Micronization of Polymer in an Extrusion Process using Supercritical Carbon Dioxide

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Agenda

- Introduction
- Research Objective
- Literature Review
  - Supercritical CO_2
  - Supercritical Particle Formation Methodologies
  - Extrusion process
- Experimental
  - Materials and Equipment
  - Preliminary Experiments
  - Characterization
- Result and Discussion
  - Particle Size
  - Particle Size Distribution
  - Particle Morphology
- Future Work
- Conclusion
- References

Introduction

- **Used in powder industries such as paints, toners and drugs**
  - **Common production methods: milling, grinding, spray drying or re-crystallization from solvents**
- **Drawbacks**
  - **High-temperature and high mechanical stress: not suitable for thermolabile compounds**
    - **Not sufficient control on the powder characteristics: particle size variability, broad size distribution**
    - **Uses liquid organic solvent precipitation**
      - **Product pollution**
      - **Waste stream generation and emissions of VOCs**
      - **Solvent recovery**
      - **Increased cost**

Research Objective

- **Feasibility of producing micron sized polymeric particles via the extrusion process using supercritical CO_2**
  - **Design Criteria: Attain minimal particle size and narrow particle size distribution**

- **Investigate the effect of processing parameters on particle properties:**
  - **Particle size**
  - **Particle Size Distribution**
  - **Morphology**

Literature Review: Supercritical Fluids

- Pressure and temperature above critical value
- It has gas-like viscosity and liquid-like density
- Thermodynamically defined by the conditions

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial^2 V}\right)_T = 0$$

- Density can be tuned easily with a small change in pressure

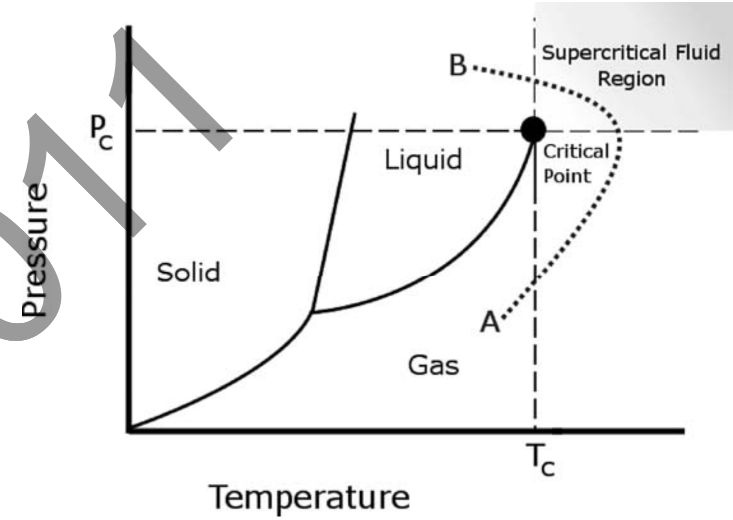


Table 1: List of Some Supercritical Fluids that are viable VOC replacements:

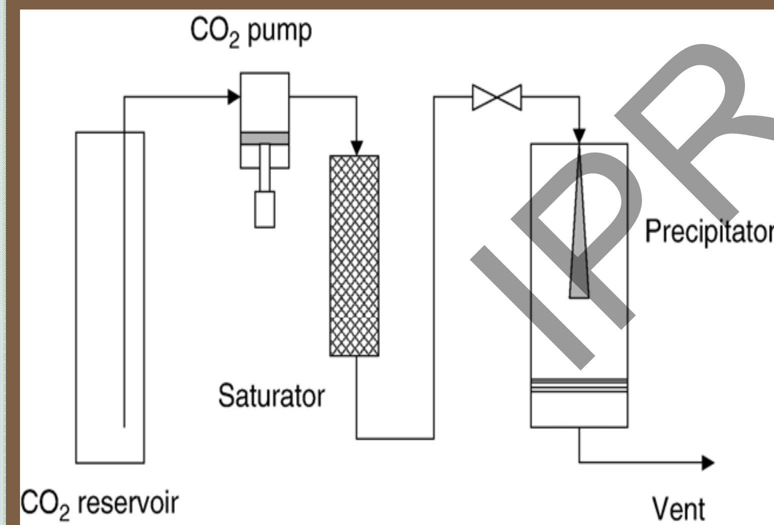
Substances	Critical Temperature (K)	Critical Pressure (MPa)
Carbon Dioxide	304.1	7.38
Dimethyl Ether	400.0	5.24
Acetone	508.1	4.70
Water	647.3	22.1

Literature Review: Supercritical CO_2

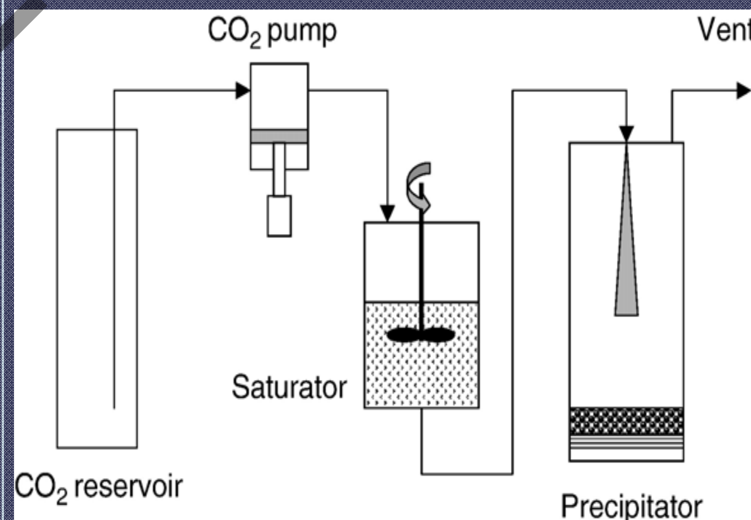
- **The polymer industry expels over 20 million tons of volatile organic compounds (VOCs) each year**
- **A promising alternative to VOCs**
- **Benefits:**
  - **Non-toxic and chemically inert**
  - **Inexpensive**
  - **Easily attainable supercritical conditions**
  - **High purity products**
  - **CO_2 is gaseous at ambient conditions, which simplifies the problem of solvent residues**
  - **Dissolved CO_2 causes a considerable reduction in viscosity due to increase in free volume of the polymer**
    - **Allows processing thermolabile compounds**
    - **Less energy is consumed during the process**
  - **Alters physical properties of the polymers: viscosity, diffusivity**

Literature Review: Supercritical Particle Formation Methodologies

Rapid Expansion of Supercritical Solutions (RESS)



Particles from Gas Saturation Solution (PGSS)



Extrusion Process

- **Particles production in an Extrusion Process:**
  - SCF or SC-CO_2 is first dissolved in the polymer matrix
  - Dissolved CO_2 increases free volume and reduces viscosity of the polymer
  - Passed through a narrow die space and out through a micron-size nozzle hole
    - Reduction of gas solubility
    - Nucleation of Bubbles
  - Vigorous expansion of the dissolved gas breaks up the polymer melt
  - **Expansion of Gas-Saturation with Excess Gas (EGSEG)**

Why use Extrusion Process?

