Characterization of carbon nanotube containing polymer membranes

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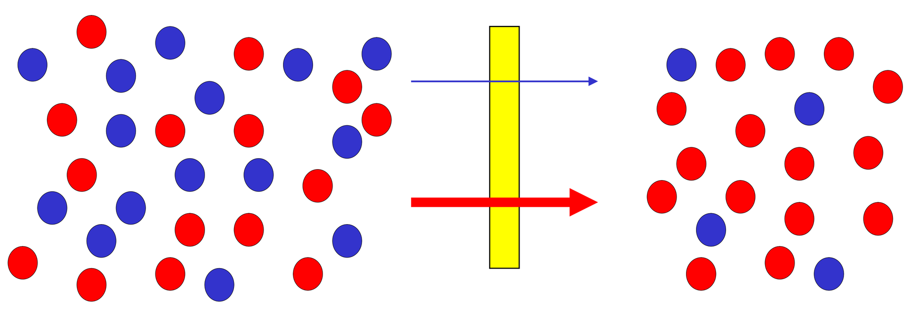
Motivation - membranes

Separation of gas mixtures

High permeability **P** = high solubility **S** * high diffusivity **D**

with $D \propto \exp\left[-\frac{v^*}{v_f}\right]$



Selectivity for two components A and B: $\alpha_{AB} = \frac{P_A}{P_B}$

Why polymers?

- Changes in ***free volume*** affects diffusivity directly without changes in solubility
- Structural modifications
- Ease of preparation and handling

Motivation – This Work

Why PIM-1?

- High permeability
- High free volume

⇒ promising membrane material

Why mixed matrix membranes / MWCNTs?

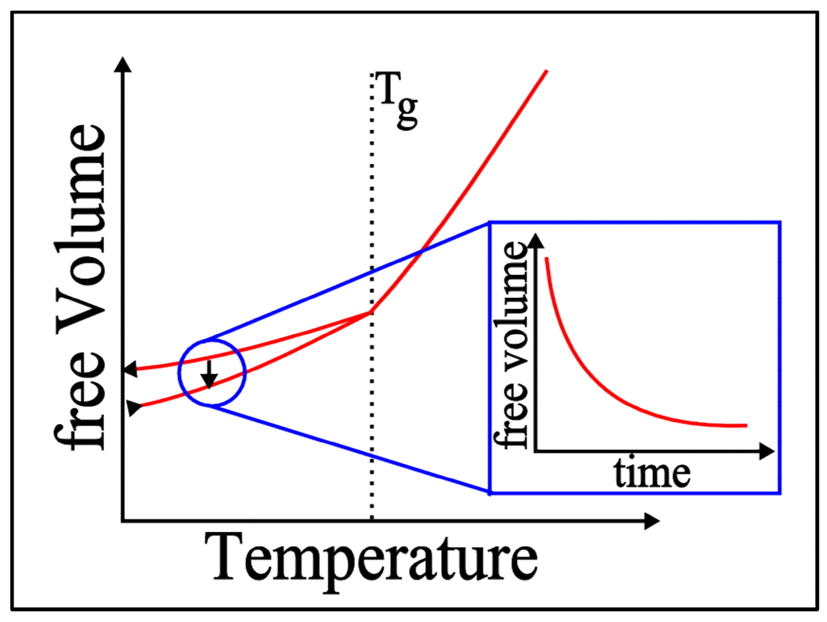
- Mechanical performance of material increased – effect on long term stability?
- Increasing membrane and mechanical properties of an known and very good membrane material.

This Work

- Aging (storage at room temperature) leads to reduction in free volume*
- Here usage, i.e. how does free volume change comparing freshly prepared and used membranes.
- How is the effect of CNT on aging / usage ?

*Stephan Harms et al, JOURNAL OF ADHESION, 88(7), 608-619, 2012

Physical aging



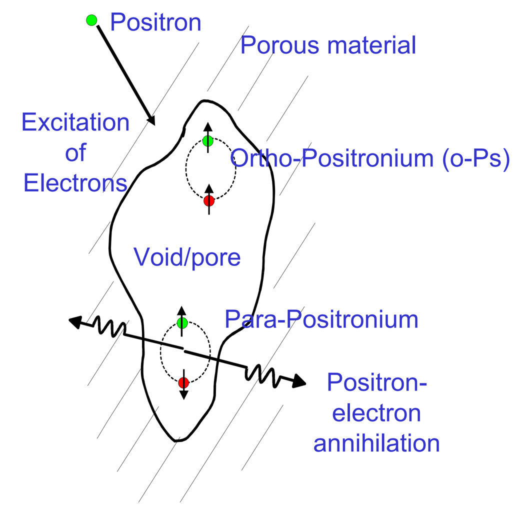
- Decrease of **P** over time / while usage
- Reason: Reduced free volume holes?

