on the material properties and membrane performance. In this study, we propose an efficient protocol for the hydroxyl group functionalization of PVDF flat sheet membranes. The reaction conditions were selected to enhance flat sheet membrane morphology and performance. The method involves two-step non-aqueous chemical modification including dehydrofluorination of the virgin polymer followed by hydroxylation step using H_2SO_4 . Extensive physicochemical (CA, SFE, W_{adh} , γ_{cr}), material (mean flow pores, bubble point) and surface (roughness, S, F_{adh}) characterization were performed on the prepared membranes, applying goniometric, microscopic, surface and spectroscopic methods. Moreover, the deep wetting characterization analysis was done by determining the mechanism of wetting (dynamic measurements), critical surface tension (γ_{cr}), and spreading pressure.

2. Experimental section

2.1. Materials

The polymer, solvent, and non-solvent used to make the membrane were PVDF (HSV900, Arkema, MW 92840 Da), dimethylacetamide (DMAc, Sigma Aldrich, $\geq 99.5\%$), and deionized water (Elix, Millipore) respectively. Sulfuric acid (95-97%), Methanol (98 %) and potassium hydroxide ($\geq 85\%$) were purchased from Sigma Aldrich (USA). All the chemicals were used as received.

2.2. PVDF modification and membrane fabrication

In this study, pristine and modified membranes were fabricated through immersion precipitation method. Initially, for the pristine membrane, PVDF powder (10 g) was dissolved in DMAc (90 g) by stirring for 24 h to obtain 10 wt. % polymeric dope solution. For the modified membranes, a dehydrofluorination step was performed, by mixing PVDF powder (10 g) with 5 wt. % KOH in methanol (100 mL) for 5 and 30 minutes at room temperature. In

both cases, the PVDF powder was separated from the solution by centrifugation, decantation and subsequent washing with pure methanol (5x) to remove excess of KOH, followed by drying at 70°C for 24 h prior to further treatment. The resulting PVDF powder was further treated with 98% H₂SO₄ (50 mL) at 80°C for 12 h in order to complete the second step of modification. The resulting suspension was centrifuged, decanted, and dried at 80°C for 24 hours. In the case of 30 min KOH treatment, centrifugation was essential due to the presence of some agglomerations in the final dope. Dope solutions were kept idle for ~ 24 h for degassing and further homogenization. Membranes were formed by casting the polymer dope on a non-woven support (Novatexx 2483, Freudenberg-Filter, Germany) using a thin film applicator (3580 Elcometer) with a solution gap of 250 µm at 24°C followed by immersion in a coagulation bath containing deionized water for 1 h. Membranes were then dried at room temperature for 24 h. A commercial flat-sheet PVDF membrane was treated with 30% aqueous NaOH solution followed by 12 h treatment with conc. H₂SO₄ in order to assess its compatibility with a mild alkali and conc. acid.

2.3.Membrane characterization

Contact angle and surface free energy. Pristine and modified PVDF membranes were characterized by determination of apparent contact angle (CA) using 3 µL drop of ultra-pure liquid. Static (sessile drop) and dynamic contact angles were measured at room temperature using goniometer (Krüss Easy Drop Analyzer, Germany) and deionized water (15 MΩ.cm) as a liquid. The apparent CA values were calculated from Krüss Easy Drop Analyzer software with an accuracy of ± 0.5°. The measurements of static CA were repeated 20-30 times (mean accuracy ± 3%) and shown as an average value. The following testing liquids at 20°C were used during the static mode of measurements: water ($\gamma=72.7 \text{ mN m}^{-1}$), glycerol ($\gamma=63.4 \text{ mN m}^{-1}$), 1-methyl-2-pyrrolidone ($\gamma=40.8 \text{ mN m}^{-1}$), N,N-dimethylformamide ($\gamma=37.1 \text{ mN m}^{-1}$), xylene ($\gamma=30.1 \text{ mN m}^{-1}$), toluene ($\gamma=28.5 \text{ mN m}^{-1}$), tetrahydrofuran ($\gamma=27.4 \text{ mN m}^{-1}$), n-

dodecane ($\gamma=25.4 \text{ mN m}^{-1}$), cyclohexane ($\gamma=25.2 \text{ mN m}^{-1}$) and hexane ($\gamma=18.5 \text{ mN m}^{-1}$). Based on the obtained contact angle values for the presented liquids, Zisman and Owens-Wendt theories were implemented to determine critical surface tension (γ_{cr})⁵⁷⁻⁵⁹. Wettability behavior of virgin and modified PVDF samples were investigated by measuring dynamic contact angle using DI water.