- **Used in industry since 1930's**
- **Primary method of polymer production**
  - Potentially eliminate: milling, grinding, RESS , GAS and SAS
- **Particle shape, size, and size distribution can be controlled**
  - Processing parameters
  - Nozzle size and geometry
- **Permits operation at lower temperature**
  - Allow micronization of thermolabile compounds

Material

- **Polyethylene Wax (PE wax)**
  - **Low molecular weight PE**
  - **Synthetic wax produced by polymerization of high density low MW ethylene**

Table 2: Characteristic Properties of PE Wax

CHARACTERISTICS	POLYETHYLENE WAX
Melting point (^{0}C)	95-100
Molecular Weight	2,000-4,000
Density	0.93-0.94
Colour	White

  - **Good electrical , remoulding , resistant properties**
  - **Micronized PE wax: Inks , coating and personal care products**

- **Supercritical CO_2**
  - **99.997% product purity with an initial pressure of about 1900 psi (~13.1 MPa)**

Experimental Setup

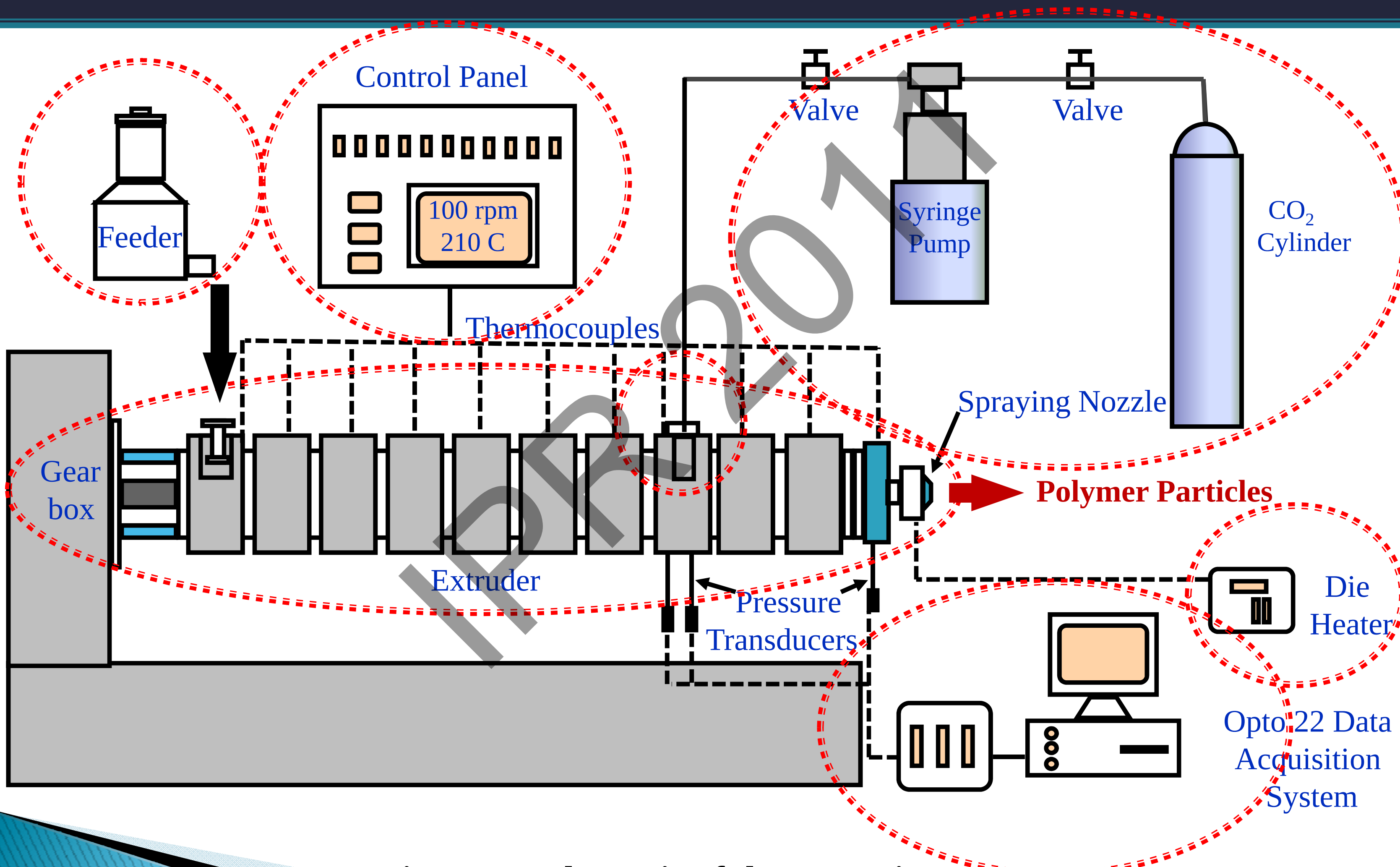


Figure 1: Schematic of the Extrusion System

Collection Chamber

- Manufactured in-house
- Material: Lexan (clear polycarbonate sheet) of ½" thickness

