The effect of mixing on the molecular weight and size distribution in emulsion polymerization

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Introduction

Mixing and heat transfer have significant influence on the colloidal stability of latex particles during polymerization. Mixing, which results in bulk movement of the fluid, plays a significant role in maintaining the homogeneity of the reaction mass in emulsion polymerization. Good mixing is necessary to prevent local concentrations of added surfactants and water soluble monomers. Maintaining homogeneity is especially important in large-size reactors. Mixing is also essential to enhance the rate of the mass transfer in to the reaction medium.. The shear due to agitation is another important factor that can strongly influence coagulum formation in high-solid concentration emulsions. In fact, shear can accelerate coagulation through the development of fluid velocity gradients, which can increase collision forces between particles as well as the frequency of particle collisions inside the reactor. Therefore, mixing parameter has a major effect on the particle size and molecular weight distributions of the polymer, which in turn can significantly influence the product final properties in the emulsion polymerization. In particular, for MMA batch polymerization either macro or mini emulsion, the rate of monomer conversion decreases with an increase in particle size of latex.

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The main objective of this study is to investigate the effects of the impeller speed, baffles, and the temperature on the conversion, molecular weight and size distribution of the polymer. Factorial experimental design approach is used to analyze the effects of the process variables.

Experimental

Polymerization was carried out in a stainless steel tank reactor equipped with a six-bladed pitched 45° turbine- type impeller with a width of half the vessel diameter, a thermocouple, a port for nitrogen purge, an inlet for feeding ingredients and sampling and the mixer power was 1/4 hp. Methyl methacrylate (MMA), Azobisisobutyronitrile (AIBN), and Potassium per sulfate (KPS) were employed as monomer, initiator, and surfactant (emulsifier), respectively. Deionized water (DDI) was used as an inert medium. The impeller speed and temperature were kept constant and the operating conditions range is given in Table 1. The reactor was initially charged with water and surfactant. The reactor then was heated to the required temperature. Gradually, initiator and monomer were poured in to the reactor. The conversion was measured by gravimetric method.

For particle size measurement, a 2 ml sample of latex was diluted with DDI water; the diluted samples were therefore used for particle size distribution measurements. Gas permeation chromatography (GPC) was used to determine molecular weight distribution of polymer. Figure 1 shows a detailed diagram of the experimental set up.

Currently the experimentation is being performed and the results will be discussed at the IPR symposium.

Table 1: Operating Conditions Range

Parameter	**Range**
Temperature	55- 65° C
Residence time	30- 150 min
Impeller Speed	0- 600 RPM
Baffles	Yes/No
Surfactant Concentration	4- 8 g/L