Why PALS?

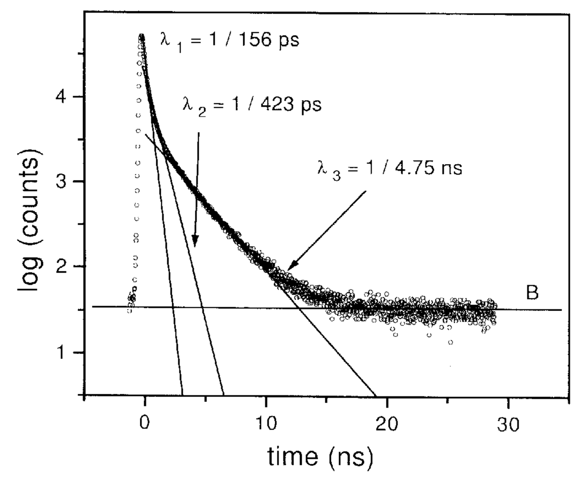
- PALS can detect microscopic free volume

$D \propto \exp\left[-\frac{v^*}{v_f}\right]$

Positron Annihilation Lifetime Spectroscopy (PALS)



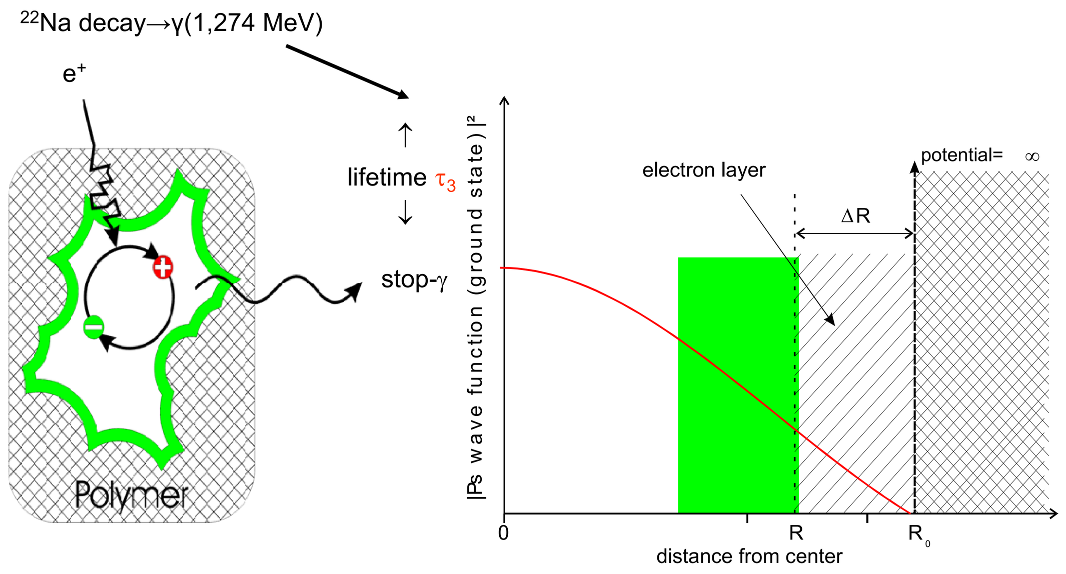
Positron annihilation in porous materials



Typical PALS spectrum

Tao-Eldrup Model: $\tau_3 \leftrightarrow$ average hole size

- radioactive decay → positron
- positron + electron → ortho-positronium (o-Ps)
- trapping in voids
- decay by interaction with electrons from wall



- average free volume void sizes determine average ortho-positronium lifetime
- ortho-positronium intensity depends on concentration of holes, spur electrons and positron acceptors

Hole radius $r\uparrow$ ⇒ overlap wavefunction, $\Delta R\downarrow$ ⇒ decay probability ↓ ⇒ lifetime $\tau_3\uparrow$