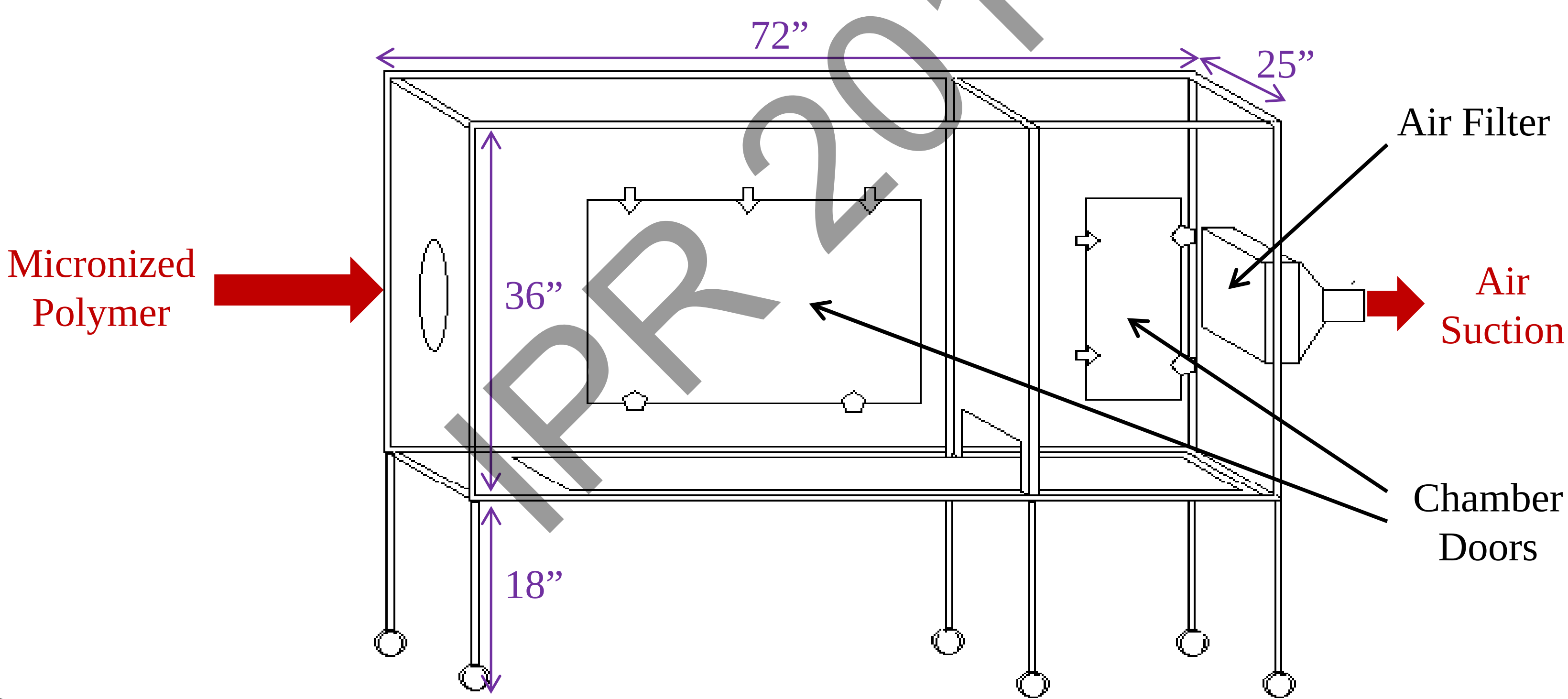


Figure 2: Schematic of the Polymer Collection Chamber

Experimental: Characterization

- Optical Microscope
  - Estimate particle size
  - Generate particle size distribution
- Scanning Electron Microscopy
  - Analyze particle size and morphology
- Differential Scanning Calorimeter
  - Measure thermal transition points
- Capillary Rheometer
  - Measures shear viscosity of polymer

Experimental Design

- Preliminary Experiments:
  - To establish a stable micronization process
  - To analyse the effect on pressure

- Effect **of** processing variables
  - Polymer Feed Rate (13 - 26 g/min)
  - CO_2 Feed Rate (25 - 55 ml/min)
  - Nozzle Temperature (10-200 ^oC)

- Effect **on** characteristics of produced particles
  - Particle Size
  - Particle Size Distribution (PSD)
  - Morphology

Results and Discussion

- Successful production of particles
- Particles sized in the range of 0.01 to 190 µm
- Best Results:

(a) **(b)**

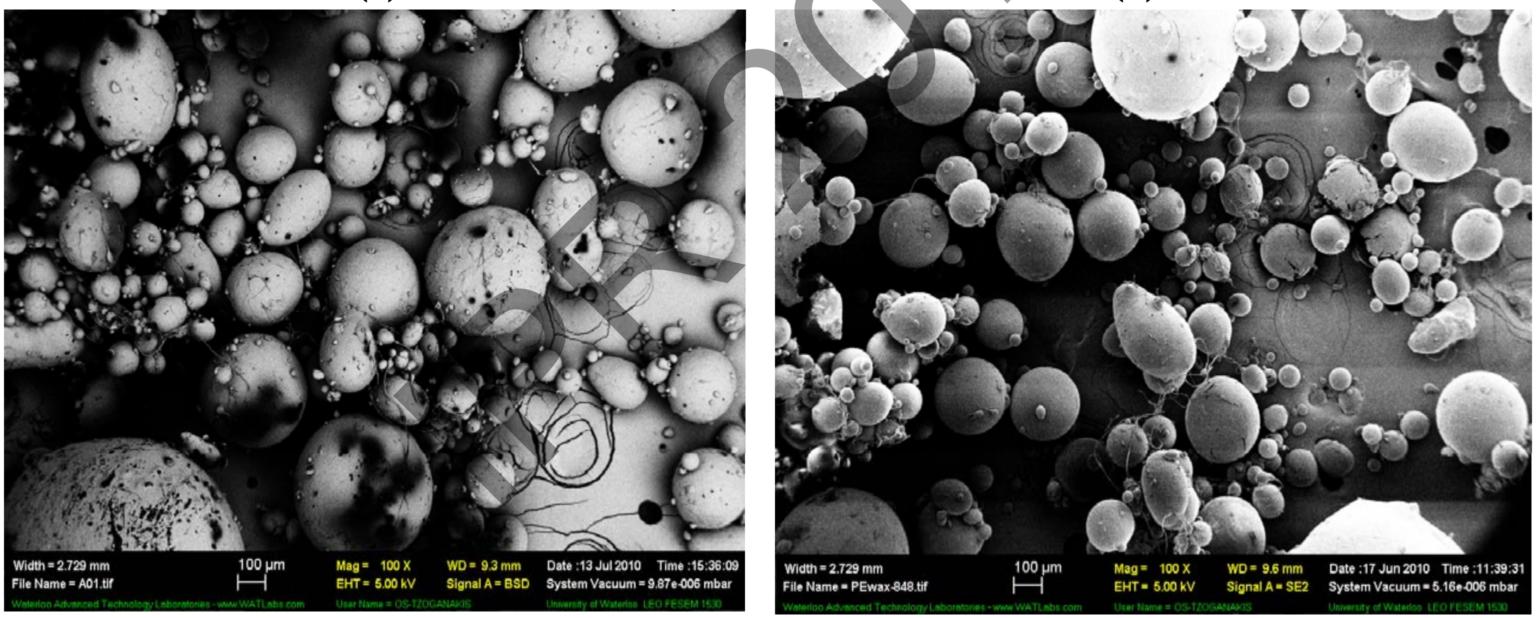


Figure 3: SEM Images of Particles Produced at CO_2 Feed Rate of 25 ml/min, Screw Speed of 50 rpm, and Nozzle Temperature at 200^0C:
(a) Polymer feed rate = 13 g/min, and (b) Polymer feed rate= 26 g/min

Results and Discussion: Particle Size

- **Effect of Nozzle Temperature:**
  - Nozzle temperature ↑ causes an ↑ in mean particle diameter

Table 3: Mean Particle Diameter at Different Polymer Feed Rates and Nozzle Temperatures (CO_2 feed rate =25 ml/min, screw speed= 50 rpm)

Polymer Feed Rate (g/min)	Nozzle Temperature (^0C)	Mean Diameter (µm)	Sauter Mean Diameter (µm)	Volume Mean Diameter (µm)
13	140	5.41	17.49	28.95
	160	5.91	10.97	13.73
	180	6.33	11.59	13.21
	200	6.66	26.56	35.48
26	140	5.46	18.86	26.18
	160	5.58	12.27	16.64
	180	9.60	16.72	19.11
	200	9.73	19.31	24.46

Unreliable

Results and Discussion: Particle Size

- **Effect of Polymer Feed Rate (PFR):**
  - Polymer feed Rate ↑ results in an ↑ in pressure
  - No significant effect on particle size

