Institute for Polymer Research
27th Annual Symposium

Symposium documents for

Costas Tzoganakis

Abstract

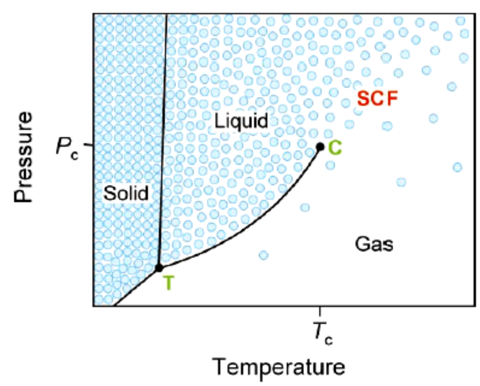
Presentation

PROCESSING OF POLYMERS WITH SUPERCRITICAL CO_2

Professor Costas Tzoganakis
Department of Chemical engineering
University of Waterloo
200 University Avenue West
Waterloo, Ontario N2L 3G1
CANADA
E-mail: ctzogan@uwaterloo.ca

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.

PROCESSING OF POLYMERS WITH SUPERCRITICAL CO_2

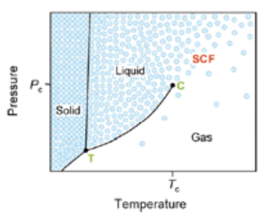
Prof. Costas Tzoganakis
Institute for Polymer Research
Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario
CANADA

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**

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**

INTRODUCTION

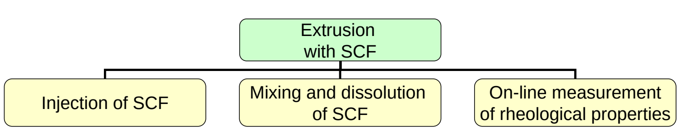
Supercritical Fluids (SCFs) / Applications

Motivation for using sc CO_2 in polymer extrusion

- **Benign solvent**
- **Changes in mechanical and physical properties of polymers**
- **Higher diffusivities improve mass transfer characteristics**
- **Lower viscosities assist in reduced energy for pumping**

References
A.I. Cooper, J.Mat. Chem., 10, 207-234 (2000).
S.G. Kazarian, Polymer Science, Ser.C., 42, 78-101 (2000).
P.G. Jessop and W. Leitner, "Chemical Synthesis Using Supercritical Fluids", Weinheim, Wiley-VCH (1999).
J.L Kendall, D.A. Canelas, J.L. Young and J.M. DeSimone, Chem. Rev., 99, 543 (1999).
C.A. Eckert, B.L. Knutson and P.G. Debenedetti, Nature, 382, 313 (1996).

POLYMER EXTRUSION APPLICATIONS



POLYMER EXTRUSION APPLICATIONS

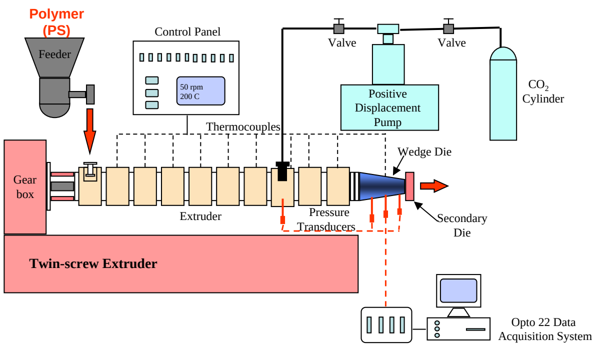
Plasticization / Effects on viscoelastic behavior

- **Supercritical CO_2 ($scCO_2$)**
- **Research Studies**

- Shear Viscosity
  - Capillary, Slit, Wedge Dies
  - $\eta = \eta(\dot{\gamma}, P, T, C_{CO_2})$
  - Free Volume Scaling Model
- Entrance Flow
  - Entrance Pressure Drop
  - Elongational Viscosity

