Institute for Polymer Research
27th Annual Symposium

Symposium documents for

Kerry Li

Abstract

Presentation

Extrusion and fibre spinning of Nylon-6,6 / supercritical CO_2 mixture

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Abstract:
A novel technical to spin nylon fibre was developed: Addition of supercritical CO_2 to nylon melts and spinning those mixtures under different conditions were performed. CO_2 works co-ordinately with thermal to disrupt nylon-6,6 inter-chain hydrogen bond. In sequent, the intended improvement in stretching along with tensile properties of nylon fibres was evaluated.

As an elementary exploration, the rheological behaviour of nylon-6,6 / supercritical CO_2 mixture was explored through a custom extrusion. Results indicate that the CO_2 as a plasticizer reduce the bulk shear viscosity. The combined effects of temperature and hydrostatic pressure on shear viscosity were investigated accordingly.

Introduction.

Nylon-6,6 is one of semi-crystalline polymers with very polar characteristic amide groups in the symmetrical backbone chain. The amide group -(-CO-NH-)- provides high density hydrogen bonding between polyamide chains, giving nylon high strength at elevated temperatures, toughness at low temperatures, combined with its other properties, such as stiffness, wear and abrasion resistance, low friction coefficient and good chemical resistance. These properties have made nylons the strongest of all man-made fibers in common use.

Mechanical, thermal and optical properties of fibers are strongly affected by orientation and crystallinity. Basically, higher fiber orientation and crystallinity will produce better properties. In order to achieve desirable properties through molecular orientation and crystallinity, two-step melt spinning, comprised of spinning and drawing, is considered to be the conventional method to manufacture nylon filaments.

Multiple drawing stages were invented to achieve high levels of orientation. The mechanism is to obtain relaxation allow for drawing in the later stages. However, the tensile strength of nylon-6,6 produced through this technical is less than 1.0Gpa and much lower than their theoretical strength. The highest orientation and crystallinity are hard to achieve by this technical since the high density of hydrogen bond in nylon crystal stem restrict the further drawing. Therefore, disruption of the hydrogen bonds is necessary to obtain further stretching and improved tensile properties.

Lewis acid-base complexion, such as carbon dioxide interact with carbonyls, was found to be able to scission the hydrogen bond in nylon-6,6 inter-chain. Most recently, a technique to draw polymer in high pressure gases has been presented in this purpose. The drawing process has been monitor in specified temperature and pressure range. Also the gas or liquids act mostly as plasticizer in drawing process. In those attempts, the use of

$scCO_2$ only evaluates the ability of $scCO_2$ to plasticize amorphous fibres. Meanwhile, the discussion of interaction of carbon dioxide with electron donor species (e.g. carbonyls) is absent.

Ideally, if we are able to disassociate inter-chain hydrogen bond of nylon before drawing and recover them after drawing, the highest stretching may be achieved, as well as the tensile strength. In our spinning and drawing approaching, the addition of CO_2 during extrusion of nylon-6,6 melts presents complex effects attributed to both chemical structure (interact with carbonyls) and supermolecular (plasticize). The reduction of bulk shear viscosity rally with the weakness of polymer hydrogen bond may facilitate higher degree of stretching when spinning, the existing of CO_2 in subsequent drawing process function as plasticizer which promote further stretching. The CO_2 selected as a media during process leave no trace in the end, the whole process is simple and environmental benign.

In order to estimate the plasticize performance of $scCO_2$, a custom extrusion process designed to study the mixing and rheological behaviour in a systematic manner.

Experimental:

The viscosity behavior of nylon-6,6 / supercritical CO_2 mixture was studied in a custom extrusion process, see Diagram 2.; A wedge die was used to connected with extruder to measure shear viscosity, the following formula apply in this measurement:

$$\Delta P = \frac{K}{\tan\theta}\left(\frac{6Q}{W}\frac{2n+1}{3n}\right)^{n}\left[\frac{1}{2n}\left(\frac{1}{h_2^{2n}}-\frac{1}{h_0^{2n}}\right)+\frac{1}{W(2n-1)}\left(\frac{1}{h_2^{2n-1}}-\frac{1}{h_0^{2n-1}}\right)\right]$$

$$\eta = K\left(\frac{2n+1}{3n}\right)\left(\frac{6Q}{Wh^2}\right)^{n-1}$$

The spinning and drawing process show in Diagram 1. A custom high-pressure chamber will be used to avoid the foam in some instance. The design of chamber shows in Picture 1.