(a) **(b)**

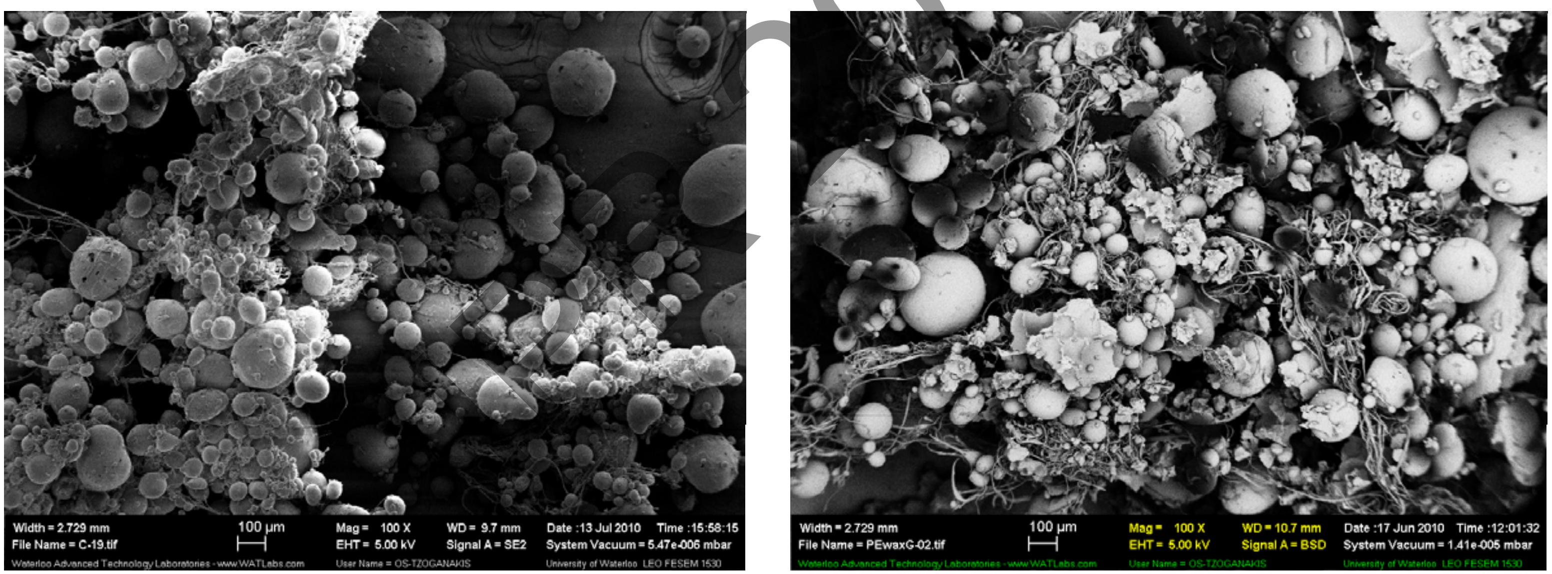
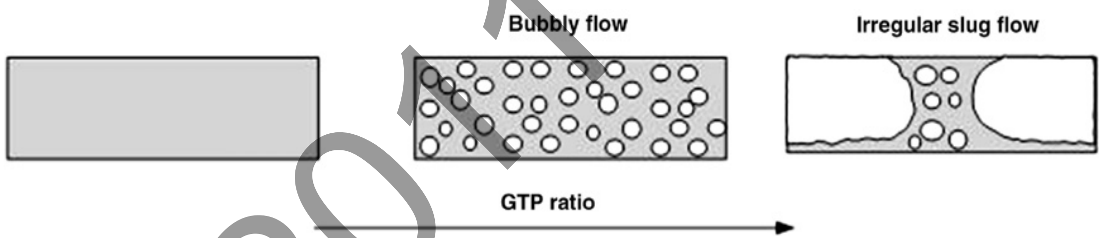


Figure 4: SEM Images of Particle Produced at Different Polymer Feed Rate (CO_2 feed rate = 25 ml/min, screw speed = 50 rpm, nozzle temperature = 160^0C): (a) 13 g/min and (b) 26 g/min

Results and Discussion: Particle Size

- **Effect of CO_2 Feed Rate:**
  - GTP ↑



  - GTP ↑ results in an ↑ particle size

Table 4: Mean Particle Diameter at Different CO_2 Feed Rates for a Constant Polymer Feed Rate of 52 g/min (Screw Speed = 55 rpm and Nozzle Temperature = 140^{0}C)

CO_2 Feed Rate (ml/min)	Mean Diameter (µm)	Sauter Mean Diameter (µm)	Volume Mean Diameter (µm)
25	8.45	19.49	34.80
35	10.31	31.82	45.14
45	20.50	77.45	97.66
55	9.68	20.24	24.85

Unreliable

Results and Discussion:

- **Particles Size Distribution (PSD)**
  - Based on optical microscopic measurements performed
  - 150 particles divided into 26 size classes
  - Particle sizes against the % frequency of occurrence of particles in a given size class
  - The distributions were normalized

Results and Discussion: PSD

- **Effect of Nozzle Temperature:**
  - The PSD broadens as nozzle temperature ↑ at high PFR
  - The position and number of modal peaks changed for high PFR