Ortho-positronium intensity = hole concentration × o-Ps formation probability

S. J. Tao, J. Chem. Phys. 56, (1972) 5499, M. Eldrup et al., J. Chem. Phys. 63, (1981) 51

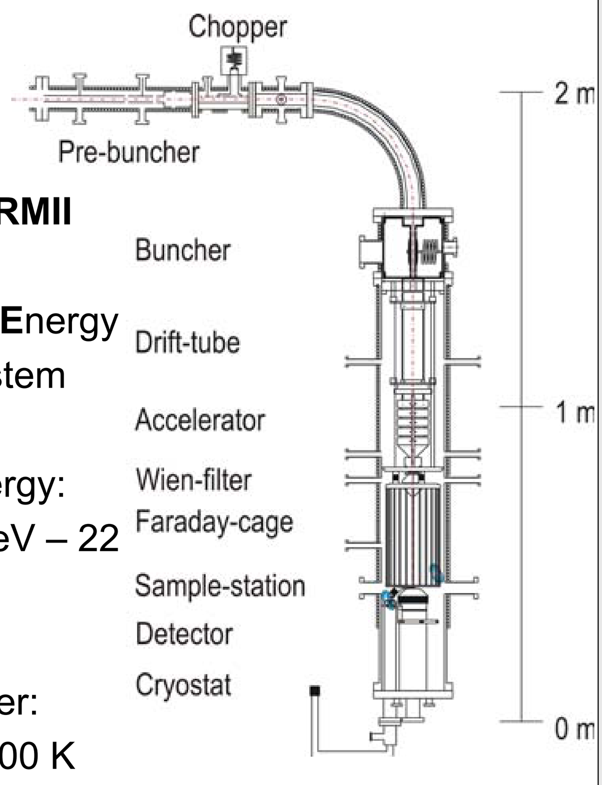
PLEPS

PLEPS at FRMII

Pulsed Low Energy Positron System

Positron energy: Ekin = 0.2 keV – 22 keV

sample holder: T = 80 K – 500 K



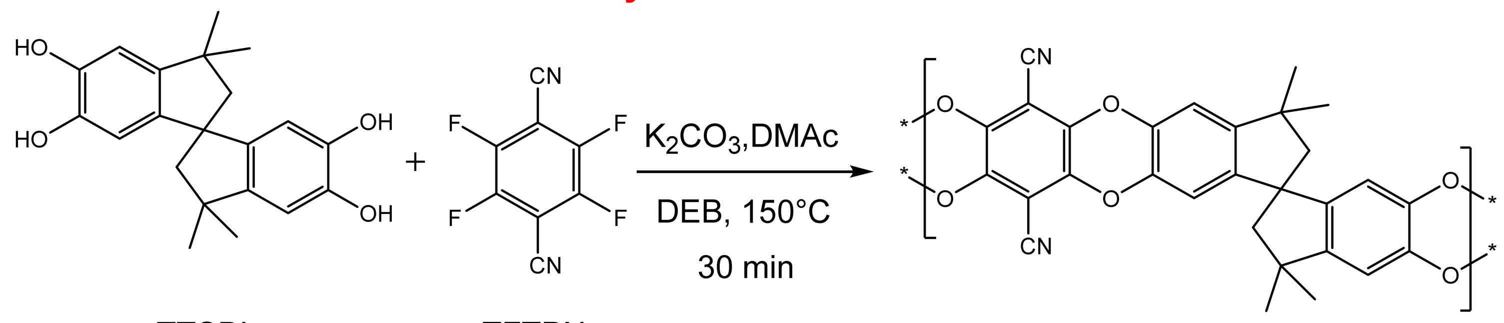
PLEPS setup at FRMII

W. Egger, L. Ravelli
University of armed forces Munich, Neubiberg and FRM II Munich

