Influence of silicon oxide (SiO₂) and sulfosuccinic acid (SSA) loading on properties of poly(vinyl alcohol) (PVA) derived composite membranes.

Tomáš Remiš, Jaroslav Kadlec
New Technologies - Research Center, University of West Bohemia, Plzeň 306 14, Czech Republic
Email: tremis@ntc.zcu.cz

Abstract. New anhydrous proton conducting membranes based on poly(vinyl alcohol) (PVA), tetraethyl orthosilicate (TEOS) and sulfosuccinic acid (SSA) were prepared in a single step using the solution casting method, with the aim to improve the mechanical properties of PVA membranes. SSA has been used as a sulfonating agent for crosslinking the membrane structure and also as a source of protons. TEOS has been used as crosslinking agent to increase the thermal and mechanical properties of the membranes and membranes stability in aqueous environment. In order to verify that all the substances were immobilized into the matrix, the membranes were analyzed by means of Fourier transform infrared spectroscopy (FTIR). The thermal, mechanical and rheological properties of the membranes were investigated by means of thermogravimetry (TGA), dynamic mechanical analysis (DMA) and Ares G2 rheometer. Water uptake (Wu) of composite membranes was determined. The properties were investigated for various PVA solutions and for each dried membrane. The analysis of mixed PVA solutions exhibited unique behaviour of viscosity with increasing the crosslink density. TGA and DMA measurements showed increased thermal and mechanical resistance of membranes depending on the extent of their crosslinking. Due to incorporation TEOS, the resistance of PVA membranes to the aquatic environment has increased. These properties can increase the resistance of the membranes during the processes occurring in the fuel cells.

1. Introduction
PVA membranes are used in many applications, especially in organic/inorganic separation, pervaporation, biomedical applications, catalytic processes, controlled release of drugs, etc. These membranes are very hydrophilic, which is considered an advantage for some applications, but mostly becomes as problem due to the high swelling of the membranes in the water. The properties of new proton conductive membranes based on PVA, tetraethylorthosilicate (TEOS) and sulfosuccinic acid (SSA) have been determined for different stoichiometric ratios. SSA has been used as a sulfonating agent, for crosslinking the membrane structure and also as a source of protons. SiO₂ has been used to increase the thermal and mechanical properties of membranes and to reduce membrane solubility in water. Thermal and rheological properties of the membranes were investigated using thermogravimetry (TGA) and Ares G2 rheometer. The absorption of the membrane and its resistance to the water has been investigated.
2. Experimental

2.1. Material
PVA (hydrolyzed 99+%, $M_w = 86000–98000$) and SSA (70 % in water) were obtained from Sigma-Aldrich (USA). TEOS and hydrochloric acid (HCl, 37 wt %) were purchased from Merck Chemicals (Germany). All the chemicals were of analytical grade and used as received. Deionized water was utilized for all the membrane preparation experiments.

2.2. Membrane preparation
Composite PVA membranes were prepared by the solution casting method. At first, a 5 wt% solution of PVA in water was prepared by continuous stirring at 90 °C until the complete dissolution was achieved. The PVA solution was mixed with SSA for 24 h at room temperature. Further, TEOS mixture was prepared by mixing H$_2$O, HCl and TEOS in the molar ratio of 4:0.1:1, which was stirred at room temperature for 2 h [1] and added to the PVA-SSA solution. The composition of each solution is specified in Table 1. The prepared solution was poured into the automatic film applicator (TQC, Germany) equipped with a plexiglass plate and was fabricated into membranes with uniform thickness and dried at 40 °C.

2.3. Characterization
FTIR reflectance spectroscopy studies were performed on the samples using NICOLET 380-FTIR spectrometer, in a spectral range of 400 – 4,000 cm$^{-1}$.

The rheological studies of the PVA solutions were measured on a rheometer ARES G2 from TA Instruments. The polymer solutions were inserted between two parallel plate geometries (d =25 mm). For each measurement, the shear rate from 0.1 to 100 s$^{-1}$, for a duration 30 s was carried out at room temperature.

TGA was used to evaluate the relative thermal stability of modified PVA membranes. The TGA curves were obtained with a TGA Q500 thermogravimetric analyser (TA Instruments, USA). Samples of about 5 mg were heated at a rate of 10 °C/min in N$_2$ atmosphere. The weight of the samples was measured as a function of temperature.

The temperature dependence of the storage modulus was determined by DMA using a DMA Q800 instrument (TA Instruments, USA). Membrane samples with a size of 20 x 6 mm and a thickness of about 0.1 mm were used to measure the mechanical properties. Experiments were conducted in N$_2$ atmosphere at frequency 1 Hz, starting from ambient temperature up to 100 °C with a heating rate of 5 °C/min.

