Institute for Polymer Research
27th Annual Symposium

Symposium documents for

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Abstract
Presentation
ABSTRACT

Supercritical fluids (SCF) have recently achieved a widespread attention in the synthesis and processing of thermoplastic polymers. A supercritical fluid (SCF) is a substance that is compressed beyond the critical pressure and heated above the critical temperature (see figure). At these conditions, the vapour and liquid phases become indistinguishable and the substance behaves as a single phase. Although the SCF remains as a single phase, its density can be easily “tuned” from gas to liquid values merely by changing the pressure of the fluid. While the density of an SCF is liquid like, the diffusivity and viscosity are intermediate between the gas and liquid values. The motivation for using SCFs in polymer processing stems not just from the environmental impetus for their use as benign solvents. Sorption of SCFs into polymers results in their swelling and changes in mechanical and physical properties of these polymers. The higher diffusivities of SCFs provide a means of improving mass transfer characteristics, while lower viscosities assist in reduced energy for pumping. In polymer extrusion, SCFs are injected in extruders for the purpose of plasticizing a polymer, reducing the melt viscosity and increasing diffusion rates. This leads to reduced pumping requirements and thermal degradation as well as it provides interesting potential for chemical modification in reactive extrusion operations.

In this presentation, results will be presented from studies in four different areas. In the first one, the effect of supercritical CO$_2$ on the viscosity and elasticity of polymer melts during extrusion will be highlighted for polyethylene and polystyrene resins. In the second one, the effect of
supercritical CO$_2$ on the morphology of binary blends will be addressed in view of the influence of scCO$_2$ on the interfacial tension. In the third study, we will address the role of supercritical CO$_2$ in reactive extrusion processes by discussing results from grafting and reactive blending experiments. In the fourth study, the application of scCO$_2$ in an extrusion process for the devulcanization of rubber crumb will be presented. Finally, current research efforts on the development of a scCO$_2$-assisted fibre spinning processes will be highlighted.
INTRODUCTION

Supercritical Fluids (SCFs) / Applications

- Vapour and liquid phases are indistinguishable
- SCF density can be easily "tuned" from gas to liquid values merely by changing the pressure of the fluid
- Density is liquid like / diffusivity and viscosity are intermediate between the gas and liquid values

OUTLINE

- Introduction
  - Supercritical Fluids (SCFs) / Applications
- Polymer Extrusion Applications
  - Plasticization / Effects on viscoelastic behavior
  - Polymer Blending / Interfacial tension and morphology
  - Reactive Extrusion
  - Rubber Devulcanization
- Closing Remarks
- Acknowledgements

POLYMER EXTRUSION APPLICATIONS

Plasticization / Effects on viscoelastic behavior

- Supercritical CO₂ (scCO₂)
- Research Studies

\[ \eta = \eta(\gamma, P, T, C_{CO₂}) \]

References

POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Viscosity of PS/CO₂ Solutions

- Dissolution of 1.0 wt% of CO₂
- Increasing CO₂ content
- Decreasing Pressure

<table>
<thead>
<tr>
<th>Increasing Temperature</th>
<th>Increasing CO₂ content</th>
<th>Decreasing Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C → 210°C</td>
<td>1.35 wt%</td>
<td>13.3 MPa</td>
</tr>
<tr>
<td>260°C → 270°C</td>
<td>0.9 wt%</td>
<td>8.7 MPa</td>
</tr>
</tbody>
</table>

- Pressure Profile within the Slit Die

<table>
<thead>
<tr>
<th>PT #1</th>
<th>PT #2</th>
<th>PT #3</th>
<th>PT #4</th>
<th>PT #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>24</td>
<td>24</td>
<td>24</td>
<td>52</td>
</tr>
</tbody>
</table>

PT — Pressure Transducer
TS — Temperature Sensor
All dimensions are in mm
**Entrance Pressure Drop of PS/CO₂ Solutions**

- Entrance pressure drop of PS and PS/CO₂ increases with upstream pressure.
- CO₂ decreases the entrance pressure drop of PS melts. Entrance pressure drop, plotted versus wall shear stress, coincide on a master curve.
- CO₂ decreases both shear and extensional viscosities of PS.