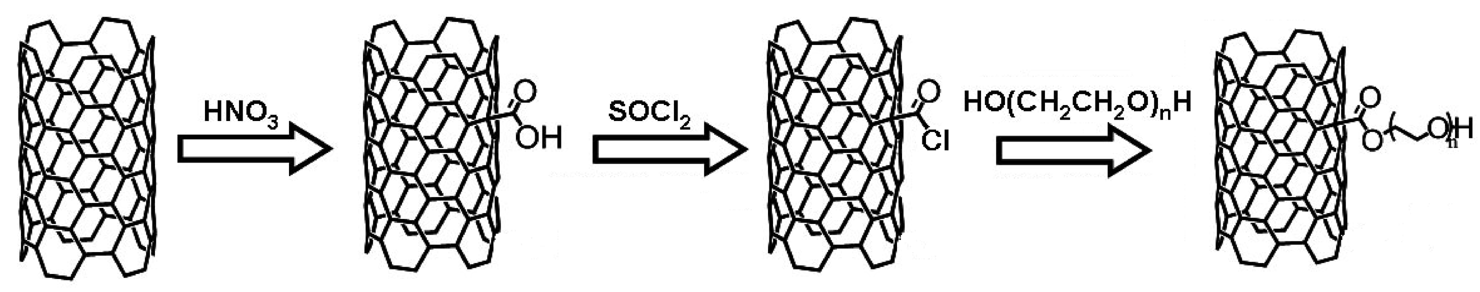
Werner Egger et al, phys. stat. sol.c, 4(10), 3969-3972 2007

Sample preparation

Polymerization PIM-1



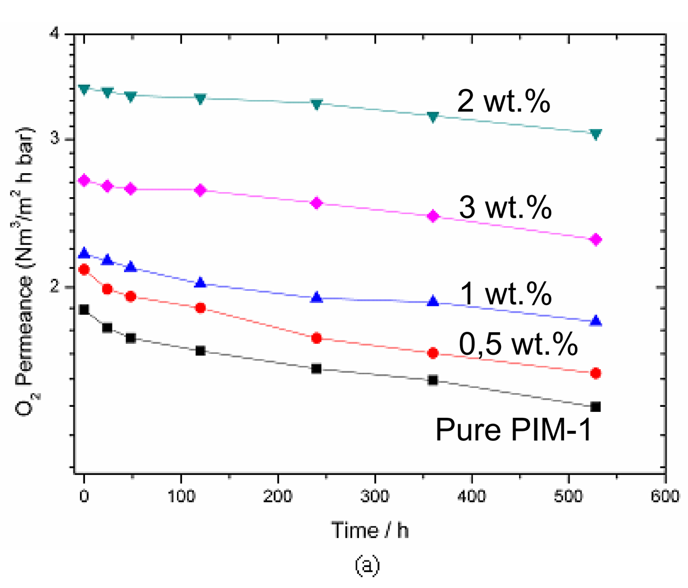
Functionalization of MWCNTs



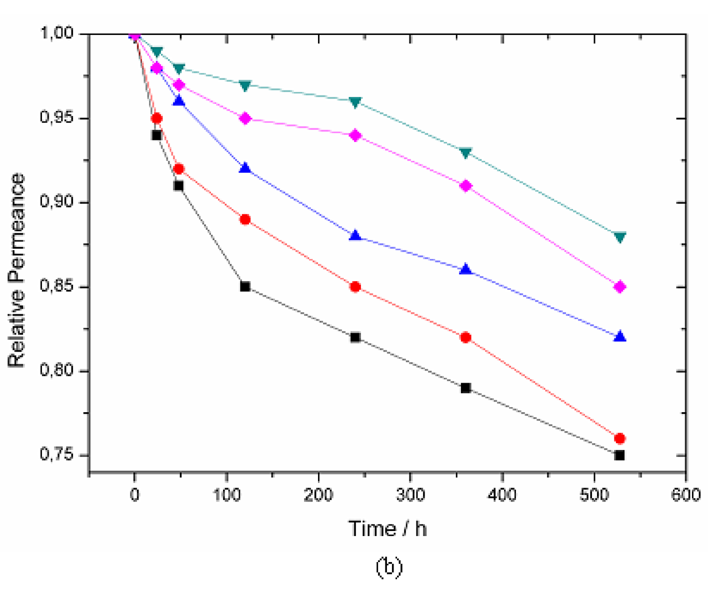
- Upto 2wt.%, f-MWCNTs dispersed in PIM-1 matrix.
- Thin (700 nm) PIM-1 and PIM-1 f-MWCNT MMM prepared on PAN support layer
- Used (~300 days for gas separation) and as-cast samples prepared for PALS measurements.

