Polymer membranes for flue gas treatment

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# Typical composition flue gas

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Water vapor selective polymers

- Pebax® 1074

\[
\text{HO-}\left[\text{C-PA-C-O-PE-O}\right]_n\text{H}
\]

- Sulfonated poly (ether ether ketone) (SPEEK)
Water vapor selective polymers

PEBAX®
- Rubbery
- Block copolymer
- Hydrophilic soft blocks and hydrophobic hard domains

SPEEK
- Glassy
- Ionic groups
- Highly hydrophilic
Gas separation with polymer membranes

\[ P = D \cdot S \]

\[ \alpha = \frac{P_i}{P_j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j} \]

Diffusivity
Size dependent:
\[ \text{H}_2\text{O} < \text{CO}_2 < \text{N}_2 \]

Solubility
\[ T_c \text{ dependent:} \]
\[ \text{N}_2 \ll \text{CO}_2 \ll \text{H}_2\text{O} \]
Water vapor sorption
Water vapor sorption

PEBAX®
Flory Huggins sorption

SPEEK
Dual Mode
Flory Huggins sorption

$T = 50^\circ\text{C}$
Water clustering phenomena

Cluster integral $G_{ww}/N_w$ vs. Activity

- PEBAX®
- SPEEK

$T = 50^\circ C$
Water vapor diffusion
Water vapor diffusion

$T = 50^\circ\text{C}$

Fickian diffusion coefficient/ $\times 10^{-12} \text{ m}^2/\text{s}$

- Pebax
- SPEEK

Activity / -

T = 50°C
Water vapor (H₂O) permeation
Water vapor permeation ternary mixtures

T = 50°C; Ternary feed: H₂O/N₂/CO₂
Water vapor permeation ternary mixtures

$T = 50\, ^\circ\text{C};$ Ternary feed: $\text{H}_2\text{O}/\text{N}_2/\text{CO}_2$

Sorption + desorption

SPEEK

PEBAX®
Gas (CO$_2$ and N$_2$) permeation
Gas and vapor permeation

**Binary mixtures**

- $\text{N}_2/\text{H}_2\text{O}$
- $\text{CO}_2/\text{H}_2\text{O}$

**Ideal, hypothetical permeability and selectivity $\text{CO}_2/\text{N}_2$ in ternary mixtures**

**Ternary mixtures**

- $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$

**Real permeability and selectivity**
Permeation binary (ideal) mixtures

\[ T = 50^\circ\text{C}; \text{H}_2\text{O/N}_2 \text{ or } \text{H}_2\text{O/CO}_2 \]
Permeation binary (ideal) and ternary mixtures

$\text{CO}_2$ Sorption and desorption (binary + ternary)

$\text{PEBAX}^\circledR$

Desorption ternary

Sorption ternary

Ideal behavior

binary feed

$T = 50^\circ\text{C}$; Binary: $\text{H}_2\text{O}/\text{N}_2$ or $\text{H}_2\text{O}/\text{CO}_2$; Ternary: $\text{H}_2\text{O}/\text{N}_2/\text{CO}_2$
Permeation binary (ideal) and ternary mixtures

T = 50°C; Binary: H₂O/N₂ or H₂O/CO₂; Ternary: H₂O/N₂/CO₂
Selectivity binary and ternary mixtures

\( T = 50^\circ\text{C} \); Binary: \( \text{H}_2\text{O}/\text{N}_2 \) or \( \text{H}_2\text{O}/\text{CO}_2 \); Ternary: \( \text{H}_2\text{O}/\text{N}_2/\text{CO}_2 \)
Conclusions

• Rubbery PEBAX®
  – Relaxation or hysteresis not observed
  – Permeation performance independent on mixture composition

• Glassy polymer SPEEK
  – Relaxation, hysteresis phenomena
  – Strong dependence of permeation performance on mixture composition (binary vs. ternary mixtures)
Conclusions

• Impact of water vapor strongly dependent on polymer structure and morphology

• High water permeabilities combined with high water/light gas selectivities

• Reasonable CO₂ permeabilities combined with high CO₂/N₂ selectivities
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References


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