The water uptake studies were carried out at 24, 48 and 120 h at room temperature. The membranes were placed in deionized water for specified time. The wet membranes were then wiped with a filter paper and weighted. The water uptake was calculated using the following equation:

$$W_u = \frac{W_s - W_d}{W_d}$$

where $W_s$ and $W_d$ are the weights of swollen and dry membranes, respectively.
Table 1. Composition of polymer solutions, PVA, SSA, TEOS.

| Sample           | Solution mixture          | Composition                                      |
|------------------|---------------------------|--------------------------------------------------|
| 5PVA             | 5% PVA                    | 25ml H₂O, 1.25g PVA                              |
| 5PVA_0.5SSA      | 5% PVA, 0.5%SSA          | 25ml H₂O, 1.25g PVA, 0.125ml SSA                 |
| 5PVA_1SSA        | 5% PVA, 1%SSA            | 25ml H₂O, 1.25g PVA, 0.25ml SSA                  |
| 5PVA_2SSA        | 5% PVA, 2%SSA            | 25ml H₂O, 1.25g PVA, 0.5ml SSA                   |
| 5PVA_5SSA        | 5% PVA, 5%SSA            | 25ml H₂O, 1.25g PVA, 1.25ml SSA                  |
| 5PVA_1TEOS       | 5% PVA, 1%TEOS           | 25ml H₂O, 1.25g PVA, 0.25ml TEOS (0.00625ml HCl, 0.0625ml H₂O) |
| 5PVA_2TEOS       | 5% PVA, 2%TEOS           | 25ml H₂O, 1.25g PVA, 0.5ml TEOS (0.0125ml HCl, 0.125ml H₂O) |
| 5PVA_5TEOS       | 5% PVA, 5%TEOS           | 25ml H₂O, 1.25g PVA, 1.25ml TEOS (0.032ml HCl, 0.32ml H₂O) |
| 5PVA_10TEOS      | 5% PVA, 10%TEOS          | 25ml H₂O, 1.25g PVA, 2.5ml TEOS (0.064ml HCl, 0.64ml H₂O) |
| 5PVA_0.5SSA_1TEOS| 5% PVA, 0.5%SSA, 1%TEOS  | 25ml H₂O, 1.25g PVA, 0.125ml SSA, 0.25ml TEOS (0.00625ml HCl, 0.0625ml H₂O) |
| 5PVA_0.5SSA_2TEOS| 5% PVA, 0.5%SSA, 2%TEOS  | 25ml H₂O, 1.25g PVA, 0.125ml SSA, 0.5ml TEOS (0.0125ml HCl, 0.125ml H₂O) |

3. Results and discussion

3.1. FT-IR

Figure 1 shows the FT-IR spectra of the M1 and M7 membranes. It was reported that the absorption band of ester (–COO–) appeared at 1730–1735 cm⁻¹. This results indicate the spectral changes are an evidence of a crosslinking by the esterification between –OH in PVA and –COOH in SSA. The absorption band at 2369 cm⁻¹ indicate the presence of sulfonic acid group, which is formed by the introduction of SSA [2]. The band at approximately 1040 cm⁻¹ is assigned to stretching vibrations of Si–O–Si. The absorption band, at 900 cm⁻¹ can be attributed to the stretching vibration of Si–OH or Si–O– groups. A broad absorption band, situated between 3,000 and 3,600 cm⁻¹, are assigned to O–H stretching and O–H bending vibrations, respectively [3].

![Figure 1. FT-IR spectra of composite PVA membranes](image_url)
3.2. Rheology
The viscosity of the pure PVA solution changed after the incorporation of SSA (Figure 2). At low SSA content, the viscosity was initially increased due to the interaction between the acid groups of SSA and PVA. However, the viscosity was reduced slightly when the SSA loading percentage exceeded 0.5 wt%. The slight reduction in our observed viscosity can be explained by the limited dispersion behaviour of SSA in the PVA matrix. Agglomeration of particles resulted in the reduced surface area between the SSA and PVA, and caused the decrease in viscosity.

![Figure 2. Rheological spectra of pure PVA solution and different SSA loadings of PVA/SSA solutions](image)

3.3. TGA
Figure 3 shows thermogram of composite PVA membranes. Thermal stability increase with each additional added component, which means higher crosslinking extents for the composite membrane with SiO$_2$, with SSA and with combination of SiO$_2$-SSA particles, respectively. This results correspond with rheological properties of modified membranes and show better thermo-mechanical properties of membranes compared to pristine PVA membrane.

![Figure 3. TG thermograms of composite PVA membranes](image)
3.4. DMA

DMA analysis was performed to investigate the thermomechanical properties of the composite PVA membranes. The temperature dependence of the storage modulus was measured in the range from 30 to 100 °C. In the case of composite membranes, storage modulus increased with the increasing SiO$_2$ and SSA loading, respective (Figure 4). Thanks to SSA content in composite 5PVA_0.5SSA_2TEOS membrane, storage modulus decrease compared 5PVA_2TEOS membrane. This indicate stronger crosslinking extents for the composite membrane with silica particles.

![Figure 4. DMA of composite PVA membranes](image_url)

3.5. Water Uptake

Figure 5 shows the decreasing ability of PVA composite membranes to absorb water depending on the increasing SiO$_2$ content, while increasing the water resistance of PVA-SiO$_2$ membranes. SSA increases $W_u$ of composite membranes.

![Figure 5. Water uptake of PVA-SiO$_2$ and PVA-SiO$_2$-SSA membranes](image_url)

4. Conclusion

The results of this study can be useful for next research of composite PVA membranes. Rheological studies show that ideal motion of used SSA is 0.5 wt%. Incorporation of SiO$_2$ in the PVA matrix
increases the mechanical and heat resistance of membranes and water resistance of PVA membranes. SSA increases $W_o$ of PVA membranes. Advantageous is a combination of SiO$_2$ and SSA in the PVA matrix.

**Acknowledgements**
The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, cofounded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI program and, in the follow-up sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the "National Sustainability Program I.

**References**
[1] Kim, Dae, et al 2007 *Macrom. Res.* 15
[2] Rhim, Ji-Won, et al 2004 *J. Memb. Sci.* 238 143
[3] Katumba G, Mwakikunga B W, and Mothibinyane T R 2008 *Nanosc. Res. Lett.* 3 421