Results and discussion:

The pressure, gas uptake and temperature effects on bulk shear viscosity shows in plot1, 2,3 respectively:

Spinning and drawing of mixture is ongoing, some spinning results show in plot 4,5,6:

Schematic diagram of the continuous-draw apparatus

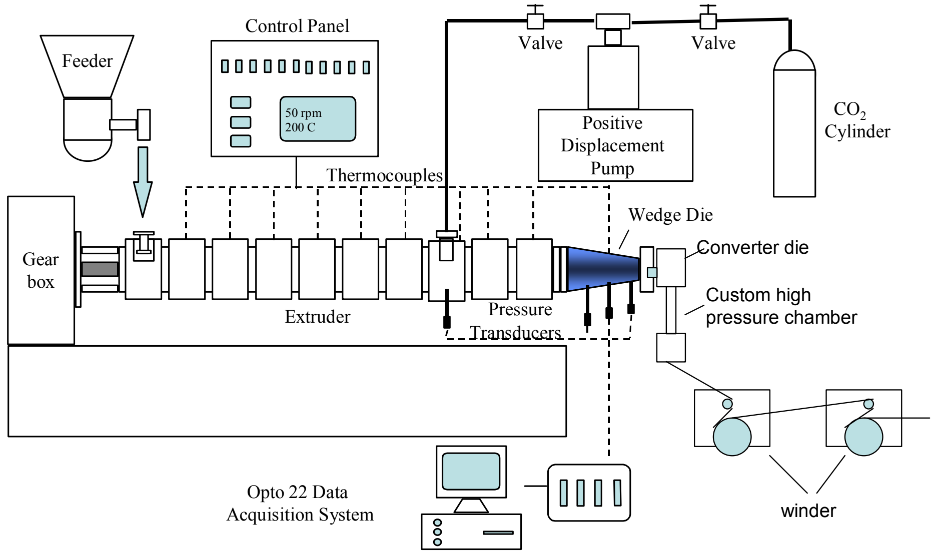
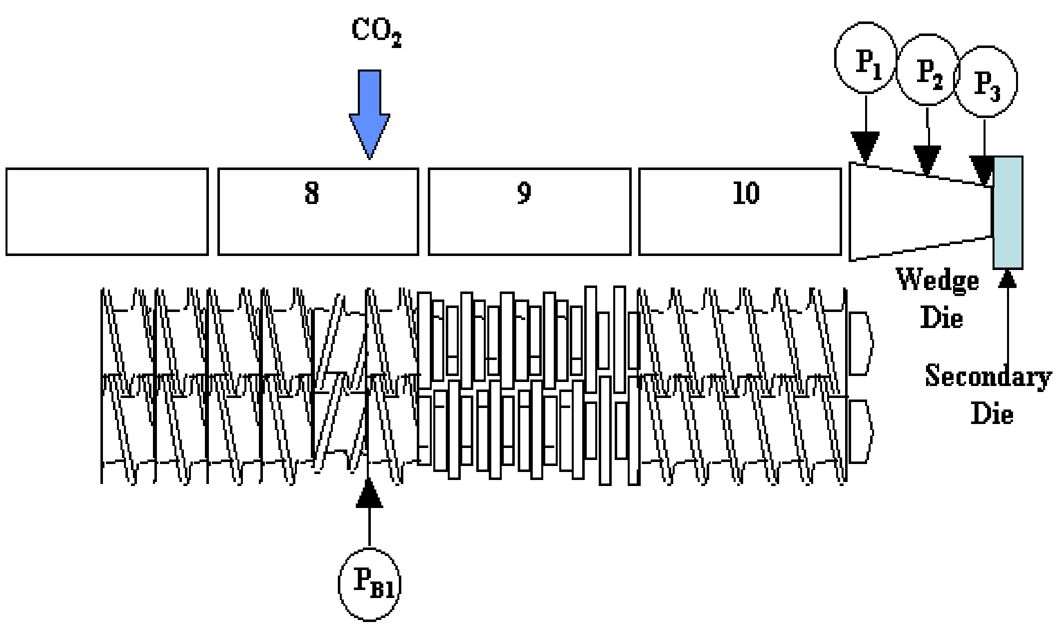
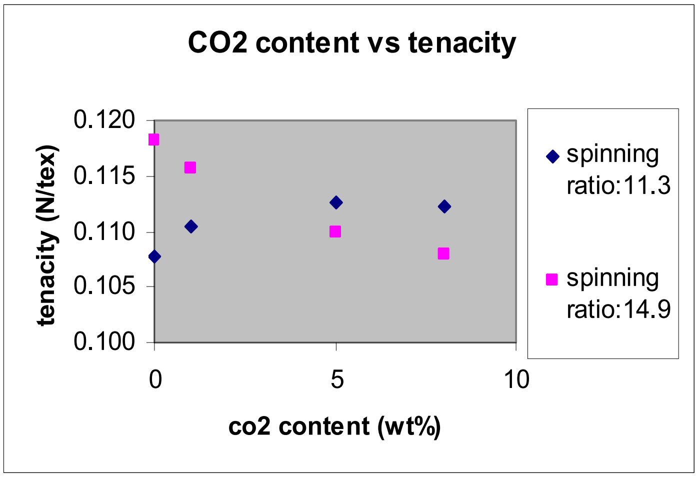
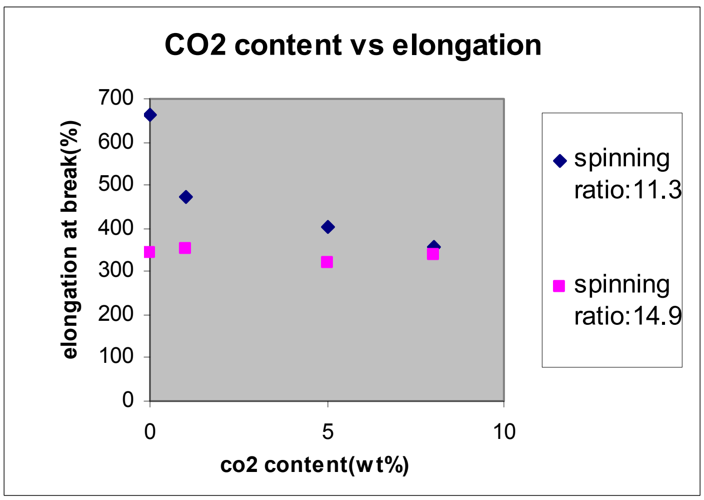