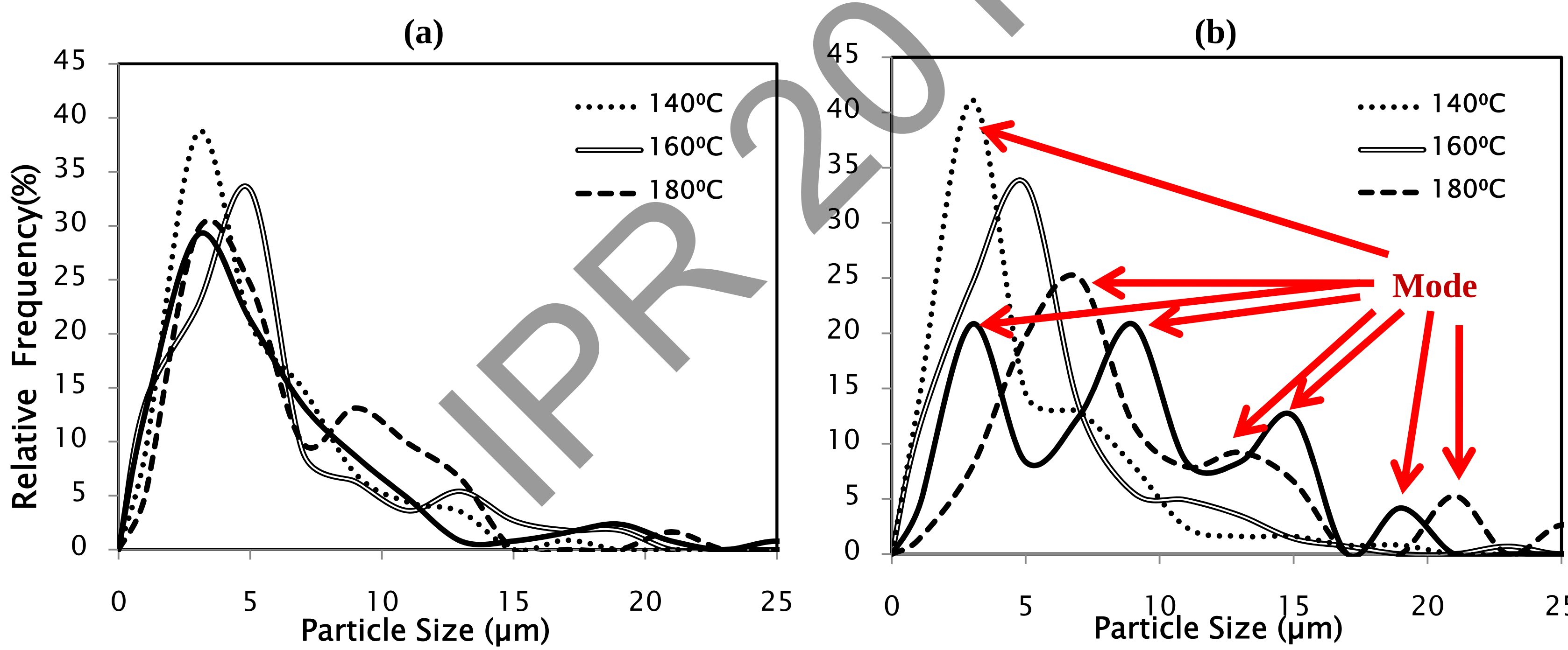


Figure 5: Normalized Particle Size Distributions at Different Polymer Feed Rates (CO_2 Feed Rate = 25 ml/min, Screw Speed = 50 rpm): (a) 13 g/min, and (b) 26 g/min

Results and Discussion: PSD

- **Effect of Polymer Feed Rate (PFR):**
  - Insignificant at low temperature

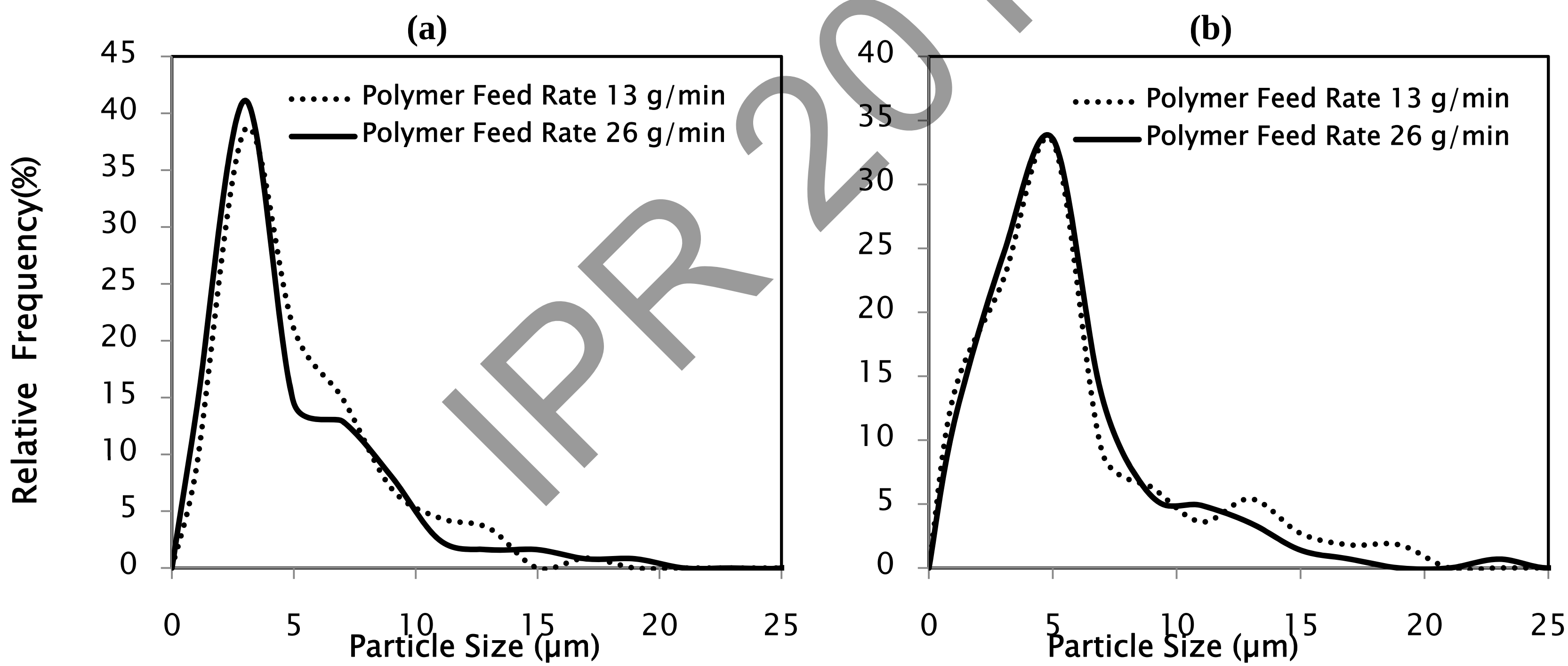


Figure 6: Normalized Particle Size Distribution at Lower Nozzle Temperatures (CO2 Feed Rate = 25 ml/min, Screw Speed = 50 rpm): (a) 140 ^{0}C and (b) 160 ^{0}C

Results and Discussion: PSD

- **Effect of Polymer Feed Rate (cont'd):**
  - At high temperature, differ in both size and shape