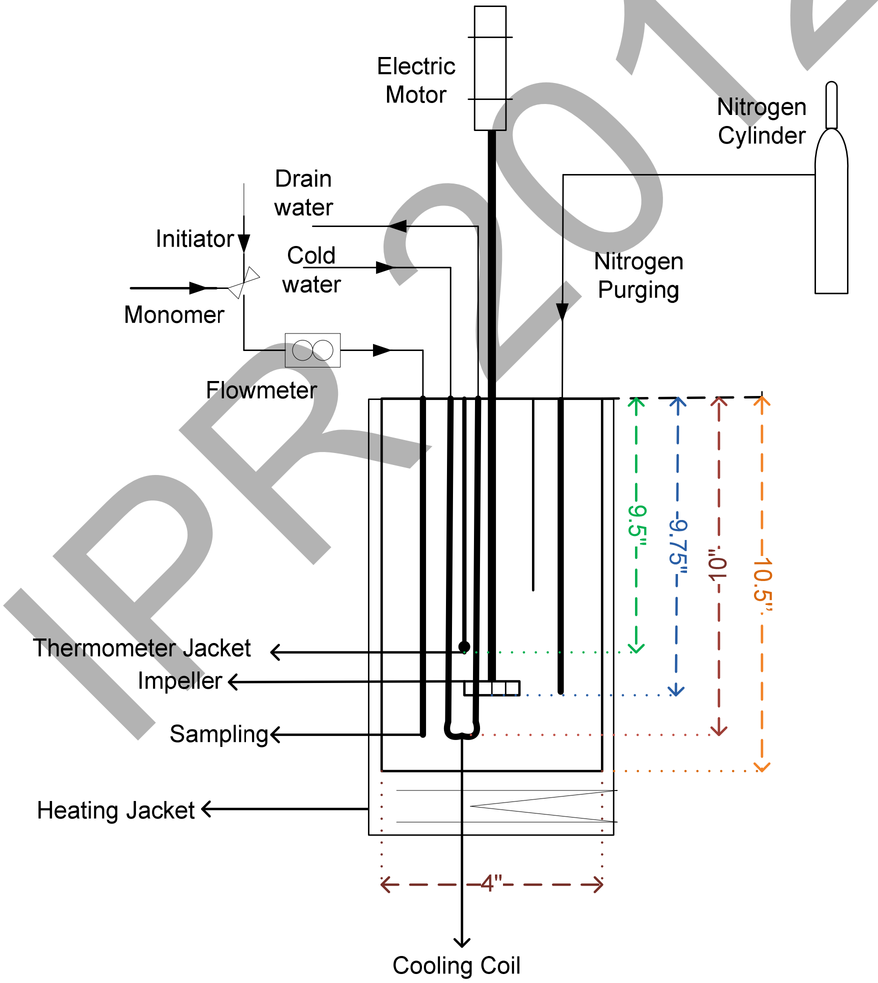

Figure 1: Schematic Diagram of the Polymer Reactor System

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The Effect of Mixing on the Molecular Weight and Size Distribution in Emulsion Polymerization

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May 2nd, 2012

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Outline

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- Literature Review
- Research Objective
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- Results
- Concluding Remarks
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Emulsion Polymerization

- Production of latex paints, rubbers, coatings and adhesives.
- Emulsification of monomer in water & polymerization.

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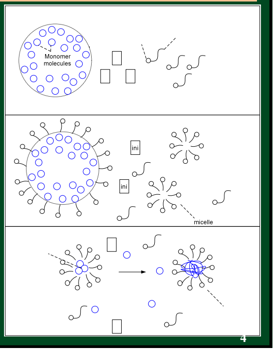
Emulsion Polymerization

- Free radicals enter micelles and form polymer particles.
- Particles grow as they absorb monomer from monomer droplets.
- Polymerization continues within the particles until the monomer is consumed.



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Emulsion Polymerization
Experimental Previous Studies

Parameter	Researcher	System	Description
Mixing	Choi and Lee (2010)	VAC, ET & NMA Impeller: Rushton Turbine Semibatch	Coagulation increased with impeller speed.
	Dobie and Boodhoo (2010)	MMA and MA Impeller: 3-blade marine propeller Batch	Intensive mixing resulted in aggregation of the smaller particles.
	Ozdeger et al. (1998)	Styrene and n-butyl acrylate Impellers: A310 fluidfoil & Rushton	At high solids (50%), Conversion with Rushton impeller was higher. Bimodality was more significant for the A310 Fluidfoil impeller.
Particle Size	Fontenot and Schork (1993);	MMA, Batch	Cosurfactant (HD) increased particle numbers. The miniemulsion particles had higher polymerization compared to mircoemulsion.
	Yu et al. (1995)	MMA Batch	Polymerization rate was faster and particle size was smaller when decreasing the ratio of the water/monomer or increasing the temperature of polymerization or the amount of the emulsifier.
Temperature	Okaya et al. (2004)	MMA, PVA colloid Batch	Lower temperature than cloud point of PVA, resulted in coagulation.
	Dimitratos et al., (1989)	copolymerization of vinyl-acetate-n-butyl acrylate Semibatch	Process disturbances and measurement errors were investigated.
	Tanaka, (1997)	MMA CSTR	PID control of Temperature was investigated.
Feed rate	Penlidis (1986); Lin et al. (1982)	VAC , Batch Vinyl Chloride, Batch	Emulsifier feed rate control and monomer to water ratio control were studied.