In the case of SFE determination, various approaches can be considered. The most general methodology involves CA measurements of various solvents possessing different polarity and SFE^{57, 62}. In the presented work, the Owens–Wendt methodology was implemented for the evaluation of SFE. According to Owens–Wendt theory, surface free energy (SFE) is composed of two parts, dispersive and polar components^{57, 60-61}. The dispersive component of SFE is related to the dispersive interactions due to the temporary differences in electron density among the molecules⁶². The resulting electron anisotropy generate dipoles that further induce momentary dipoles in nearby molecules. It should be pointed out that dispersive interaction are generally weak and known as London forces^{57, 60-61}. The polar types of interactions are associated with hydrogen, polar, induction (Debye) as well as acid-base forces^{57, 60-62}. It occurs in molecules possessing permanent dipole moment. Those molecules possess stable inequity in the electron density because of moderate electronegativities of the bonding partners, having concurrently asymmetrical geometry (e.g., water). In the case of more hydrophobic surfaces, lower contribution of polar interaction will be observed^{57, 60-61}.

Work of adhesion (W_{adh}) is another important parameter related to the physicochemistry of modified membranes that reflect the wetting process⁶⁷. The value of W_{adh} is the equivalent energy released in the process of wetting⁶⁸. The knowledge of this parameter is valuable in the evaluation of such processes like, hydrophobic or hydrophilic coating^{5, 18, 20, 27, 43, 45, 64, 68}, bonding, dispersion^{28, 45}.

Scanning electron microscopy (SEM). The SEM imaging of the membranes was performed using a scanning electron microscope (SEM, Quanta FEG 250 SEM, FEI). Prior to the analyses, samples were sputtered with a 100 Å layer of gold–palladium in order to create conductive surfaces and achieve higher quality images.

Atomic force microscopy (AFM). AFM (Nano-Observer AFM Microscope, Y-Travel, CSI, France) machine was implemented for surface analysis (topography and phase analysis) of investigated membranes. Tip scanning mode was used for the surface roughness determination of samples. The root mean squared (RMS) roughness was used as a parameter describing heterogeneity of the samples. In this study, scan size areas were equal to 5µm x 5µm. All membrane were tested at least five times and an average value was calculated (accuracy $\pm 4\%$).

Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) ATR-FTIR (Bruker Vertex 80v ATR-FTIR apparatus, Germany) was utilized to obtain the FTIR spectra of the membrane samples and to assess the efficiency of the modification process.

Raman spectroscopy

Raman spectra were collected using Raman Witec Alpha 300 RAS, Germany. The 532nm laser line was chosen. The spectra were gathered with an integration time of 2 sec and accumulation equal to 50.

Thermogravimetric analysis coupled with mass spectrometry (TGA-MS)

The thermal stability of the pristine as well as modified membranes was assessed applying TGA method coupled with Mass spectrometer (TGA NETZSCH STA 449 F3 Jupiter with MS QMS 403D Aëolos, NETZSCH, Germany).

Differential scanning calorimetry (DSC)

A differential scanning calorimetry analyzer (DSC 4000, Perkin Elmer, Germany) was used for examination the melting point of modified samples. The measurements were done under the ambient condition of nitrogen with a speed of 10°C/min starting from 80°C, and the flow velocity of gas was 20 mL/ min.

Capillary flow porometry and gas permeability

Mean flow pore sizes and the bubble point (maximum pore size) of the membranes were determined using capillary flow porometer (CFP, Porous Materials Inc., Ithaca, USA).

The ‘wet up/calc dry’ flow method was used where the sample was initially wetted with a low surface tension wetting liquid (GalwickTM) and subsequently placed in a sealed chamber through which gas (dry air) flows. Gas permeability of the membranes were also measured using the same equipment (CFP). In this case, the sample is sealed in the chamber such that gas flows through the sample only in the direction in which permeability is to be determined. Detailed procedure can be found elsewhere ^{8,14}.

Results and discussion

3.1 Membrane fabrication

Commercial flat sheet PVDF membrane, treated with aqueous NaOH (30 wt. %, 30 min) has major drawbacks concerning its material integrity. They showed a deep brown color and underwent a severe shrinking after the treatment with aqueous alkali and became highly brittle. Further treatment (such as hydroxylation with conc. H₂SO₄) was not possible (**Fig. 1**). This justifies the modification of the polymer directly rather than treating the membrane. To avoid any unwanted reactions, chemical stability of the non-woven support should also be considered, especially when strong acids or bases are applied. It should be noted that, treatment of PVDF with aq. NaOH (30 wt. %) followed by acid treatment failed to achieve a homogenous membrane surface without holes. Nucleation and aggregation were clearly

observed during the initial steps of treatment. Various other treatment conditions were also tried (as shown in **Table 1**) and it was not possible to achieve membranes with good material integrity and homogeneous surfaces.