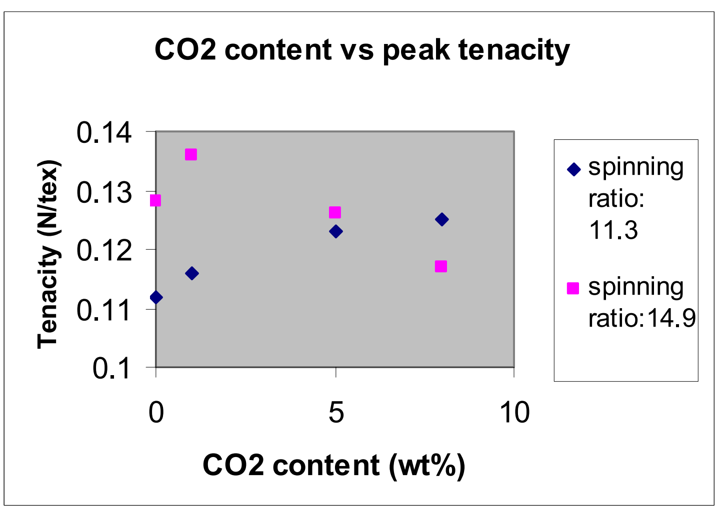
Diagram 2: Screw configuration



Plot 4,5,6: spinning results

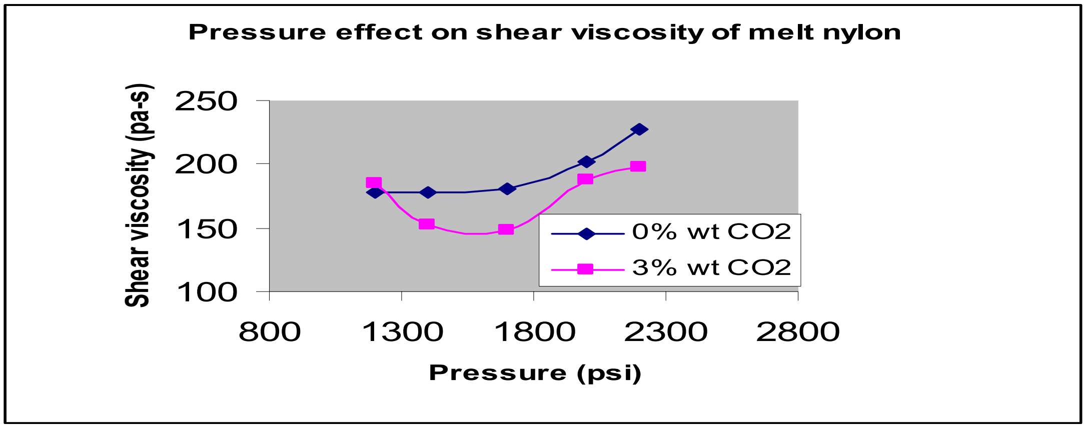


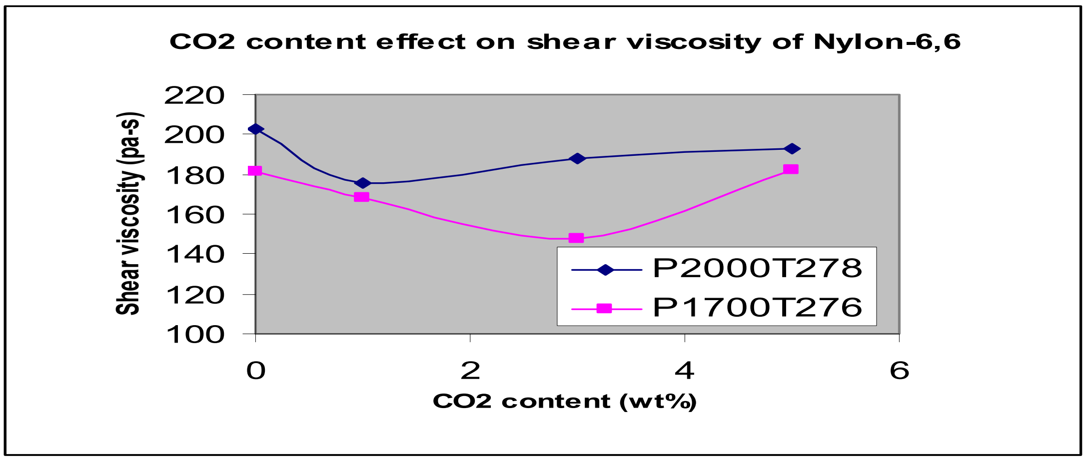


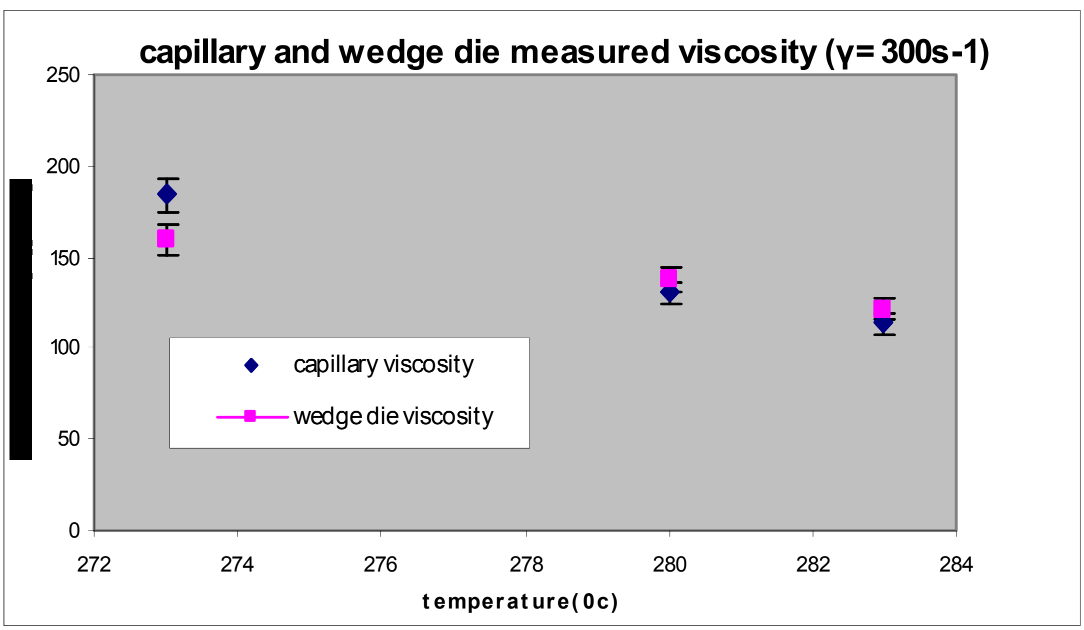


Pic.1. high-pressure chamber

Plot 1,2,3: The pressure, co2 uptake and temperature effects to shear viscosity







Extrusion and fiber spinning of Nylon-6,6 / supercritical CO_2 mixtures

Presented by: Ziqiang Li
Supervisor: C. Tzoganakis

IPR Symposium: May 18, 2005

Content

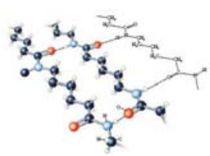
Objective

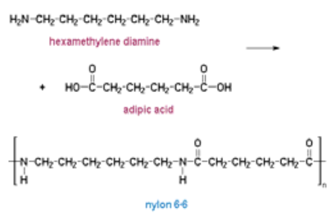
- Investigate the effects of supercritical CO_2 on nylon-6,6 viscosity:
  - Prepare the supercritical CO_2 / nylon-6,6 mixture in extruder, on-line measure the effect of T,P,CO_2 content ,shear rate to shear viscosity via connected wedge die.
- Implement the spinning and drawing of supercritical CO_2 / nylon-6,6:
  - Spinning supercritical CO_2 / nylon-6,6 mixture or / and in custom chamber.
  - Investigate the effect of uptake of CO_2 to filament's mechanic properties (tenacity, strength).