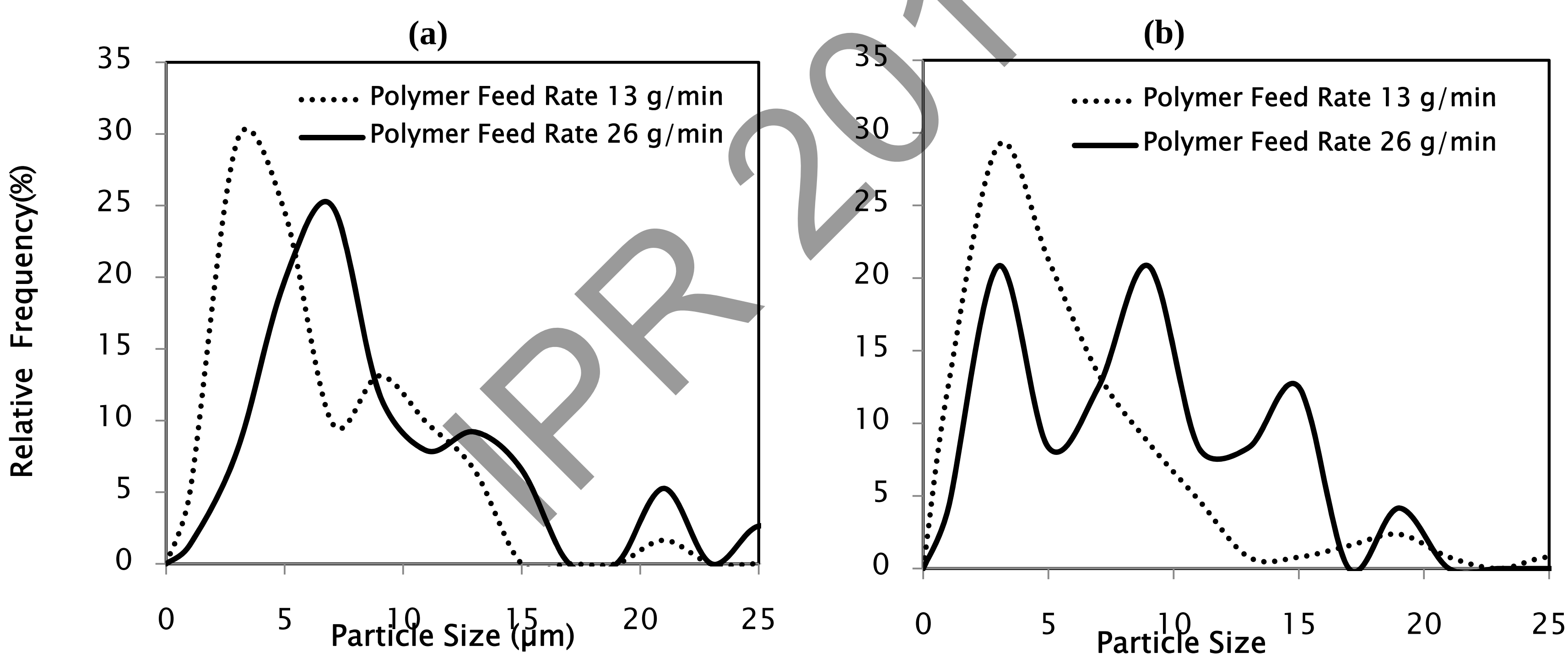


Figure 7: Normalized Particle Size Distribution at Higher Nozzle Temperatures (CO_2 Feed Rate = 25 ml/min, Screw Speed = 50 rpm): (a) 180^{0}C and (b) 200^{0}C

Results and Discussion: PSD

- **Effect of CO_2 Feed Rate:**
  - Narrow distribution obtained for an ↑ in CO_2 feed rate

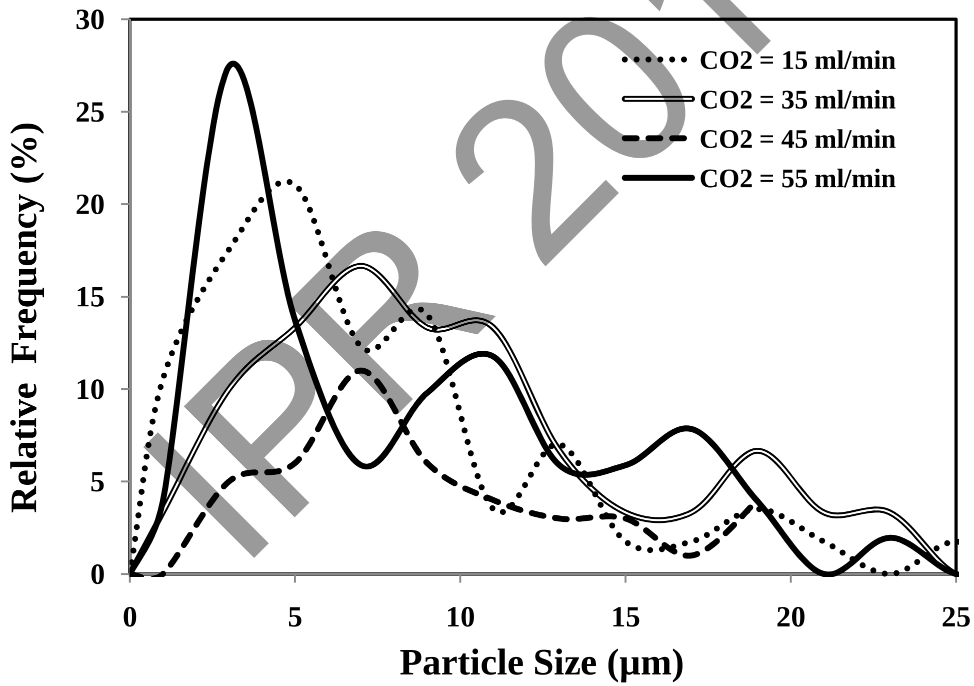


Figure 8: Normalized Particle Size Distribution at Different CO_2 Feed Rate (Polymer Feed Rate = 52 g/min, Screw Speed = 50 rpm, Nozzle Temperature = 140^{0}C)

Results and Discussion: Morphology

- **Effect of Nozzle Temperature:**
  - Solidification time defines the shape of particles
  - ↑ in temperature ↑ the solidification time
  - More spherically shaped particles formed
  - Less fibres and least agglomeration

(a) **(b)**

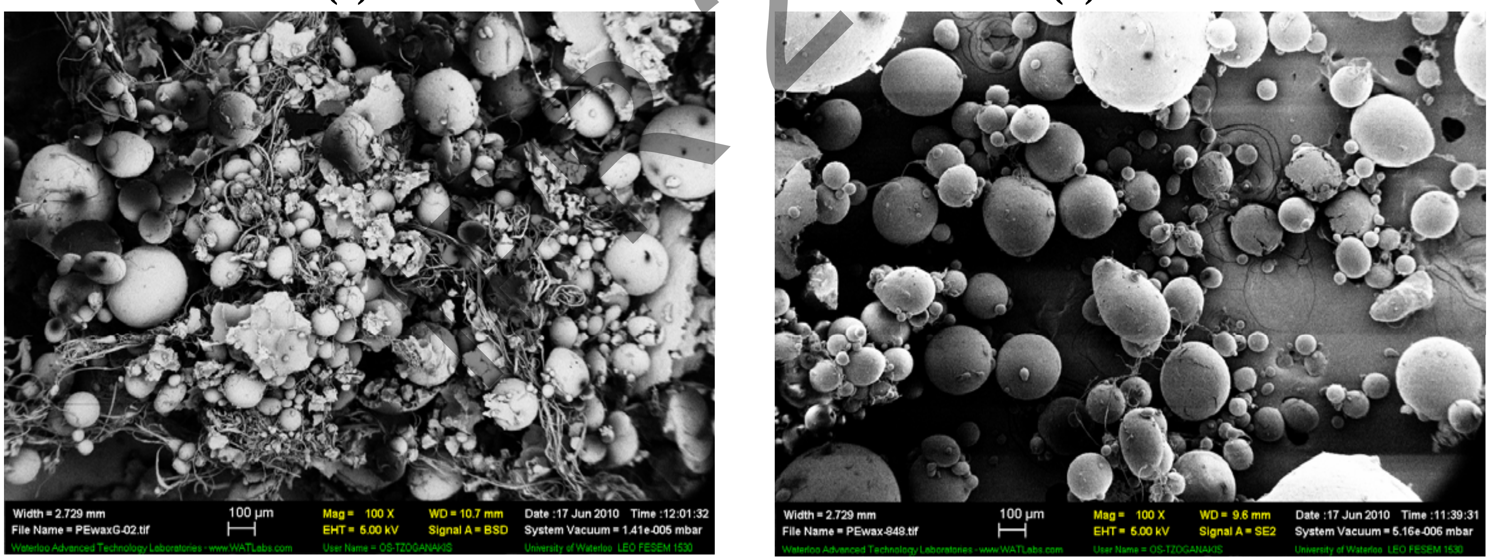


Figure 9: SEM Images of Particle Produced at Different Nozzle Temperatures at a Polymer Feed Rate of 26 g/min (CO_2 Feed Rate = 25 ml/min, Screw Speed = 50 rpm): (a) 160^{0}C and (b) 200^{0}C