A PVDF membrane has a reasonable hydrophobic character and hence treatment with aqueous solution was found to be ineffective. The limited access of reagents in aqueous media led to a highly anisotropic modification, which influences the properties of the fabricated membranes. Therefore, the polymer dope was subjected to non-aqueous treatment prior to the fabrication of flat sheet membranes. Low concentration (5 wt. %) of KOH in methanol was used for the treatment. Short and long exposure times (5 and 30 minutes) of alkaline treatment were selected. Membranes resulted from 5 min treatment showed thin film formation during phase separation, which might be due to immature dehydrofluorination step. This short treatment to the polymer chains apparently reduces the integrity of the polymer chains and limits the adhesion of the polymer film onto the support. On the other hand, extended exposure, up to 3 hours, led to partial gelation and casting was rendered difficult.

Fig. 1. (A) 30 min PVDF membranes (B) Fragile flat sheet membranes were obtained using conventional alkali treatment followed by hydroxylation.

Initially, pinholes were observed in the 30 min treated membrane (30 min-NC). This sample was also characterized by a heterogeneous top layer, high roughness and contact angle values (**Table 2**). The changes in the structure is ascribed to the aggregation and the initial nucleation

of the polymer chains. The implementation of centrifugation to the experimental protocol had a crucial effect on producing uniform membrane. A homogeneous membrane was achieved in the case of 30 min treatment with centrifugation. Presence of aggregates on the non-centrifuged samples were clearly visible in the SEM micrographs shown in **Fig. 2**. Comparing the value of contact angle for pristine and 30 min with and without centrifugation, an increase from 127° to 138° was observed. Moreover, visible changes were detected in surface free energy values. The differences between SFE for 30 min and 30 min-NC was around 25% (**Table 2**) where smaller value was calculated for 30 min-NC membrane. The contribution of polar interaction was reduced noticeably from $73 \pm 3 \text{ mN m}^{-1}$ and $25 \pm 1 \text{ mN m}^{-1}$ to $15 \pm 1 \text{ mN m}^{-1}$ for pristine, 30 min and 30 min-NC samples, respectively. Interesting observation was noticed from the critical surface tension. For instance, comparing the 30 min modified sample with 30 min-NC a step increase of 25% in γ_{cr} was observed. It indicates that the centrifugation enhances the wetting-resistance of the membranes.

Table 1: General observations during attempts for PVDF modification using various reagents and reaction conditions

PVDF (Dope)	Base treatment type, time (min)*	Acid treatment (h)	General comments
1	A, 5 – 180	12 – 48	<ul style="list-style-type: none"> a. No membrane could be fabricated due to agglomeration and precipitation b. The integrity between polymer and the support was poor c. Pinholes were noticed after application d. Application on a commercial membrane result in fragile, shrinking, disintegrated, and dark brown membrane
2 (5 min)	B, 5	12	<ul style="list-style-type: none"> a. Thin films were obtained after application which might be due to immature dehydrofluorination that might lead to polymer disintegration b. Holes were present in the resulted membrane

3	B, 30	12	a. Membrane shows good integrity and adhesion to the support b. Pinholes were present in the membranes due to some aggregation
(30 minNC)			
4	B, 30	12	a. Uniform membrane were obtained with good adhesion to the support b. No pinholes or defects observed
(30 min)			
5	B, 180	12	a. Membrane couldnot be fabricated due to gel formation

*Two methods for dehydrofluorination step were selected; A: 30 wt. % NaOH in water and B: 5 wt. % KOH in Methanol (5%)

3.2 Effect of PVDF activation on the surface properties

The changes in the membrane morphology caused by the alkali treatment modification were clearly observed in the SEM images presented in **Fig. 2**. Pristine membrane was characterized by uniform structure with small pores.

Fig. 2. SEM images of membranes prepared from pristine and modified PVDF, with and without centrifugation.

Table 2. Characterization of membranes prepared from pristine and modified PVDF.