Introduction:

NYLON-6,6:

- Very polar characteristic amide groups in the symmetrical backbone chain



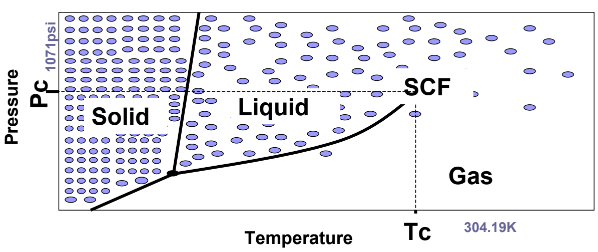


- ✓ High density of H-bond
- ✓ Semi - crystalline
- ✓ Good mechanical, thermal properties
- ✓ High DR under high temperature and moisture

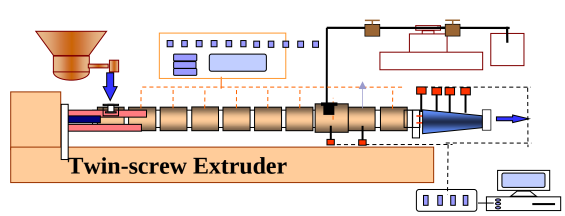
Introduction:

- Supercritical Fluids

  - A fluid is supercritical when its temperature and pressure are higher than their critical point values (Tc , Pc).
- Supercritical Carbon Dioxide



Introduction: Extrusion of PA-66 / $ScCO_2$:

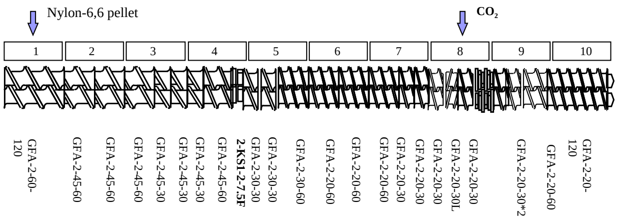


- Avoid degradation
- Maintenance high pressure
- Well mixing, avoid pressure fluctuate.
- Avoid back flow
- It is a pressure sensitive method.

- Dry and less dispersive force
- Screw arrangement
- Injection port screw arrangement
- Reverse disc applied
- Calibrate and exchange the measurement transduser

Introduction: Extrusion of PA-66 / $ScCO_2$

- Screw arrangement
  - Provide well mixing
  - Less degradation
  - Pressure build up
- Connect wedge die to
  Investigate mixture viscosity under
  - Different CO_2 uptake,
  - Temperature, pressure,
  - Shear rate.



Barrel 1: 180°C; 2: 220°C ; 3:250° C; 4-7:270°C; 8-9:275 ° C; 10-11: 280 °C

Introduction: viscosity measurement

The injection of CO2

For power-law fluids

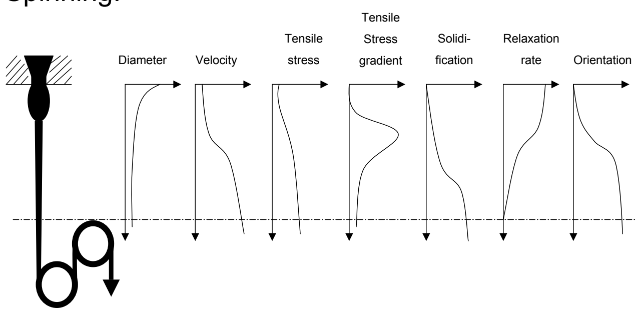
$$\Delta P = \frac{K}{\tan\theta}\left(\frac{6Q}{W}\frac{2n+1}{3n}\right)^n\left[\frac{1}{2n}\left(\frac{1}{h_2^{2n}}-\frac{1}{h_0^{2n}}\right)+\frac{1}{W(2n-1)}\left(\frac{1}{h_2^{2n-1}}-\frac{1}{h_0^{2n-1}}\right)\right]$$

$$\eta = K\left(\frac{2n+1}{3n}\right)\left(\frac{6Q}{Wh^2}\right)^{n-1}$$

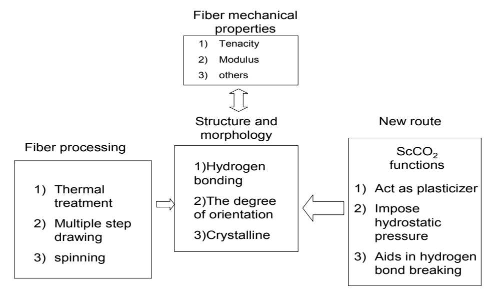
Width: 1.4 cm, θ: 0.9°

Filament spinning and drawing

- Spinning:

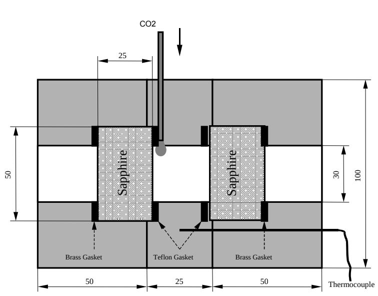


Motivation and design concepts:



Preliminary experiment - I

- **FTIR measurement of hydrogen bond breaking process of CO_2 saturated Nylon:**



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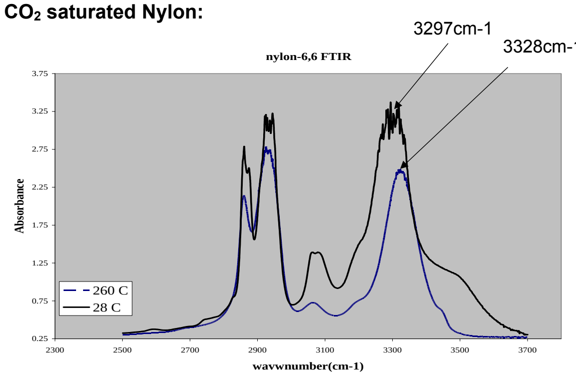

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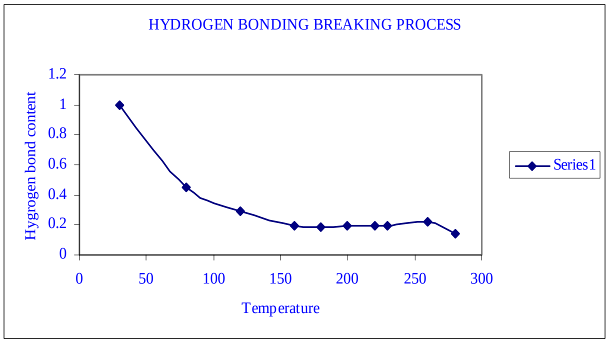


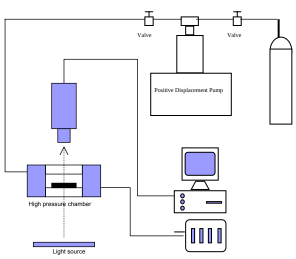
Preliminary experiment - II

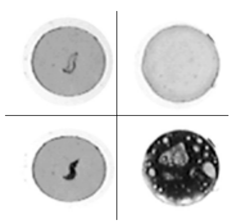
Solubility of CO_2 in molten Nylon-6,6:

- Motivation:
  - Injection limits of CO_2 during extrusion.
  - Control uptake of CO_2 during fiber spinning
- Swelling image analysis…

Preliminary experiment - III

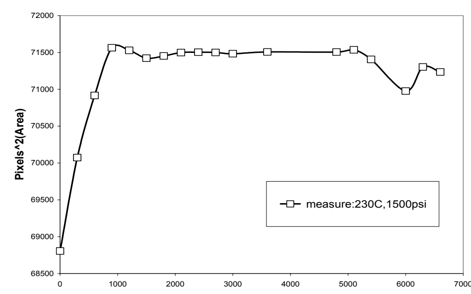
Swelling of nylon-6,6 in supercritical CO_2





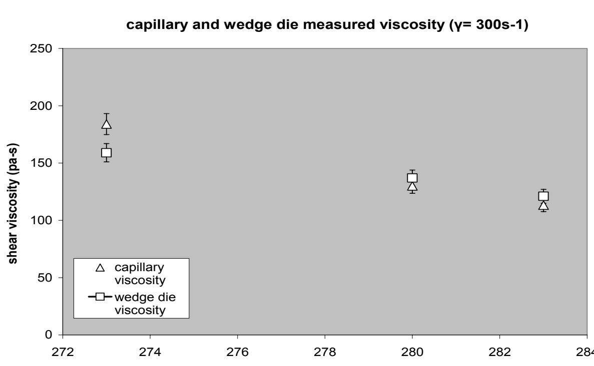
Preliminary experiment - III

Swelling of nylon-6,6 in supercritical CO_2



The expansion of polymer volume is nonlinear till equilibrium is reached. For this to be valid, the sample has to be thermally treated to be free of strain and thermal expansion has to be excluded in this measurement.