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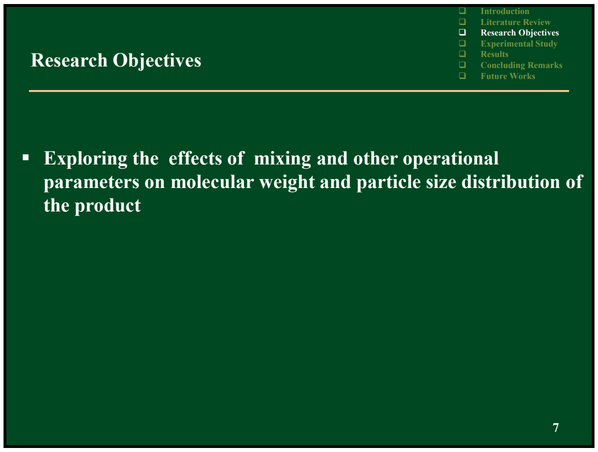
Emulsion Polymerization
Lack of Information

Effects of process parameters (mixing, temperature, and , …) on particle nucleation , growth, agglomeration and breakage are not clear.



Research Objectives

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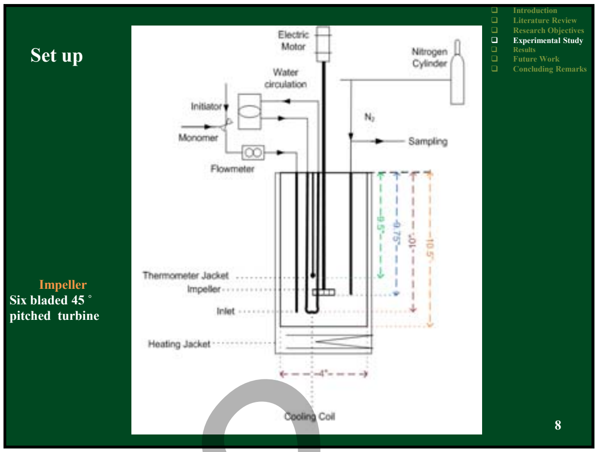
- Exploring the effects of mixing and other operational parameters on molecular weight and particle size distribution of the product



Set up

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Impeller
Six bladed 45 ° pitched turbine

Set up

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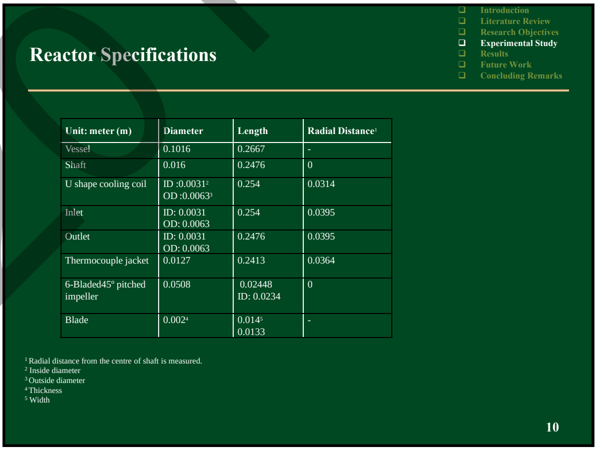

Reactor Specifications

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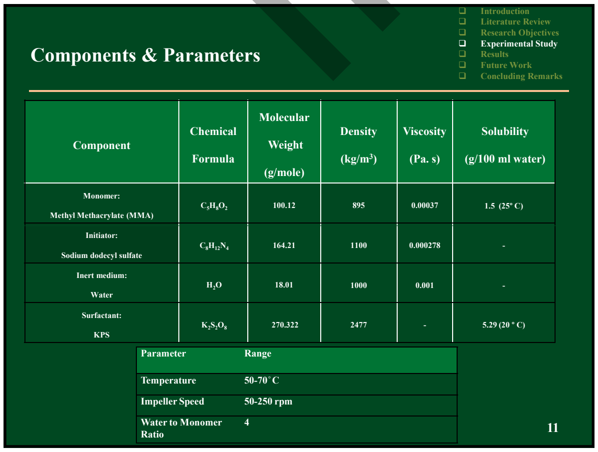
Unit: meter (m)	Diameter	Length	Radial Distance[1]
Vessel	0.1016	0.2667	-
Shaft	0.016	0.2476	0
U shape cooling coil	ID :0.0031[2] OD :0.0063[3]	0.254	0.0314
Inlet	ID: 0.0031 OD: 0.0063	0.254	0.0395
Outlet	ID: 0.0031 OD: 0.0063	0.2476	0.0395
Thermocouple jacket	0.0127	0.2413	0.0364
6-Bladed45° pitched impeller	0.0508	0.02448 ID: 0.0234	0
Blade	0.002[4]	0.014[5] 0.0133	-