Parameter	Pristine	5 min	30 min	30 min-NC
CA for water [°]	87 ± 2	120 ± 2	127 ± 1	138 ± 2
CA for glycerol [°]	85 ± 1	109 ± 2	110 ± 2	130 ± 1
Work of adhesion [mN m ⁻¹]	77 ± 2	36 ± 2	29 ± 1	25 ± 1
SFE total [mN m ⁻¹]	103 ± 4	63 ± 3	55 ± 2	44 ± 2
SFE dispersive part [mN m ⁻¹]	30 ± 1	30 ± 1	30 ± 1	29 ± 1
SFE polar part [mN m ⁻¹]	73 ± 3	33 ± 1	25 ± 1	15 ± 1
γ _{cr} [mN m ⁻¹]	31 ± 1	35 ± 1	36 ± 2	45 ± 2
RMS [nm]	83 ± 4	426 ± 17	200 ± 9	620 ± 24
F _{adh} [nN]	8.8 ± 0.4	12.9 ± 0.5	10.8 ± 0.4	20.5 ± 0.8

According to the data shown in **Table 2**, it can be stated that the modification has a significant impacts on the material and physicochemical properties of the membranes. The modification resulted in the formation of membranes with higher contact angles, when compared to the pristine membranes. After a short time of treatment (5 min) with KOH, the CA increased from 87 ± 2 ° to 120 ± 2°, whereas with a prolonged treatment (30 min), it increased to 127° (**Table 2**). This trend is the opposite of that expected, taking into consideration the generation of more hydroxyl groups on the membrane surface. This anomaly is due to the fact that CA value is also influenced by surface roughness, morphology, critical surface tension as well as the chemistry of the surface along with the hydrophobicity/hydrophilicity^{1, 51, 63-64}. Contact angle measurement alone is not holistic, when changes in physicochemistry of the modified surfaces are considered. To have a wider spectrum of information and holistic characterization of the samples, further analyzes such as critical surface tension (γ_{cr}) and roughness (RMS) of the surfaces were also determined further.

The changes in physicochemistry and wetting behavior became more noticeable, when surface free energy (SFE) and work of adhesion (W_{adh}) were taken into account (**Table 2**). It can be seen that SFE values decreased with the increase in surface hydrophobicity (**Table 2**), which is in accordance with the literature (ref). For instance, comparing membranes from pristine PVDF and from 30 min modified one, CA value was increased from $87^\circ \pm 1.5^\circ$ to $127^\circ \pm 1.3^\circ$. At the same time, the overall SFE was reduced almost twice from $103 \pm 4.1 \text{ mN m}^{-1}$ to $55.3 \pm 2.3 \text{ mN m}^{-1}$ (**Table 2**). Moreover, it was clearly noticed that polar component reduced much more than dispersive one. The dispersive components for all samples are comparable. Values of W_{adh} also changed significantly after modification (**Fig. 4D**). Membranes had W_{adh} values of $77 \pm 2 \text{ mN m}^{-1}$, $36 \pm 2 \text{ mN m}^{-1}$, and $29 \pm 1 \text{ mN m}^{-1}$ for pristine, 5 min, and 30 min respectively (**Table 2**). The reduction of W_{adh} parameter can be ascribed to the increase of contact angle values, decrease of SFE, and creation of so-called lyophilic conditions ⁶⁹ after modification. It indicates the formation of more hydrophobic and more wetting-resistant membrane surfaces.

Dynamic contact angle and spreading pressure (S) were also determined in order to assess the influence of modification on the surface wettability. During dynamic measurement of CA, the following parameters were examined: volume, base diameter and height of the drop along with the work of adhesion as a function of experimental time (**Figs. 3 and 4**). Based on the obtained parameters, the mechanism of surface wetting was determined. It can be seen that the drop volume (**Fig. 4 A**) and the height (**Fig. 4 C**) were reduced uniformly, indicating the possibility of membrane wetting by the water. However, **Fig. 4 B** shows that the drop diameter remained almost constant throughout the experiment, suggesting the occurrence of water evaporation as opposed to membrane wetting as reported in the literature ^{68, 70}. Thus, the surfaces of pristine, as well as modified membranes (5 min and 30 min), were not wetted by the testing liquid, i.e. the water did not penetrate into the structure of the

membrane. This is also proved by the calculation of the spreading pressure (S), which is developed based on the works of adhesion and cohesion. The measured values of spreading pressure were equal to -68.9, -109.2 and -116.6 mN m⁻¹ for pristine, 5 min, and 30 min, respectively. The negative values of S indicates the wetting-resistance ⁶¹. Wetting behavior was further analyzed by measuring contact angle as a function of time (**Fig. 3**). It can be seen that all the plots possessed comparable curvature. Furthermore, according to this plot (**Fig. 3**) the kinetics of liquid evaporation was determined. For the pristine and 5 min modified samples, water evaporation was described by a zeroth order kinetic reaction. However, for 30 min treated sample, a pseudo-zeroth order kinetic was noticed. Consequently, the constant rate for all changes were calculated and were equal to 0.0324, 0.0231 and 0.0145 mol dm⁻³ s⁻¹ for pristine, 5 min, and 30 min membranes, respectively. In **Figs. 3** and **4** the measurements for 30 min-NC sample was also included. Considering the data from dynamic contact angle measurements, it is possible to state that the preparation mode i.e. application of centrifugation process, has an important effect on the mechanism of surface wettability. Comparing samples 30 min and 30 min-NC, it is clear that despite higher hydrophobicity level of 30 min-NC membrane (138°), its resistance to wetting is small (**Fig. 3**). Furthermore, in the case of 30 min-NC, the evaporation of liquid as well as the wetting were observed (**Fig.4**). Namely, the volume and height of testing liquid changed non-linearly (**Fig. 4A, C**). Examining the evolution of W_{adh} during dynamic measurement (**Fig.4D**), it can be seen that in short period of time the value sharply increased. This is associated with spread of contact area between membrane surface and testing liquid. In conclusion, the most important findings were related to the fact that after alkali modification process (including centrifugation step), the surfaces became more resistant to wetting by different liquids (**Table 2** – critical surface tension). This is crucial in the further application of such materials for instance in the MD process, where the hydrophobicity as well as high water resistance is required.