Extrusion Results:



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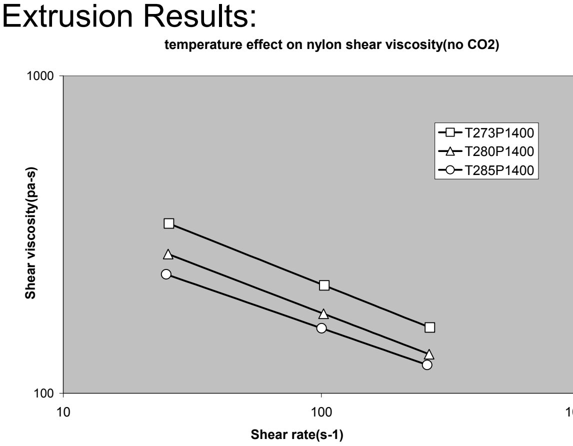

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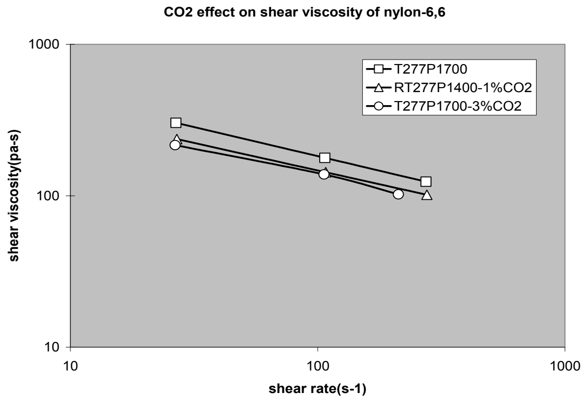

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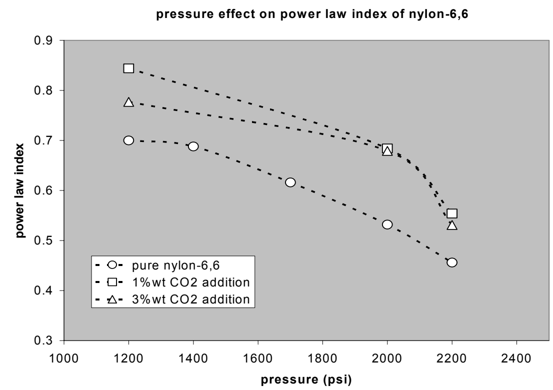
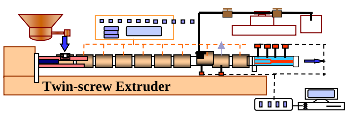
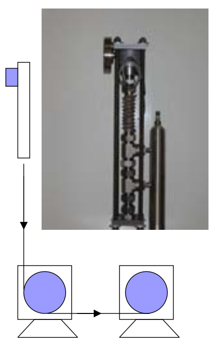


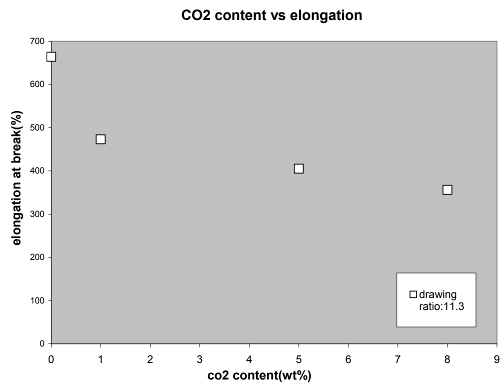
Filament spinning of PA-66 & mixtures: set up & chamber design



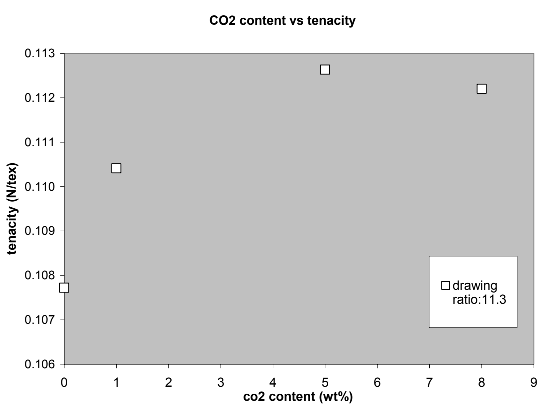


- Chamber design principle:
  - Drawing and spinning in the present of high static pressure of CO_2
  - Temperature and pressure adjustable
  - Continuous work manner

Filament spinning of PA-66 & mixtures:



Filament spinning of PA-66 & mixtures:



Conclusions:

CO_2 function as a plasticizer to:

- Reduce nylon-6,6 melt viscosity,
  And mixture viscosity is the function of shear rate, temperature, pressure and CO_2 uptake.
- The solubility of CO_2 in nylon-6,6 melt is low, partially due to the high residual hydrogen bond content in nylon-6,6 melt.