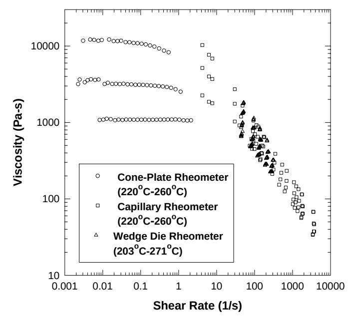
POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Viscosity of PS/CO_2 Solutions

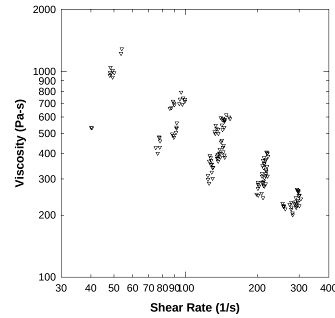


POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Viscosity of PS/CO_2 Solutions



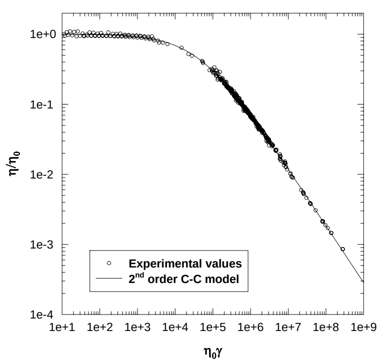
PS viscosity data



PS/CO_2 viscosity data

POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Viscosity of PS/CO_2 Solutions



POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

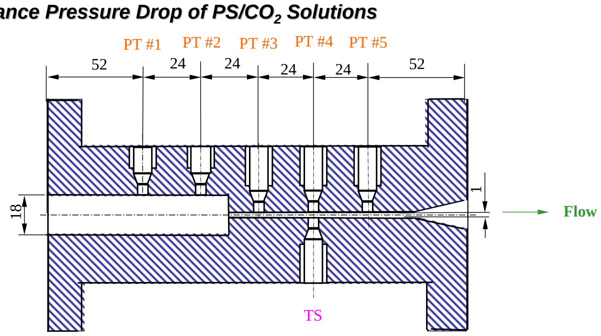
Viscosity of PS/CO_2 Solutions

Increasing Temperature	Increasing CO_2 content	Decreasing Pressure
200°C ⇨ 210°C	1.35 wt%	13.3 MPa
260°C ⇨ 270°C	0.9 wt%	8.7 MPa

- Dissolution of 1.0 wt% of $CO_2 \approx$ Decreasing pressure by 9.8 MPa
- T-P and T-C interactions depend on the absolute temperature.

POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Entrance Pressure Drop of PS/CO_2 Solutions



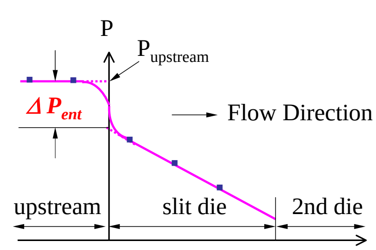
PT — Pressure Transducer
TS — Temperature Sensor

Die width is 22
All dimensions are in mm

POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Entrance Pressure Drop of PS/CO_2 Solutions

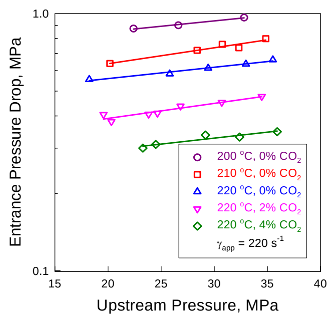
Pressure Profile within the Slit Die



$$\Delta P_{ent} = P_{upstream} - P_{extrapolation}$$

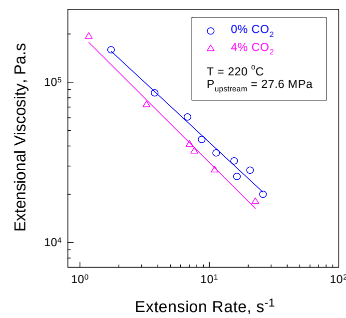
POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Entrance Pressure Drop of PS/CO_2 Solutions



POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Entrance Pressure Drop of PS/CO_2 Solutions



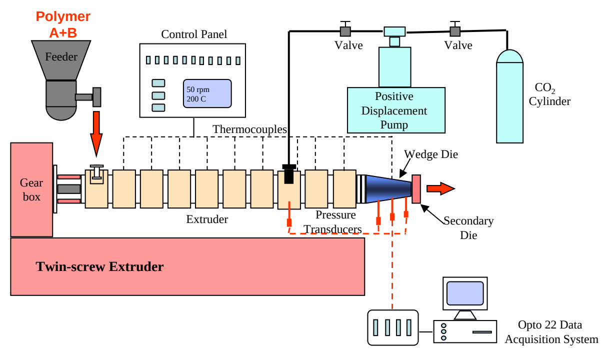
POLYMER EXTRUSION APPLICATIONS
Plasticization / Effects on viscoelastic behavior

Entrance Pressure Drop of PS/CO_2 Solutions

- Entrance pressure drop of PS and PS/CO2 increases with upstream pressure
- CO_2 decreases the entrance pressure drop of PS melts. Entrance pressure drop, plotted versus wall shear stress, coincide on a master curve
- CO_2 decreases both shear and extensional viscosities of PS

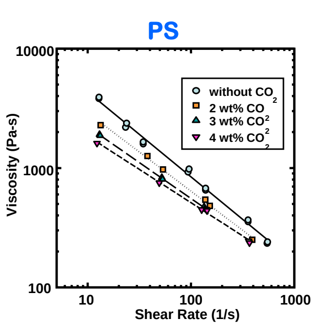
POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