Fig. 3. The evolution of contact angle during dynamic measurements for pristine and modified (5 min and 30 min) samples.

Fig. 4. The evolution of (A) volume, (B) drop base diameter, (C) height and (D) work of adhesion, during dynamic measurements for pristine, 5 min, 30 min, and 30 min-NC samples.

From a practical point of view, it is important to define and analyze the water repellence and material wettability of the surfaces and critical surface tension (γ_{cr}) is very useful in doing so. Values of critical surface tension (γ_{cr}) for all investigated samples were calculated based on the Zisman method ⁷¹. A growing value of critical surface tension was noticed as an effect of modification (**Table 2** and **Fig. 5**). γ_{cr} value for pristine was equal to $31 \pm 1 \text{ mN m}^{-1}$. However, for 5 min and 30 min of treatment with KOH solution, the values increased to $35 \pm 1 \text{ mN m}^{-1}$ and $36 \pm 2 \text{ mN m}^{-1}$, respectively. This observation is ascribed to the fact that more hydroxyl groups were created on the membrane surface treated for longer-time (30 minutes).

Fig. 5. Zisman plots for pristine, 5 min, and 30 min membranes.

To fulfill the holistic characterization of the prepared samples, the roughness of the membrane surface was determined. The surface roughness parameter was expressed as a root mean square (RMS) average of height deviations taken from the mean data plane. This parameter

was obtained based on the built-in mathematical algorithm in Gwyddion 2.45 Software (Freeware version). RMS is suitable to examine progressive changes on the surface of material as a result of chemical modification. It is also very sensitive to divergences with respect to the mean line ⁷². In **Fig. 6**, the topography images of pristine and 30 min samples were presented (**Table 2**). It can be seen that RMS values increased from 83.3 nm for pristine to 200 nm for 30 min treated membrane, indicating the impact of modification on the roughness of the membranes.

Fig.6. AFM topography of the pristine and 30 min samples.

AFM technique was also applied for the adhesion force (F_{adh}) determination. This parameter belongs to the data describing tribological properties of the materials. Based on the data presented in **Table 2** for pristine and modified samples, it can be pointed out that modification has a visible impact on the value of adhesion force. Sample characterized by smaller value of F_{adh} possessed also the lower hydrophobicity level and smoother surfaces (**Table 2**). This observation is associated with fact that the friction forces are controlled by the surface interactions under low contact pressures ⁷²⁻⁷³, where adhesion plays the main role. The

presence of adhesive forces has origin in chemical covalent bonding, electrostatic, van der Waals forces, as well as capillary forces between two contacting surfaces⁷²⁻⁷³. The determined values for all investigated samples were in the range of 8.8 ± 0.4 and 20.5 ± 0.8 . As a result of modification by OH groups, increase of F_{adh} of 1.2 to 2.3 times was noticed. The value of F_{adh} was directly related with the roughness of the sample, having a higher F_{adh} value for a rougher membrane (**Table 2**). This phenomenon can be explained by stronger adhesion on more heterogenic surface, due to the extended contact with membrane surface. From the results presented above, it is clear that modification process have an important influence on the physicochemistry (CA, SFE, γ_{cr} , W_{adh}) as well as on the morphology (RMS) of the PVDF membranes.

Fig. 7. **A** – TGA curves for pristine and modified 30 min samples, **B** – DTG curves for pristine and modified 30 min samples and MS spectrum of modified 30 min sample.