Spinning and drawing process:

- Is setting up to conduct a new route to produce fibre in the present of high hydrostatic pressure CO_2
- CO_2 work to increase the fibers tenacity after post-drawing, but as a trade off, its elongation at break reduced

Future work:

- Estimate solubility of CO_2 in molten nylon-6,6 by viscosity measurement.
- Run spin experiments at high drawing ratio.
- Investigate the effect of CO_2 on fibre spinnability.

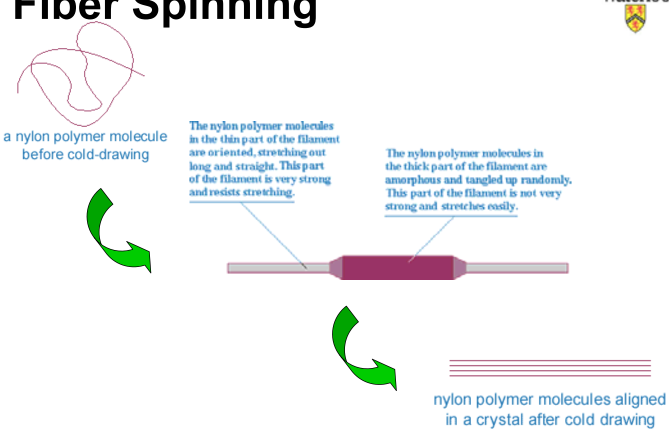
Acknowledgements:

- My sincere thanks to my supervisor, Professor Costas Tzoganakis
- Financial support from "Materials and Manufacturing Ontario" (MMO) is gratefully acknowledged.
- Donation of material from Invista is gratefully acknowledged.

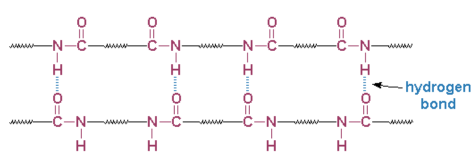
Question??

Thank you!

Fiber Spinning



Fiber Spinning



Parallel nylon chains are bound together through hydrogen bonding between amide groups.

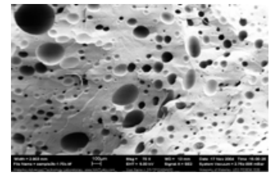
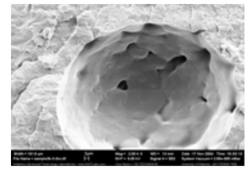
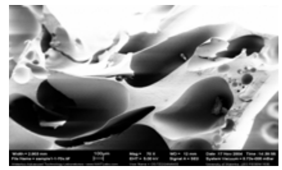
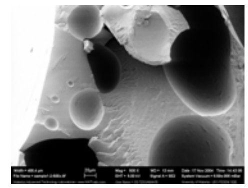
http://www.chemheritage.org/EducationalServices/nylon/nylon.html

Interactions of scCO2 with Polymers

- FTIR spectroscopic studies
- Lewis acid-base interactions between CO2 and electron donor species (e.g. carbonyls)

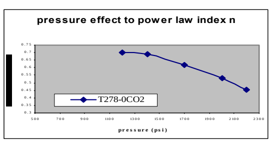
O=C=O	O=C=O	O=C=O	+ - + O=C=O
Symmetric (v_1) 1333 cm^{-1}	Anti-symmetric (v_3) 2350 cm^{-1}	Bending (v_2) 667 cm^{-1}	

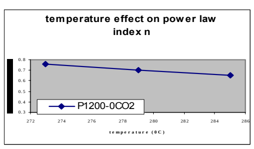
Extrusion Results: foam structure and others

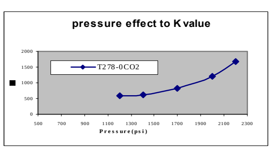





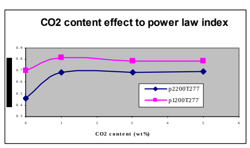
Extrusion Results:

- Power law index n and K value:





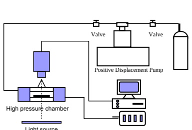


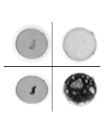


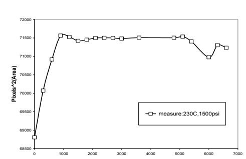
Existing technologies are either too complicated to achieve or less precise:

FTIR; Gravimetric; Pressure decaying; Barometric, Volumetric, Quartz crystal Microbalance; Phase separation measurement;

Swelling of nylon-6,6 in supercritical CO_2







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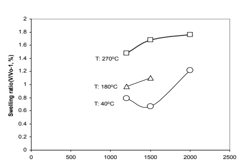

It is elucidated that the increase of temperature and hydrostatic pressure (or gas density) enhanced the swelling ratio of polymer. We have to calibrate the volume expansion in order to get the real contribution from interaction between gas and polymer.