Morphology and visco-elastic properties of Nafion: Deformation studied by ²H-NMR, SAXS and Tensile Tests

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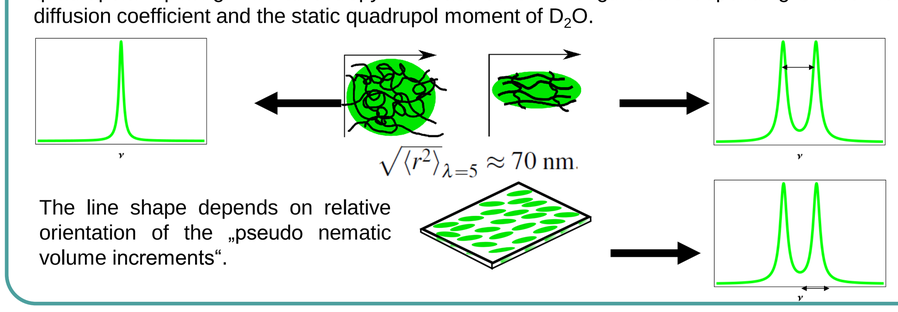
Introduction

Nafion N117 as received and stretched at a wide range of temperatures and relative humidity including wet conditions has been investigated combining ²H goniometer NMR, tensile tests, and small angle x-ray scattering (SAXS). In ²H goniometer NMR we exploit the pseudo nematic effect, i.e. the residual quadrupolar splitting of diffusing D_2O constraint in an anisotropic polymer. The anisotropy of Nafion polymer is measured on the 70*nm* scale by NMR and correlation on the low *nm* scale (ca. 3*nm*) are probed by SAXS. Comparing the influence of stretching conditions on those different length scales and on tensile tests provides insight into the interactions driving morphology and visco-elastic properties in PFSAs.

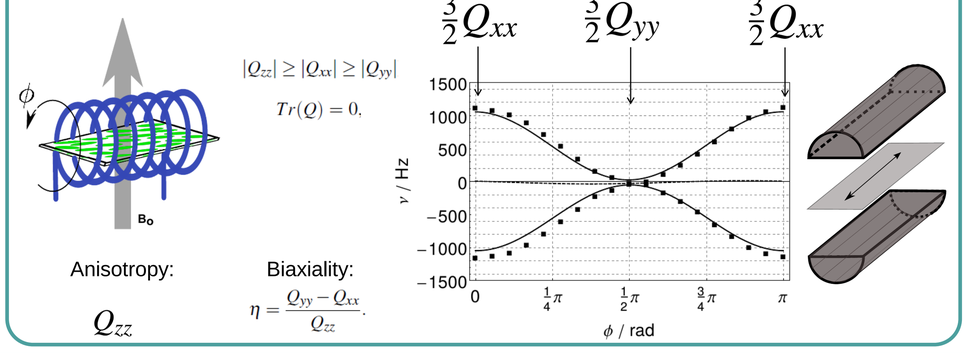
Pseudo Nematic Effect

Constraint movement of the D_2O molecules by an anisotropic polymer matrix results in residual quadrupolar splitting. The anisotropy is measured on a length scale depending on the water diffusion coefficient and the static quadrupol moment of D_2O.



The line shape depends on relative orientation of the „pseudo nematic volume increments“.

Deuteron NMR at different goniometer angles



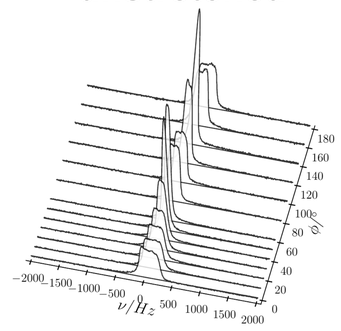
Anisotropy: Q_{zz}

Biaxiality: $\eta = \frac{Q_{yy} - Q_{xx}}{Q_{zz}}.$

Stretching at different relative humidity and temperature

unstretched

All Nafion samples have been standardized (2h 8M HNO_3, 1h bidistilled water) and measured at λ=5 D_2O.

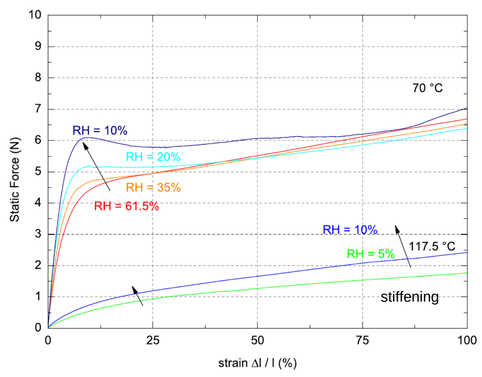


Small splittings and angular dependence are due to the extrusion process.