Taking into account the data from thermogravimetric analysis, it can be seen that temperature in which samples start to decompose was changed (**Fig. 7A**). Namely, for pristine sample this temperature was equal to 420°C, however after treatment, for the 30 min, temperature increased up to 450°C. All samples possessed an excellent thermal stability. The maximum observed peaks on the DTG curves were detected at 460°C and 467°C for non-

modified and treated PVDF sample, respectively (**Fig. 7B**). This observation may be ascribed to the intermolecular interaction in the polymeric chains due to the presence of OH groups. The achieved data are consistent with the scientific literature related, however, to one-step treatment with alkali media.^{55, 74} The efficiency of the alkali treatment was evaluated additionally by mass spectroscopy. Monitoring of ions possessing mass value equal to 19 [H₃O⁺] that related to the decomposition of hydroxyl groups, was presented in **Fig.7B**. The presence of strong peak (6.9×10^{-9} A) at the temperature of 506°C is related to the water formed upon the dehydration of the polymer chain carrying OH groups in the modified PVDF surface.

Fig. 8. DSC curves for pristine and modified (5 min, 30 min) samples.

DSC results for pristine, 5 min, and 30 min membranes were gathered in **Fig. 8**. A reduction of melting temperature (T_m) was observed after modification. This diminution of melting temperature was an effect of OH formation. Similar observation were documented in

the case of C=C bond generation ^{55, 75}. On the other hand the increased values of heat of fusion (ΔH_f) and crystallinity (χ) level were detected (**Table 3**). After 5 min of modification, about 10% increase was observed for ΔH_f and χ . However for longer treated sample (30 min) the difference between pristine and modified sample was equal to 19% for both parameters ΔH_f and χ . These observations were associated with the phenomenon of creating more organized structure. Namely, the symmetrical structure of main chain created i.e. hydroxyl groups formation. The modification condition i.e. application of KOH in the first step, destroys the previous degree of polymer net order and create the more ordered structure. The modification time has a clear influence on the chemistry of the PVDF investigated samples (**Table 3**).

Table 3. Heat of fusion (ΔH_f) and total crystallinity (χ) of virgin PVDF and modified PVDF samples.

Parameter	Pristine	5 min	30 min
Melting temperature [°C]	162.0	160.1	158.3
Heat of fusion [J g ⁻¹]	45.06	49.37	53.56
Total crystallinity [%]	43.0	47.2	51.2

Attenuated total reflectance (ATR) FTIR spectroscopy modes were applied to assess the chemical composition of the pristine and modified PVDF membrane samples. Spectra for both configurations were presented in **Fig. 9**. In the case of ATR-FTIR, the limit of the infrared penetration is generally less than 1 μm and hence it can provide an information on the top layer of membranes. Based on the FTIR spectra in the range of wavenumber of 700 – 1500 cm^{-1} , the crystalline phase of PVDF can be determined. α and β phases of PVDF and modified PVDF membranes are related to the bands located at 764 cm^{-1} and 840 cm^{-1} , respectively ⁷⁶. Applying the Beer-Lambert law, it is possible to determine the crystallinity degree of α and β phases on the membrane surface by comparing peak absorbances at the

wavenumber of 764 cm^{-1} (characterized for α phase) and 840 cm^{-1} (characterized for β phase). The ratio of α to β phase was equal to 0.4 in the case of the pristine sample. However, for both modified samples the majority was for β phase. This is due to the lack of characteristic bands in the range of 764 cm^{-1} and the presence of strong peaks at 836 cm^{-1} (**Fig. 9B**). Moreover, based on the literature ⁷⁵ an increase of β phase can be explained by the creation of better oriented, well-packed PVDF structure of $\text{CH}_2\text{-CF}_2$ dipoles (TTT conformation) on the surface. Moreover, a CF_2 rocking band was observed in 5 min, and 30 min samples at 441 and 445 respectively. Red shift of about 10 cm^{-1} were recorded for these samples with respect to the pristine one at 480 which can be assigned to CF_2 deformation. The new frequencies are 471 and 470 assigned to 5 and 30 min, respectively. These frequencies are related to the formation of β phase of the polymer. The CF_2 wagging of the pristine was observed at 612 cm^{-1} which indicated predominant α phase. Red shift also observed in the CF_2 symmetric stretching which was 1177, 1169, and 1164 assigned to pristine, 5 min, and 30 min respectively. Further analysis of the data presented in **Fig. 9**, shows that after modification, the visible changes in the so-called dactyloscopic region of the infrared spectra was noticed. Comparing the pristine and modified samples, a reduction in the intensity of the following peaks at $762, 796, 974\text{ cm}^{-1}$, which are characteristic for α phase, can be observed. On the other hand, other peaks at $841, 1274$ and 1403 cm^{-1} became more intense which correlated to β phase. To clearly visualize the frequencies between 1500 and 3500 cm^{-1} , thin film of the polymers was prepared by mechanical pressing (**Fig. 9A**). The first step of the alkali treatment i.e. dehydrofluorination process resulted in the creation of following peaks: in the range of $1550 - 1650\text{ cm}^{-1}$ assigned to the double bonds ($\text{C}=\text{C}$) and in the range of $1700 - 1800\text{ cm}^{-1}$ assigned for carbonyl bonds, respectively (**Fig. 9A**). On the other hand, in the pressed film, OH absorption band can be clearly observed as a weak wide signal between 3300 and 3500 cm^{-1} .