Results and Discussion: Morphology

- **Effect of Polymer Feed Rate:**
  - Agglomeration ↑ with ↑ in polymer feed rate
  - More fibrous and misshapen product
  - Caused by the large stretching effect experienced at high PFR
    - High shear experienced
    - Elongation of polymer chains

(a) **(b)**

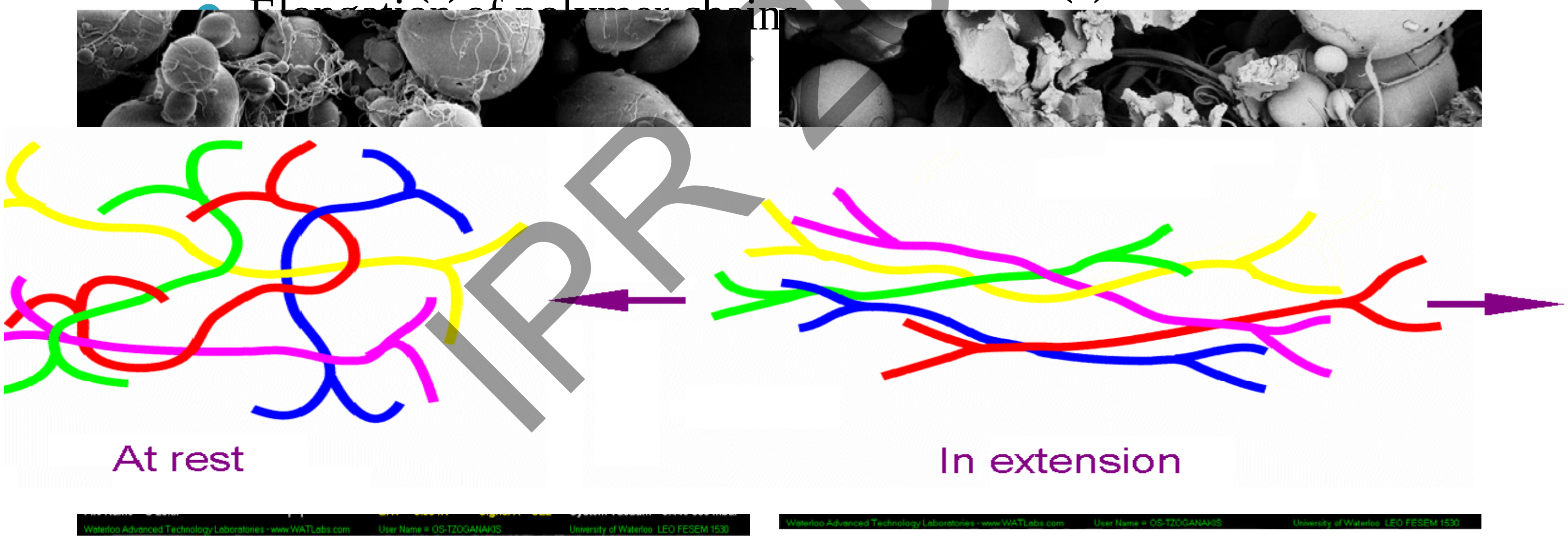


Figure 10: SEM Images of Particles Produced at Different Polymer Feed Rate at Nozzle Temperatures 180^{0}C (CO_2 Feed Rate = 25 ml/min, Screw Speed = 50 rpm): (a) 13 g/min and (b) 26 g/min

Results and Discussion: Morphology

- **Effect of CO_2 Feed Rate:**
  - More deformed particles at higher feed rates
  - Agglomeration ↑ with an ↑ in CO_2 feed rate

(a) (b)

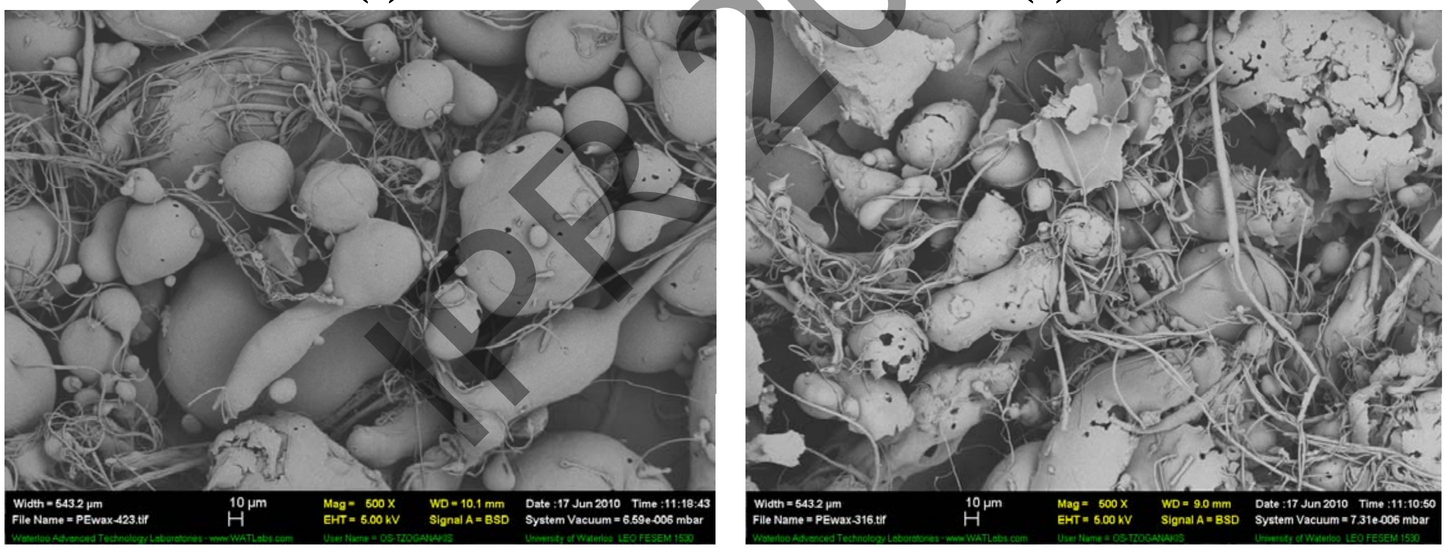


Figure11: SEM Images of Particles Produced at Different CO_2 Feed Rate at 500X Magnification (Polymer Feed Rate= 55 g/min, Screw Speed = 50 rpm, Nozzle Temperature = 140^{0}C): (a) 35 ml/min and (b) 55 ml/min

Future Work

- Statistical analysis:
  - Develop mathematical models to quantify the effect of variables
  - Optimization
- Investigate the effects of
  - Die size and geometry
  - Processing temperature
  - Molecular weight
- Feasibility of producing particles of other polymers

Conclusion

Intent:

- Micronization of polymer in a extrusion process using supercritical CO_2
- Study effect of process variables
  - Particle size
  - Particle size distribution
  - Morphology

- Benefits:
- Particle properties can be controlled
- Reduce emission of VOC and minimize waste stream generation
- Extrusion micronization can replace secondary micronization processes:
  - grinding
  - milling
  - RESS
  - SAS etc.