No randomly oriented ansiotropic volume increments exist on the scale <70nm in unstretched N117 .

No genuine anisotropy on 70 nm scale

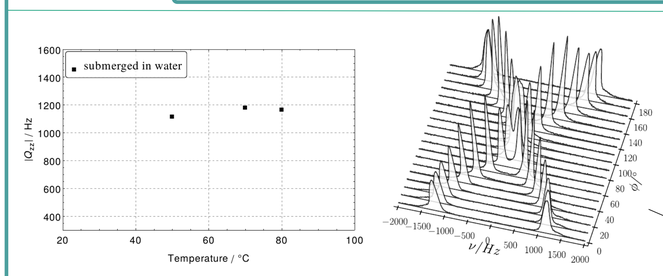
tensile tests



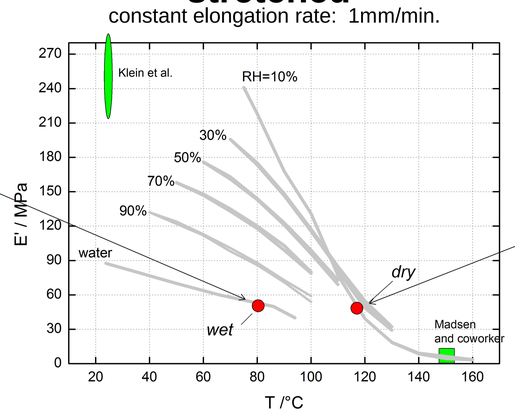
- low T / high RH: The pseudo-elastic regime is associated with reorientation of the primary polymer aggregates shearing along the water phase.
- reduced RH: Reorientation is hindered, i.e. higher elastic modulus. At a critical strain deformation inside the primary aggregates starts
- high T: Deformation occurs inside the primary aggregates. Higher water content stiffens the membrane

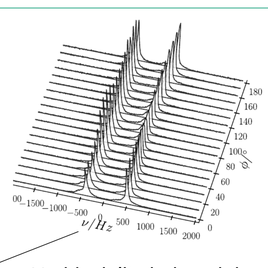
stretched

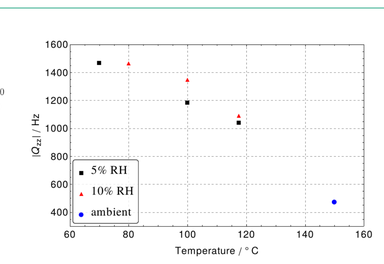
constant elongation rate: 1mm/min.



Induced Biaxiality depends on clamp size; Strong in wet Nafion.

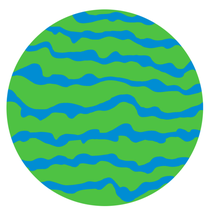






No biaxiality induced through clamp size; long range interaction weak in dry Nafion.

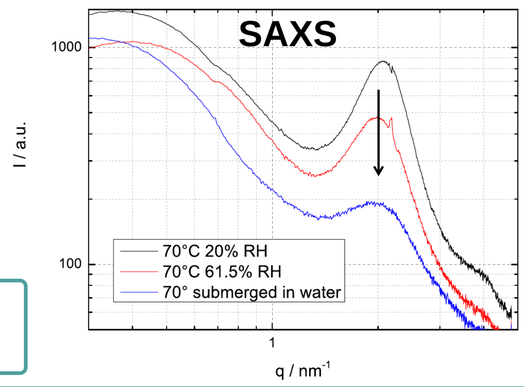
stretched under wet conditions



The polymer-water correlation causes the “ionomer peak” (q = 2nm^{-1}). Stretching at higher RH reduces the intensity of the ionomer peak.

Deuterium NMR:
Induced anisotropy virtually temperature independent.

Stretching at high RH occurs by shearing along the water phase!



stretched under dry conditions

The polymer-water correlation causes the “ionomer peak” (q = 2nm^{-1}). The peak intensity hardly changes by stretching at ambient conditions.

Deuterium NMR:
Induced anisotropy shows temperature dependence of polymer.

Stretching at low RH occurs by shearing inside the polymer phase!

Conclusions

- morphology driven by electrostatic interaction within aqueous ionic domain
- anisotropy on 70 nm scale is no genuine property of Nafion.
  - ➢ no extended elongated objects.
- anisotropy on 70 nm scale only induced by stretching.
  - ➢ low relative humidity: deformation inside the polymer phase.
  - ➢ high relative humidity: shearing along the water phase.
- induced biaxiality depends on sample shape and RH/T.

Further reading

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