Fig. 9. A – FTIR spectra for pristine and modified samples (5 min and 30 min) as a thin film.
B – ATR-FTIR spectra for pristine and modified samples (5 min and 30 min).

Raman spectra were also recorded for pristine, 5 min treated membranes. Unfortunately, we were not able to record Raman spectra for 30 min membrane using several laser sources with different intensities. This might be due to the presence of OH groups on the surface of polymer. Data were summarized in **Table 4** and **Fig. 10**. It is worth noting that Raman spectra support the hypothesis of phase change due to modification. A characteristic peak for α phase at 801 cm^{-1} , present in the pristine membrane, is almost disappeared in the 5 min treated sample. On the other hand, the characteristic peak for β phase were recorded at 839 and 856 cm^{-1} for the pristine and 5 min membrane.

Table 4. Raman shifts of REF, 5 min, 30 min treated materials

Frequency [cm^{-1}] and intensity		Vibration mode
Pristine	5min	
-	3217 W	$\nu(=\text{CH})$
-	3086 M	$\nu(=\text{CH})$
3014 S	-	$\text{CH}_2 \nu_{\text{as}}$

2976 VS	2959 M	CH ₂ v _s
-	2007 VW	
1724 W	1728 S	
1647 W	-	v(C=C)
1614 W	-	
1605 W	1609 VS	
1431 M	1444 W	CH ₂ δ
1309 W	-	CF ₂ v _{as}
1271 W	1288 M	CC v _s
-	-	CF ₂ v _{as}
1179 VW	1195 VW	CF ₂ v _s
1076 Sh	1101 Sh	CC v _{as}
-	-	CF ₂ v _s
1005 W	995 W	CH ₂ τ
885 Sh	-	CC v _{as}
-	-	CC v _s
839 M	856 M	CH ₂ ρ
801 M	805 W	CH ₂ ρ
-	636 W	CF ₂ δ, CCC δ
607 WV	-	CF ₂ ω, CF ₂ δ, CCC δ
513 W	-	CF ₂ δ
-	-	CF ₂ δ
-	-	CF ₂ δ
416 W	-	CF ₂ ω, CF ₂ δ
365 VW	-	CF ₂ τ, CCC δ
289 VW	272 W	CF ₂ τ

δ – Deformation mode, v_{as} – asymmetric stretching mode, v_s – symmetric stretching mode, ρ - rocking deformation mode, τ – twisting mode, ω - wagging mode.

Fig. 10. Raman spectra of the pristine and 5 min treated membranes.

3.3 Effect of PVDF activation on membrane

The effect of PVDF membrane activation on the membrane structure and membrane morphology was also evaluated. According to the data shown in **Table 5**, it can be stated that modification process has visible impact on membrane structure. Pristine membrane possessed value of mean flow pores and bubble point equal to $0.18 \pm 0.09 \mu\text{m}$ and $0.60 \pm 0.32 \mu\text{m}$, respectively. After modification, more open structure was achieved. This observation was also proved by SEM analysis (**Fig. 2**). In the case of 5 min membrane, an increase of both aforementioned parameters, bubble point and mean flow pores were observed. The mean flow pores and bubble point equal to $0.19 \pm 0.02 \mu\text{m}$ and $1.47 \pm 1.19 \mu\text{m}$, accordingly. On the other hand, 30 min membrane show values for bubble point and mean flow pores as 0.16 ± 0.02 and $0.33 \pm 0.03 \mu\text{m}$, respectively. Due to aggregation present in 30 min-NC membrane, the bubble point was $14.04 \pm 0.65 \mu\text{m}$ which is extremely large pores and cannot be used as membrane.

Similar effect was observed for the 5 min membrane where polymer film disintegration limits the formation of good quality membrane.

Table 5. Pore size characterization of membranes prepared from pristine and modified PVDF.