**PS/LDPE Blends**

<table>
<thead>
<tr>
<th>Shear Rate (1/s)</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10000</td>
</tr>
<tr>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>1000</td>
<td>100</td>
</tr>
</tbody>
</table>

- Without CO₂
- 3 wt% CO₂
- 5 wt% CO₂
- 7 wt% CO₂

**PS/LDPE Blends PE/PS=80/20**

- 0 wt% (x1000)
- 3 wt% (x5000)

**Schematic**

- Gearbox
- Extruder
- Positive Displacement Pump
- Control Panel
- Thermocouples
- 50 rpm
- 200 °C
- Polymer A+B
- Twin-screw Extruder
- CO₂ Cylinder
- Opto 22 Data Acquisition System
- Secondary Die
- Wedge Die
- Schematic cell
POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

0 wt% CO₂  PS/LDPE=60/40  4 wt% CO₂

POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

0 wt% CO₂  PS/LDPE=50/50  4 wt% CO₂

PS/LDPE Blends

(a) t = 0.5 hr  (b) t = 3 hr  (c) t = 6 hr
(d) t = 7 hr  (e) t = 8 hr  (f) t = 9 hr

POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

Necking Drop  Stable Drop

IFT (mN/m)

Time (hr)

POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

CO₂ Pressure (MPa)

IFT (mN/m)

200°C  220°C

0  4  8  12  16  20

4.0  4.5  5.0  5.5  6.0  6.5  7.0  7.5  8.0
### POLYMER EXTRUSION APPLICATIONS

**Reactive Extrusion**

**Grafting of MAh on PP**

![Grafting process diagram](image)

**Diagram: Grafting Process**

1. **CH**
2. **CH**
3. **R**
4. **Rh**
5. **H**
6. **C**
7. **O**
8. **CO2**
9. **PP/MAh**
10. **Peroxide Solution**

**Graph: MAh Content vs. Melt Flow Index**

- **MAh Content (wt. %):** 0.30, 0.40, 0.50, 0.60
- **Melt Flow Index (g/10 min):** 10, 20, 30, 40, 50

**Graph: T = 190°C, Load = 1.2 kg**

- **2% MAh Level without CO2**
- **2% MAh Level with CO2**
- **4% MAh Level without CO2**
- **4% MAh Level with CO2**

**Graph: Interfacial Reaction (PE-MA / LDPE / PA-6)**

- **CO2 Concentration, wt%:** 0, 1, 2, 3, 4
- **MA Conversion, %:** 0, 20, 40, 60, 80, 100

**Graph: PE-MA / LDPE / PA-6**

- **MA Conversion, %:** 0, 20, 40, 60, 80, 100
- **CO2 Concentration, wt%:** 0, 1, 2, 3, 4

**Graph: Rubber Devulcanization**

- **Vulcanized rubber**
- **Crosslink**

**Diagram: Rubber Devulcanization**

![Rubber devulcanization process diagram](image)
POLYMER EXTRUSION APPLICATIONS

Reactive Extrusion

Rubber Devulcanization

Soxhlet extraction

Two-step process to separate gel
Acetone: Remove the low molecular weight content
Toluene: Extract the sol content

Extrudate
Soluble
Gel

POLYMER EXTRUSION APPLICATIONS

Reactive Extrusion

Rubber Devulcanization

SBR80 / 250 °C

Weight percent of whole sample

Sol content
Low molecular weight content

Powder 15-1% 15-2% 15-3% 30-1% 30-2% 30-3%
Rubber flow rate (g/min) – CO2 concentration (wt%)

CLOSING REMARKS

• Highlights from our research work on polymer extrusion with supercritical CO2 have been presented
• Potential innovative applications are numerous
• Our current efforts are focused on membrane and fiber formation as well as on block copolymer and TPV preparation

ACKNOWLEDGEMENTS

Funding
Natural Sciences and Engineering Research Council of Canada (NSERC)
Materials Manufacturing Ontario (MMO)
DuPont Canada Inc.

Researchers
Dr. Minhee Lee
Dr. Anle Xue
Dr. S. Zhu
Ms. Beth Dorscht
Ms. Joy Zhang