Cross-linked PEG and 2D nano-materials based mixed matrix membranes (MMMs) for CO₂ capture

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Outline

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  - NANOMEMC2 project

- **Membrane fabrication**

- **Results and discussion**
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  - *Method 2---UV crosslinking*
  - *Method 3---Interfacial polymerization*

- **Conclusions**
PEG membrane CO$_2$/N$_2$ separation performances

- **Low Mw:**
  Liquid state, bad mechanical properties

- **High Mw:**
  Highly crystalline, low permeability (P$_{CO_2}$~12 Barrer)

- Form block copolymers
  (e.g. Pebax, polyactive)

- Form blend membranes
  (e.g. Pebax/polyactive/PSf + liquid PEG)

- Form cross-linked membranes
  (e.g., UV crosslinking, thermal crosslinking)

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S.L. Liu et al. / Progress in Polymer Science 38 (2013) 1089–1120
H.J. Liu et al., Nanoscale, 2013, 5, 9984–9987
Introduction

MMMs based on 2D materials

Advantages of 2D materials:

- High-aspect-ratio;
- Nanoporous ‘perforations’
- Small loadings (<2 wt.%)
- Favorable for thin-film composite membranes

Examples:

- Graphene/GO/RGO;
- Transition metal Di-chalcogenides; (MoS$_2$)
- 2D Metal organic frameworks(MOFs) (CuBDC/ZIF8L)
**Introduction---Nanomemc² project**

**Nanomemc²---NanoMaterials Enhanced Membranes for Carbon Capture**

- **Goals:**
  - To fully develop the potential of membranes for CO₂ capture;
  - To increase the efficiency of the capture step;
  - To reduce the overall CCS cost below the value of 40€/tonne of CO₂ avoided

- **Aims:**
  - To overcome current limitations by focusing on the development of innovative CO₂ selective membranes with high flux and selectivity,

- **Methods:**
  - Nanofibrillated cellulose (NFC), Graphene (G) and Graphene Oxide (GO) suspensions will be produced /functionalized to enhance gas transport properties.

Please refer to our poster presented by Saravanan Janakriram: **Fine tuning of separation performances in nanocellulose based membranes for CO₂ capture**

More information can be found here: [http://www.nanomemc2.eu/](http://www.nanomemc2.eu/)
Membrane fabrication

- Membrane fabrication

- PEGDGE
- PEG diaminos
- PEG diacylate
- Cross-linker
- TMC
- PEG diaminos

Method 1: Heating to 80 °C
Method 2: UV polymerization
Method 3: Interfacial polymerization

2D material
Cross-link site
PEG chain
Results—**PEG fabricated via Method 1**

**Method 1—Thermal crosslinking**

PEG + XLinker + Graphene → Mixing for a few hours → Sandwiched by two glass plate, heat at 80 ℃ for 4 hours

A-amine

[TETA][Tfa]

Jeffamine® ED-600/2003
Results—PEG fabricated via Method 1

FTIR spectrum

Results—PEG fabricated via Method 1

Single gas permeation


Single gas separation performances, dry condition
Attempts of fabricating PEG/graphene/GO MMMs

Membrane without Graphene/GO

Adding GO dispersion

Remove the water + heat treatment

heat treatment

Soak the membrane into GO solution

Can’t form membrane & bad mechanical strength

Results—PEG fabricated via Method 1
Results—PEG fabricated via Method 2

Method 2---UV crosslinking

PEG + XLinker + Graphene → Mixing for a few hours → Sandwiched by two quartz plate

PEG (35 wt.%) + XLinker (15 wt.%) + Free PEG (50 wt.%) → UV, HCPK

Results—PEG fabricated via Method 2

FTIR spectrum

C=\text{C} bond

Crosslinking time: 60 mins
## Results — PEG fabricated via Method 2

### Single gas permeation

<table>
<thead>
<tr>
<th>PEG (35wt.%)</th>
<th>X-linker (15wt.%)</th>
<th>Free PEG (50 wt.%)</th>
<th>CO₂ permeability</th>
<th>CO₂/N₂ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="PEG" /></td>
<td><img src="image2" alt="X-linker" /></td>
<td><img src="image3" alt="Free PEG" /></td>
<td>~250 Barrer</td>
<td>~35</td>
</tr>
<tr>
<td>Mw=250</td>
<td></td>
<td></td>
<td>~180 Barrer</td>
<td>~30</td>
</tr>
<tr>
<td><img src="image4" alt="PEG" /></td>
<td><img src="image5" alt="X-linker" /></td>
<td><img src="image6" alt="Free PEG" /></td>
<td>~220 Barrer</td>
<td>~30</td>
</tr>
</tbody>
</table>
Attempts of fabricating PEG/GO MMMs

X-linker + Mixing with GO aqueous solution

Mixing for a few hours

Sandwiched by two quartz plate

UV light

Bad mechanical strength (too much water from GO dispersion)

GO aggregation

Phase separation

Remove water + UV

Remove water

PEG fabricated via Method 2

Results
Results—PEG fabricated via Method 3

Method 3---Interficial polymerization via spin coating

Organic phase

Aqueous phase

Spin coating, 1000rpm, 30s

Spin coating 1000 rpm, 30s

Organic phase

Aqueous phase

TMC

Jeffamine® ED-600/2003

GO solution: 2 mg/ml

1 wt.% in Hexane

1 wt.% in H_2O

PEG fabricated via Method 3
## Results — PEG fabricated via Method 2

### Membrane characterization

<table>
<thead>
<tr>
<th></th>
<th>PDMS support</th>
<th>PDMS+PEG</th>
<th>PDMS+PEG/GO (0.5 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thickness:</strong></td>
<td></td>
<td>1~1.3µm</td>
<td>1~1.3µm</td>
</tr>
<tr>
<td><strong>Contact angle:</strong></td>
<td></td>
<td>~20 degree</td>
<td>~20 degree</td>
</tr>
<tr>
<td><strong>CO₂ permeance:</strong></td>
<td></td>
<td>25~40 GPUs</td>
<td>12~18 GPUs</td>
</tr>
<tr>
<td>( \alpha_{CO₂/N₂} ):</td>
<td></td>
<td>11~14</td>
<td>20~30</td>
</tr>
</tbody>
</table>
Conclusion remarks

- **Thermal, UV and interfacial crosslinking** have been employed to fabricated PEG-based membranes;

- Thermal crosslinking resulted in PEG membranes with superior CO$_2$/N$_2$ separation performances which surpass the Robeson upper bound;

- Attempts have been made to fabricate PEG/graphene/GO MMMs via thermal and UV crosslinking but not successful;

- PEG/Graphene MMMs have been successfully fabricated on PDMS support via spin coating. Adding GO into PEG significantly increased selectivity while sacrificing the gas permeance.

- More process parameters for the interfacial polymerizations (e.g., concentration, spin coating speed) are under optimization.
Thank you!

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