Improving the mechanical properties of sulfonated polysulfones by blending with polybenzimidazole

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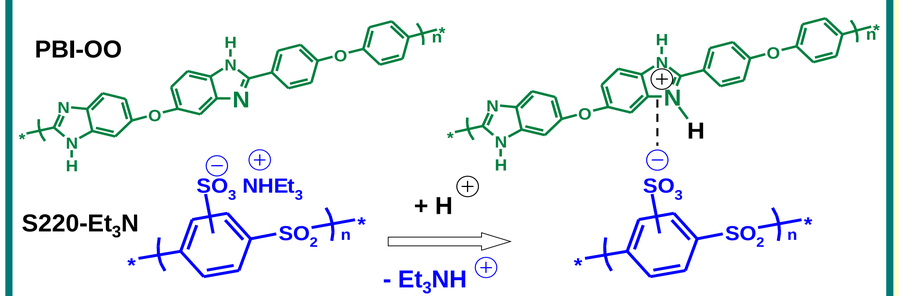
Introduction

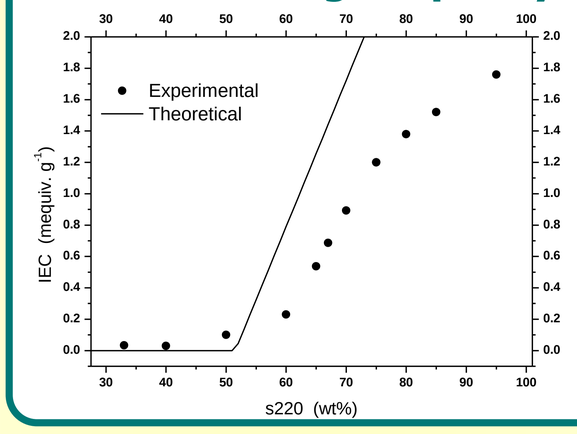
Recently, sulfonated polysulfones with high durability, very high proton conductivity and even some methanol rejection properties have been reported [1, 2]. The advantageous properties are most pronounced for high ion exchange capacities (IEC > 2.5 meq./g) for which the highly polar character of the ionomer leads to brittleness in the dry state and low elasticity in the wet state.

In an attempt to improve the mechanical and film forming properties, we have prepared blends of high IEC polysulfones (s220, IEC ~ 4.5 meq./g) and a polybenzimidazole (PBI-OO). This is expected to lead to ionic cross-links between the two polymers, which have already been proven to reduce the water uptake of similar systems [3].

Preparation



Ion-exchange capacity



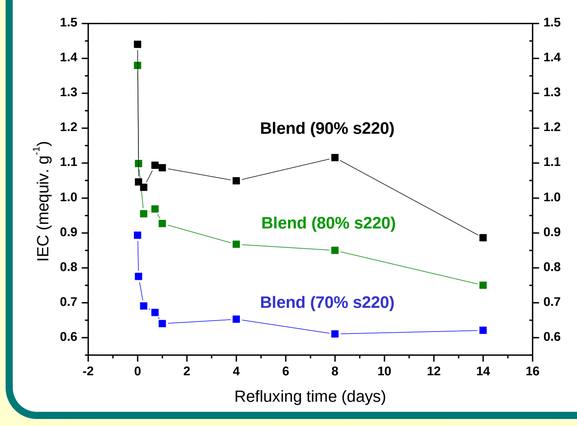
Method of measuring: indirect titration (exchange of the membrane protons with NaCl solution and titration of the formed HCl with NaOH)

Titration was repeated until full exchange of the membrane protons was achieved.

Possible reasons for the observed lower IEC:

- Inaccessibility of the sulfonic function in the PBI-OO matrix;
- incomplete cleavage of the Et_3NH group;
- loss of the sulfonic function due to condensation reaction.

Reflux of the blends in water

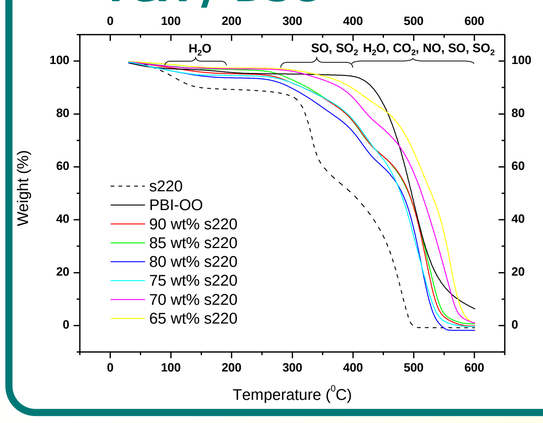


Known: acid-base interactions (coulomb attraction) are weakened at temperatures above 80ºC.[3]

Observations: In this case the elevated temperature will lead to extraction of the water soluble s220 and thus, the IEC will decrease with time. However, we observed a relatively fast decrease in IEC within the first few hours, followed by moderation of the IEC decrease within the next 2 weeks.

Possible reason: entanglement between the polymer chains.
At the beginning mostly the s220 at or just below the surface is extracted (leading to the initial drop of the IEC), while, the s220 inside the polymer blends matrix is hindered by the polymer entanglement.

