Foaming of Cyclic Olefin Copolymer (COC) and Nanocomposites by Carbon Dioxide

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1. Introduction

Cyclic Olefin Copolymer (Topas 6017)  
($M_w = 2.14 \times 10^5$ g/mol; $M_n = 1.05 \times 10^5$ g/mol)

Norbornene unite

Flexible PE unite

$T_g = 180 \degree C$

Glass Transition Temperature

Norbornene Content in COC in weight %
Why the Interest in COCs

✓ Mechanical properties
  ✓ Modulus higher than HDPE and PP, similar to PET and PC

✓ Optical properties
  ✓ Exceptional transparency, low birefringence, high Abbe number and high resistance

✓ High electric resistivity ($>10^{13} \, \Omega \cdot \text{cm}$), low dielectric constant and dielectric losses

✓ Exceptional solvent resistance

✓ Low water absorption, < 0.01% and oxygen permeability

✓ Thermal stability
**Water and Oxygen Permeability**

I. Low water absorption, < 0.01%

II. High electrical resistivity, >10^{13} \, \Omega \cdot \text{cm}

COC is superior to any known positively charged polymer (PET, PEN, FEP, PTFE, PETP, etc.)
COCs are ideal for use in high performance film, optical lens and packaging application such as DVD players, shrink film and in pharmaceutical packaging such as blister packs.
Our Previous Work on COCs

COC piezoelectres

The cellular voids with charges of opposite signs on the upper and lower walls form macroscopic dipoles.

<table>
<thead>
<tr>
<th>Applied pressure (kPa)</th>
<th>Sensitivity Raing (pC/N)</th>
<th>Max Operating Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w = 3 mm</td>
<td>1000</td>
<td>60</td>
</tr>
<tr>
<td>w = 2.5 mm</td>
<td>750-1000</td>
<td>120</td>
</tr>
<tr>
<td>w = 2 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>w = 1.5 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>w = 1.5 mm (no offset)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Yan Li, Changchun Zeng, Macromolecular Chemistry and Physics 2013, 214, 2733-2738.
2. Thermoplastic foam

Mathematical Formulations

\[ N \propto \exp\left[-\frac{16\pi\gamma^3}{3kT\Delta P^2}\right] \]

\[ P_g - P_a + 2\int_R^\infty \frac{\tau_{rr} - \tau_{\phi\phi}}{r} dr - \frac{2\gamma}{R} = 0 \]

\[ \frac{d\left(P_g R^3\right)}{dt} = 3D\pi R^2 \frac{\partial c}{\partial r} \bigg|_{r=R} \]

\[ \frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} = D \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) \]

\[ \frac{\tau}{\tau} + \left( \dot{\varepsilon} n + \frac{1}{\lambda} \right) \tau = G(0)(2D - \dot{\varepsilon} n \delta) \]

3. Solid-State Foaming of COC by CO$_2$
Effect of Foaming Conditions
Saturated at low pressure (≤ 7 MPa)

COC saturated at 7 MPa and foamed at varied temperatures

- Average cell diameter ($\mu$m)
  - Foaming temperature ($^\circ$C)

- Cell density (cells/cm$^3$)
  - Foaming temperature ($^\circ$C)

110 °C | 130 °C | 150 °C | 180 °C

COC saturated at 7 MPa and foamed at varied temperatures
Saturated at high pressure (10 MPa)

Triaxial tension and tensile stress development resulted from the variation of CO₂ concentration (C) and resulting variation of pressure (P) and dilative strain (ε).
Sanchez-Lacombe equation of state

Gibbs-DiMarzio thermodynamic criterion

Solubility of CO₂ in COC

Predicted $T_g$ as a function of the pressure for the CO₂-COC system

The line were cracks that can only result from growth of crazes.
(a) Bubble formation from homogeneous nucleation under low saturation pressure;
(b) Crazing formation from the synergetic effect of triaxial tension and tensile stress field under high saturation pressure;
(c) Simultaneous formation of Bubble and crazing under the medium saturation pressure.
4. COC/MWCNTs Nanocomposites

Mixing in a microcompounder
Rheological Properties

At low frequencies,

The addition of MWCNTs increase \( G' \) and \( G'' \).
The nanocomposite shows a predominantly elastic response ($G' > G''$) over the entire frequency range.
Above 1 wt%, there is a significant jump in viscosity.
Rheological Percolation of COC/MWCNT Nanocomposites

The formation of an interconnected structure of nanotubes in 3 wt% MWCNT composite.
The vGP plot was useful for elucidation of change of elasticity resulting from “rheological percolation”. At 3 wt% MWCNT content, a sudden decrease of $|G^*|$ was found, indicating the existence of a rheological percolation threshold between 1 wt% and 3 wt% MWCNT.
The low-frequency conductivity changes significantly.
Electrical Percolation of COC/MWCNT Nanocomposites

\[ \sigma_{DC} (p) \propto (p - p_c)^t \]

Carbon nanotubes (wt %)

\[ p_c = 0.675 \]

\[ y = 3.724x - 4.58 \]

\[ t = 3.724 \]
5. COC and Composites Foams
As expected, the composite foams generally showed significantly increased nucleation density and smaller cell size than COC.

COC and the COC/MWCNT composites foams foamed at 180°C and 17 MPa.
COC and the COC/MWCNT composites foams foamed at 100°C and 35 MPa
Three different foaming regions was found.

At low MWCNT content (<0.1), the cell density increased vs. MWCNT content; at middle MWCNT content (0.1-1), the cell density keeps constant. At high MWCNT content (>0.7) the cell density further increases.
Effect of foaming temperature

\[ N \propto \exp \left( -\frac{16\pi\gamma^3}{3kT\Delta P^2} \right) \]

At lower temperatures (170 °C-185 °C), COC composites show an increase of cell density due to the enhanced nucleation rate, while at higher temperature (185 °C), bubble rupture and collapse reduce the cell density.
Effect of foaming pressure

For COC and the composites, the cell density increased, with the increase of foaming pressure from 10 MPa to 20 MPa. However further increase of pressure (>20 MPa), the cell density decreases.
Rheological explanation

The generalized Considère stability criterion.

Chemical Engineering Science, 66, 3656-3665.
6. Summary

- Strong COC-CO2 interaction and associated severe depression of bulk glass transition temperature.
- CO2 Foaming of COC by temperature jump was explored. Ultramicrocellular foams with a cell size of 0.5 μm and cell density over $10^{12}$ cells/cm³ were successfully prepared. Moreover, it was observed that the system, which was strongly plasticized by CO2, would transition from foaming to crazing under certain conditions.
- MWCNTs loading leads to an increase of viscosity and conductivity in this nanocomposite system.
- CO2 Foaming of COC and nanocomposites by pressure quench was explored. The foam morphology was highly sensitive to the foaming conditions (pressure and temperature). Three different foaming regions were found.
Thanks for your attention!