Muntazim M Khan et al, JOURNAL OF MEMBRANE SCIENCE, 436, 109-120, 2013

Permeation Measurements



- O_2 permeance higher with f-MWCNTs
- Degradation over time
- Agglomeration with more than 2 wt.% ⇒ Performance decrease

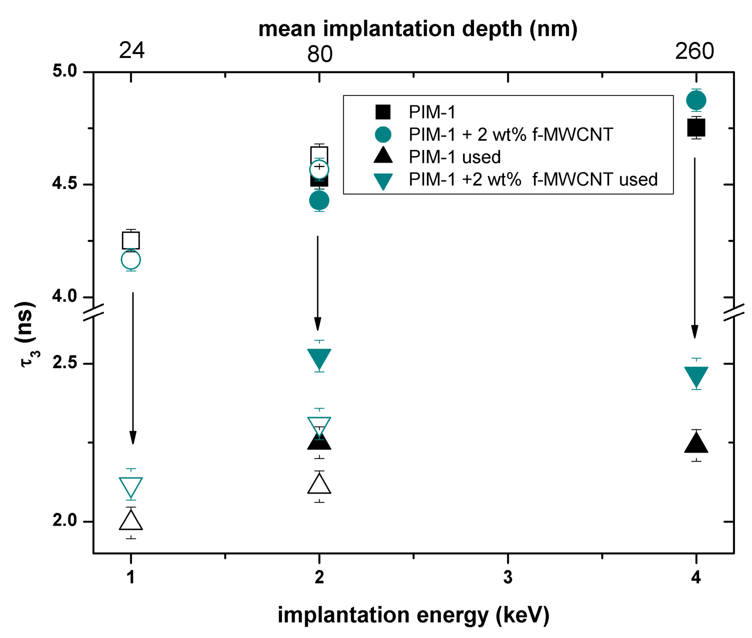


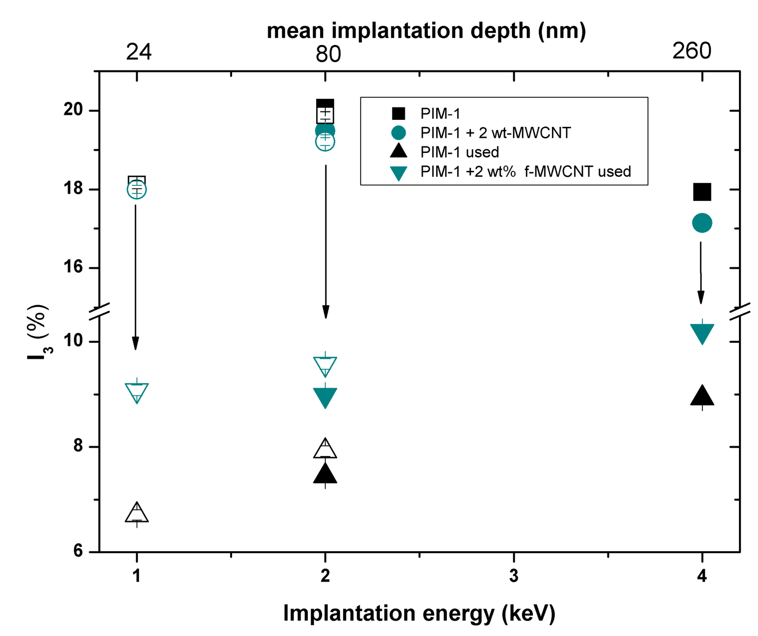
- Relative reduction of permeance slower with higher f-MWCNT content
- Better long term stability

Gas measurement condition:
Temperature = 27°C
feed pressure = 2 bar.

Muntazim M Khan et al, NANOSCALE RESEARCH LETTERS, 7, 504, 2012

PALS Measurements





Open symbols: POSWIN evaluation
Solid symbols: LT evaluation

- Lower o-Ps lifetime and intensity at the surface
- Diffusion of free volume to surface.*
- Strong **reduction** of free volume holes after usage.
- Free volume holes maybe less connected
- **Less reduction of free volume** with MWCNTs
- **Larger holes** when f-MWCNTs incorporated.
- Lifetime measurement results in expected regime for physical aging.

*Stephan Harms et al, JOURNAL OF ADHESION, 88(7), 608-619, 2012

Conclusion

- ***Better Permeation*** with added f-MWCNTs in PIM-1 matrix.
- Better mechanical stability
- **Less *free volume reduction* during usage with f-MWCNTs**
- CO_2/N_2 separation performance above Robeson 2008 upper bound

Promising mixed matrix membrane material

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