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Acknowledgements

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Thank You for Listening

Literature Review: Supercritical Fluids

Table 2: List of Some Supercritical Fluids that are viable VOC replacements:

Substances	Critical Temperature (K)	Critical Pressure (MPa)
Carbon Dioxide	304.1	7.38
Dimethyl Ether	400.0	5.24
Acetone	508.1	4.70
Water	647.3	22.1

- **Supercritical Water:**
  - Very effective reaction medium for oxidation reaction
  - Drawbacks: Corrosion and investment costs (due to extreme operation conditions)
  - Used for waste water treatment in chemical industry

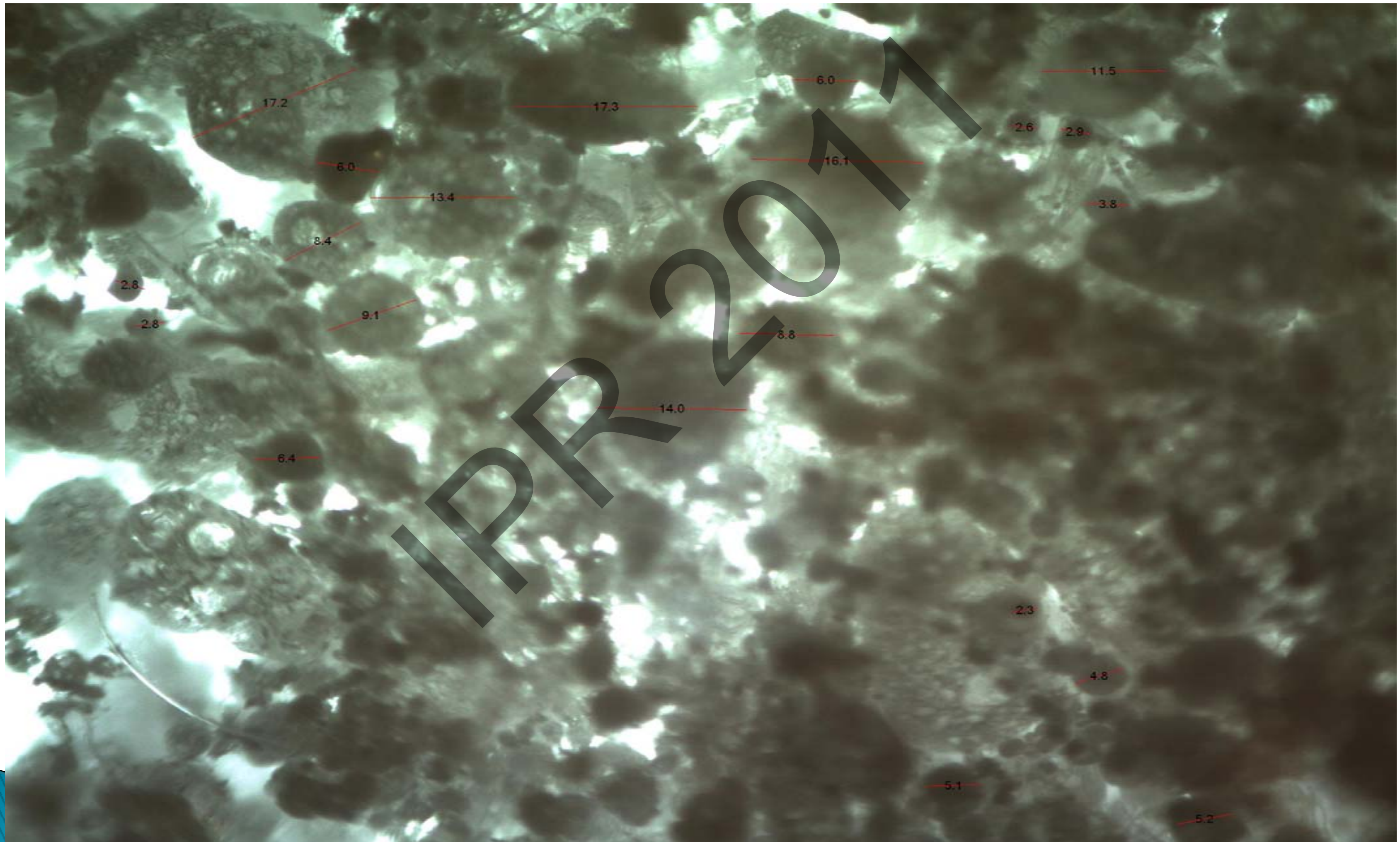
- **Ionic liquids (room-temperature molten organic salts):**
  - Salt cost is substantial
  - Separation of ionic liquid from process stream is a concern

Literature Review: Supercritical Fluids

Table 2.3: Physical Properties of Gas, Liquid and SCF

Property	Liquid	SCF	Gas
Density (g/cm^3)	1	0.5 – 1	10^{-3} -10^{-2}
Diffusivity (cm^2/s)	10^{-6}	10^{-3}	10^{-1}
Viscosity (Pa-s)	10^{-3} – 10^{-2}	10^{-5}	10^{-6}

Optical Microscope



- Quadropole moment and Lewis acidity of CO_2 contributes to it solubility in polymer
- Processing temperature and pressure.
  - At elevated temperature and pressure, the quadropole moment of supercritical CO_2 is disrupted by the thermal energy leading to a nonpolar behaviour of CO_2, allowing dissolution of a non-polar solute, such as polymer, into polar supercritical CO_2.
  - However, it is to be noted that the critical dissolution pressure and temperature rises with increasing molecular weight, i.e. larger molecules show limited solubility in CO_2.
- Polymers with flexible back bones and high free volume
  - hence low glass transition temperature molecules show higher solubility in CO_2
- The quantity of CO_2 dissolved in a polymer can also be constituted to the weak intermolecular interactions between CO_2 and functional groups, such as carbonyl group, ether group, aromatic group etc., available in a polymer.

Various theoretical models such as lattice fluid theory, off-lattice theory, cubic equation of state, are readily used to estimate CO_2 solubility in polymers. Apart from theoretical models, several experimental methods, for example phase separation method, gravimetric method, pressure decay method, are employed for solubility measurement