TGA / DSC

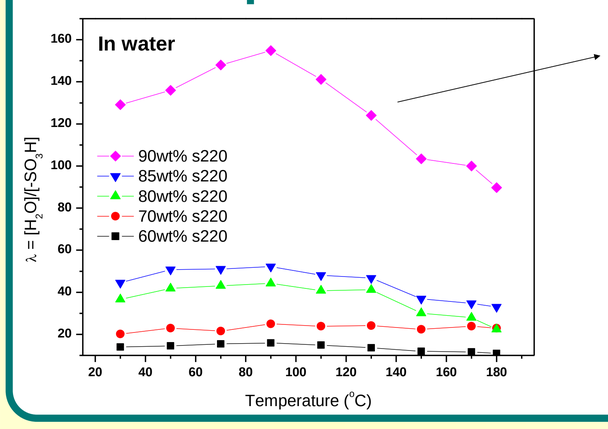


TGA conditions:
Temp. range: 30-600˚C
Envir. atm.: air
Heating rate: 2 K/min

Dynamic Scanning Calorimetry
(20-300˚C in air, rate 10 K/min)

DSC did not indicate any phase transition below 300ºC.

Water uptake



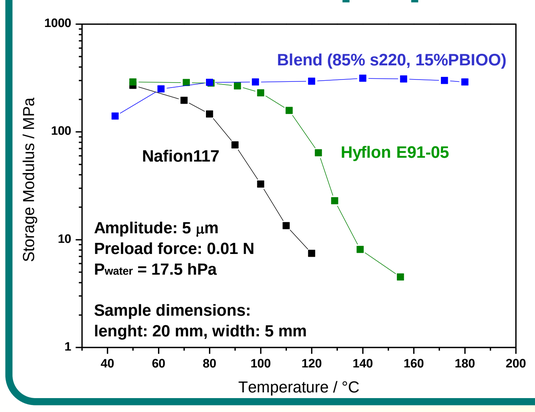
The decrease of the water uptake with temperature could be attributed to extraction of s220 from the blends. This is supported by the fact that decrease of λ is higher for blends with higher s220 content.

Observation:
Water uptake remains constant with increasing temperature in the region 30-180ºC.

Possible reasons:

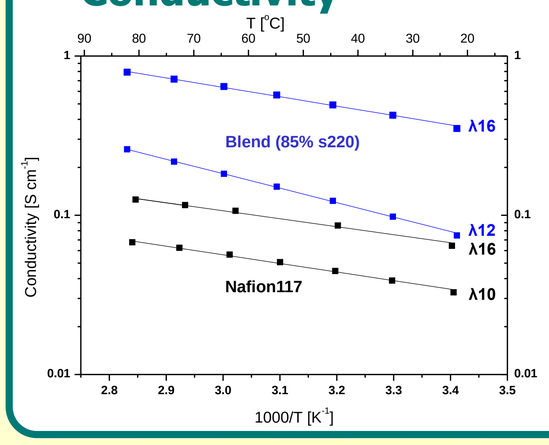
- strong multicentre intermolecular interaction;
- hydrophobicity of PBI-OO.

Mechanical properties



In comparison to Nafion and Hyflon, blends did not show any change of their elasticity with increasing temperature.

Conductivity

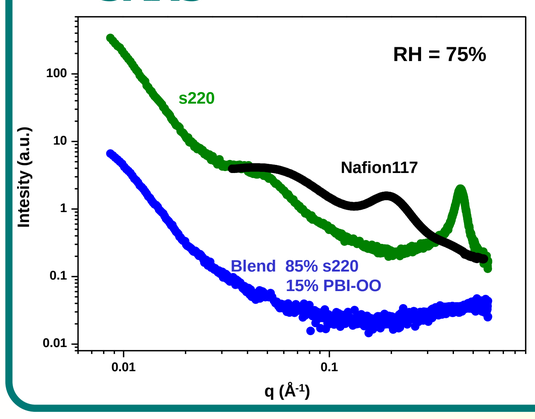


Method:
Conductivity measurements were performed in a closed cell on a stack of membrane disks with ø 4 and total thickness 1.5 mm. The water content is calculated after the measurement and is presented here as $\lambda=[H_2O]/[-SO_3H]$.

Observation:

- Blends showed higher conductivity at T=20-80ºC then Nafion117.
- Conductivities of the blends rapidly decrease with water content (results are not shown). Therefore, investigations for determining the structure and the shape of the water domains are the subject of future investigations.
- Comparing the slopes of the linear fits shows a definitely higher value of the activation enthalpy for blends than for Nafion117. This might be explained by a change of the proton transport mechanism.

SAXS



S220 showed certain periodicity of hydrophilic and hydrophobic regions. However, the distinct ordering of this polymer vanishes in blends with PBI-OO.

Conclusions & Outlook

Blending high conductive s220 with PBI-OO, which brings the softness and stabilizes the blends through acid-base interactions, gave us access to a membrane with improved mechanical toughness. Although, these are very preliminary results, this material combines high thermal and mechanical stability with high conductivity at relatively high water content. In order to prove and explain the properties of these membranes, a detailed investigation on the local microstructure and domain dimensions are in progress.

Literature

[1] M. Schuster, K.-D. Kreuer, H. T. Andersen, J. Maier, Sulfonated Poly(phenylene sulfone) polymers as hydrolytically and thermooxidative stable proton conducting ionomers, *Macromolecules, 40, 598-607 (2007)*
[2] V. Saarinen , K. D. Kreuer, M. Schuster, R. Merkle, J. Maier. On the swelling properties of proton conducting membranes for direct methanol fuel cells *Solid State Ionics, 178,* 533–537 (2007)
[3] J.A. Kerres, Blended and cross-linked ionomer membranes for application in membrane fuel cell, *Fuel Cell 5, 230-247*, (2007)

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