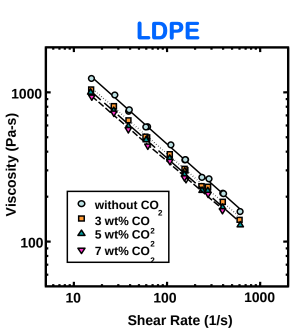
PS/LDPE Blends



POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

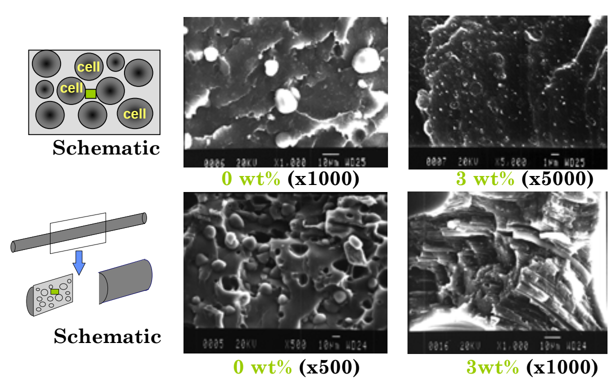




POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

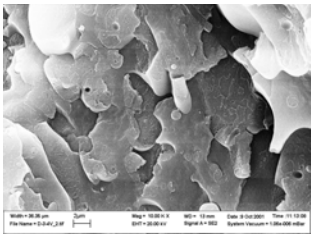
PS/LDPE Blends

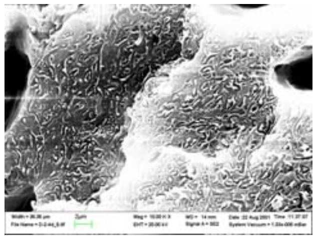
PE/PS=80/20



POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

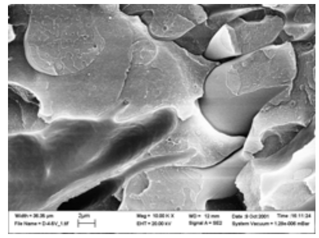


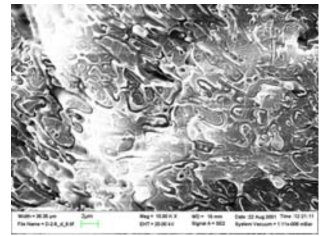


0 wt% CO_2 **PS/LDPE=60/40** **4 wt% CO_2**

POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

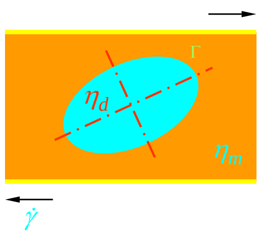




0 wt% CO_2 **PS/LDPE=50/50** **4 wt% CO_2**

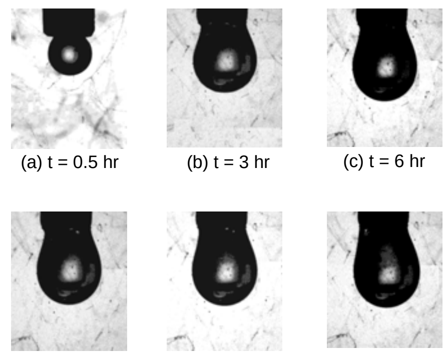
POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends



POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends

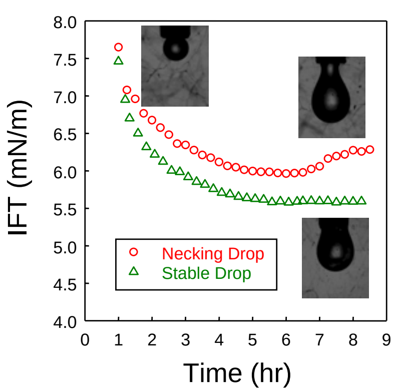


(a) t = 0.5 hr (b) t = 3 hr (c) t = 6 hr

(d) t = 7 hr (e) t = 8 hr (f) t = 9 hr

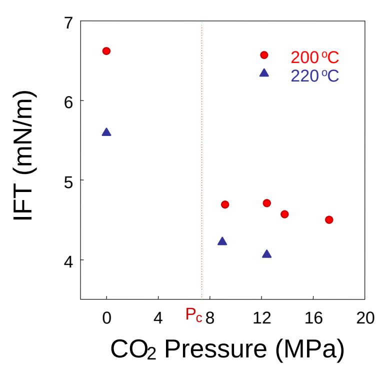
POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends



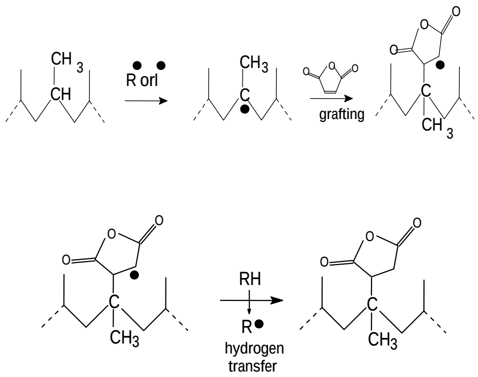
POLYMER EXTRUSION APPLICATIONS
Polymer Blending / Interfacial tension and morphology

PS/LDPE Blends



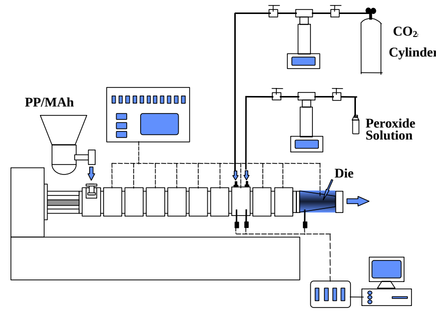
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Grafting of Mah on PP