Parameter	Pristine	5 min	30 min	30 min-NC
Mean flow pores [μm]	0.18 ± 0.09	0.19 ± 0.02	0.16 ± 0.02	4.59 ± 0.44
Bubble point [μm]	0.60 ± 0.32	1.47 ± 1.19	0.33 ± 0.03	14.04 ± 0.65

4. Perspectives

One of the most essential features in the membrane distillation is to have material with well controlled properties. The final performance of a process is a straight consequence of the physicochemical as well as structural properties of the used membranes. The efficiency of the membrane distillation process is intrinsically affected by several factors e.g. porosity, pore distribution, mean pore size, thickness, and geometry. The membrane for membrane distillation process has to be highly hydrophobic and porous, possessing excellent chemical resistance to feed solutions as well as good thermal stability. Therefore, the successful outcome of this process is reasonably predicted by the membrane capability to interface two media as well as to pose high resistance to liquid intrusion in the pores with high volumetric mass transfer.

Taking into account all abovementioned requirements, it can be stated that PVDF membranes comply with the conditions. The main limitations are related to the inert character of PVDF material, which makes its further modification difficult. However, in the current work we show new frontier to influence this inertness and chemically activate the membrane. The prepared membranes are hydrophobic, porous and characterized by good thermal and mechanical stability as well as resistance to wetting. Moreover, the polymeric membranes are active to further modification. Certainly, the prepared PVDF membrane can be used in

membrane distillation process. This step will be the point of interest of our further research. Furthermore, due to the presence of reactive hydroxyl groups on the surface, further modification are possible. The modification via covalent bonding is more effective and much stable than physical modification of the polymeric material, e.g. introducing inorganic nanoparticles to the polymeric matrix. The proposed modification on flat sheet membrane in an efficient way, can show a broad spectrum of new application using PVDF material.

3. Conclusions

A highly efficient method for PVDF membrane modification and tuning the hydrophobic/hydrophilic properties was established. Two-step experimental protocol of alkali/acid polymer treatment was proposed. The advantage of the established method was the possibility to manufacture a stable membrane with very high temperature resistance, as well as very good resistance to wetting. The other benefit from the optimized method is the short exposure to alkali media under lower concentration to reduce polymer decomposition. Efficient functionalization was achieved by using a relatively short period of time (30 min) and mild concentration of KOH (5 %).

The physicochemical as well as material properties of the modified membranes were examined by a combination of microscopic (SEM), goniometric (CA, SFE, W_{adh} , γ_{cr}) and surface methods (AFM). The influence of modification time as well as utilization of centrifugation process were examined. This set of valuated parameters is a source of interesting remarks and observations. The applied spectroscopic and dynamic goniometric contacting methods (dynamic evolution of CA, volume, height, base of drop diameter, spreading pressure) enabled a coherent view of the changes in the chemistry and structure of performed membranes. It was pointed out that the proposed treatment method has an important impact on the physicochemistry, morphology and wettability of examined polymeric materials. As an effect of alkali treatment, an increase of contact angle (from 87°

for pristine membrane to 127° for 30 min treated one) and roughness (from 83 nm for pristine membrane to 200 nm for 30 min treated one) as well as the reduction of surface free energy were noticed. Especially, the polar component for the treated samples was highly diminished (from 73.0 mN m^{-1} to 15.17 mN m^{-1}). Moreover, the strong impact of roughness on the CA value was observed. The impact of the roughness hid the real properties of the created surface i.e. the formation of higher amount of hydroxyl groups on the surface, which was proved by the TGA-MS analysis. Critical surface tension and the mechanism of wetting were determined in order to demonstrate the functionalization. Due to the high wetting resistance of the functionalized membranes, further applications such as membrane distillation or pervaporation were proposed.

List of symbols and abbreviations:

5 min – PVDF membrane sample modified by two-step process in alkali/acid treatment during 5 minutes

30 min - PVDF membrane sample modified by two-step process in alkali/acid treatment during 30 minutes (with centrifugation step)

30 min-NC - PVDF membrane sample modified by two-step process in alkali/acid treatment during 30 minutes (without centrifugation step)

CA – contact angle [$^\circ$]

DMAc - dimethylacetamide

MD – membrane distillation

MOF - metal organic frameworks

OH – hydroxyl groups

PMMA - poly(methyl methacrylate)

PTCs - phase transfer catalysts

PVDF – poly(vinylidene fluoride)

PVDF-CTFE - poly(vinylidene difluoride-co-chlorotrifluoroethylene)

PVDF-HFP - poly(vinylidene fluoride-co-hexafluoropropylene)

REF – reference PVDF membrane sample

RMS - root mean squared [nm]

S – spreading pressure [mN m^{-1}]

SFE – surface free energy [mN m^{-1}]

W_{adh} – work of adhesion [mN m^{-1}]

γ_{cr} - critical surface tension

χ – total crystallinity

δ – deformation mode,

ρ - rocking deformation mode

v_{as} – asymmetric stretching deformation mode

v_{s} – symmetric stretching deformation mode

τ – twisting mode,

ω - wagging mode.

ΔH_f - Heat of fusion [J g^{-1}]

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