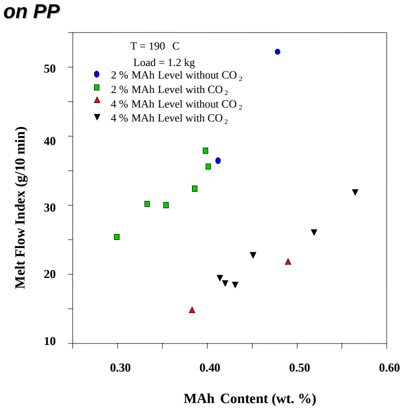
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Grafting of Mah on PP



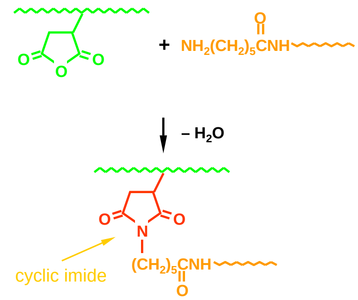
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Grafting of Mah on PP



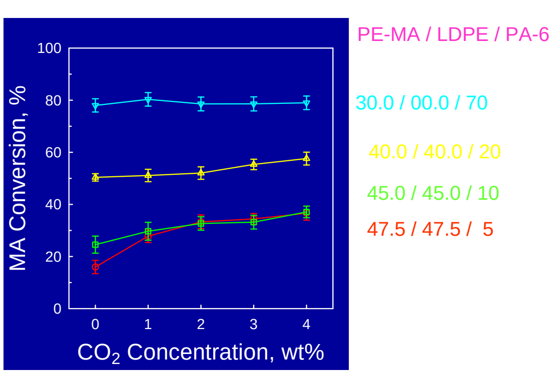
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Interfacial Reaction (PE-Mah / PA-6)



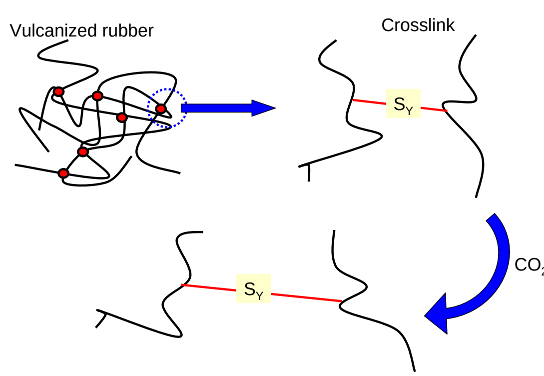
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Interfacial Reaction (PE-Mah / PA-6)



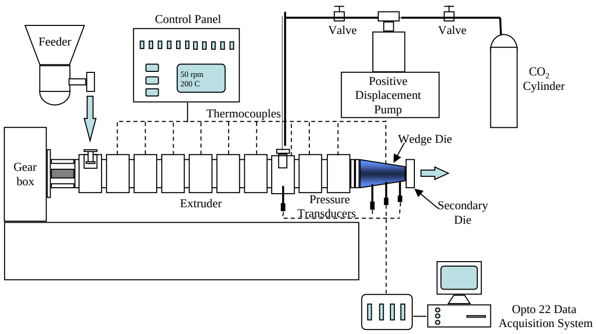
POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Rubber Devulcanization



POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Rubber Devulcanization



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

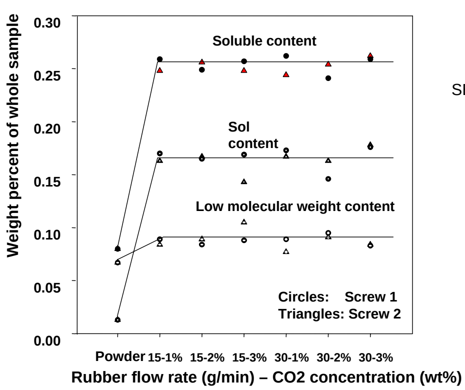
Extrudate

Soluble

Gel

POLYMER EXTRUSION APPLICATIONS
Reactive Extrusion

Rubber Devulcanization



SBR80 / 250 ºC

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