[1] Radial distance from the centre of shaft is measured.
[2] Inside diameter
[3] Outside diameter
[4] Thickness
[5] Width



Components & Parameters

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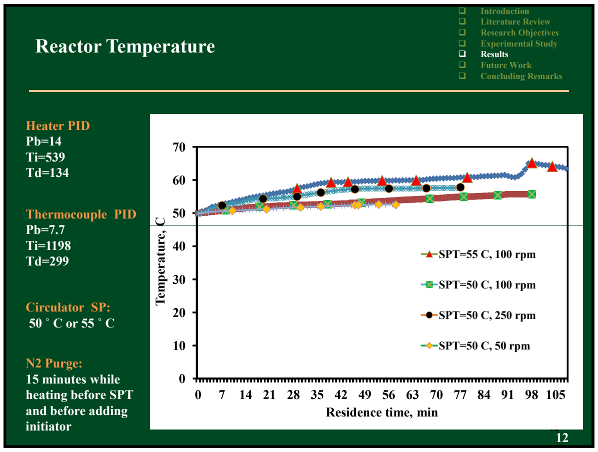
Component	Chemical Formula	Molecular Weight (g/mole)	Density (kg/m³)	Viscosity (Pa. s)	Solubility (g/100 ml water)
Monomer: Methyl Methacrylate (MMA)	$C_5H_8O_2$	100.12	895	0.00037	1.5 (25° C)
Initiator: Sodium dodecyl sulfate	$C_8H_{12}N_4$	164.21	1100	0.000278	-
Inert medium: Water	H_2O	18.01	1000	0.001	-
Surfactant: KPS	$K_2S_2O_8$	270.322	2477	-	5.29 (20 ° C)

Parameter	Range
Temperature	50-70˚C
Impeller Speed	50-250 rpm
Water to Monomer Ratio	4



Reactor Temperature

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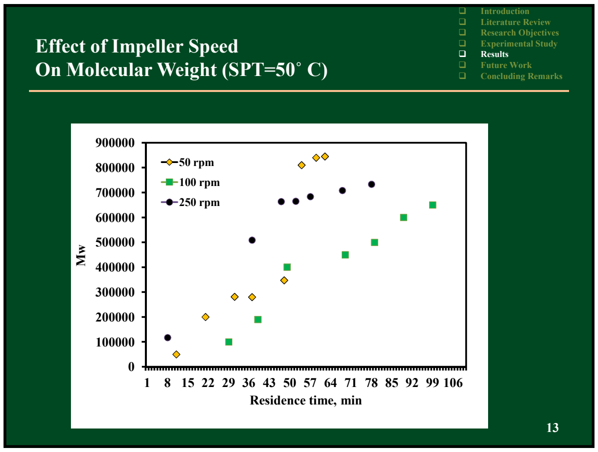
Heater PID
Pb=14
Ti=539
Td=134

Thermocouple PID
Pb=7.7
Ti=1198
Td=299

Circulator SP:
50 ˚ C or 55 ˚ C

N2 Purge:
15 minutes while heating before SPT and before adding initiator



Effect of Impeller Speed
On Molecular Weight (SPT=50˚ C)

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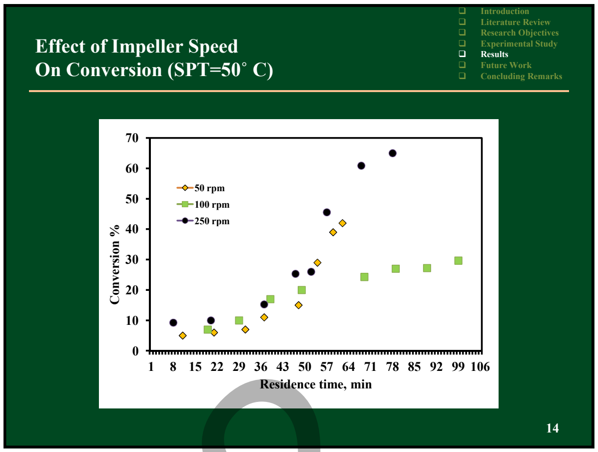

Effect of Impeller Speed
On Conversion (SPT=50˚ C)

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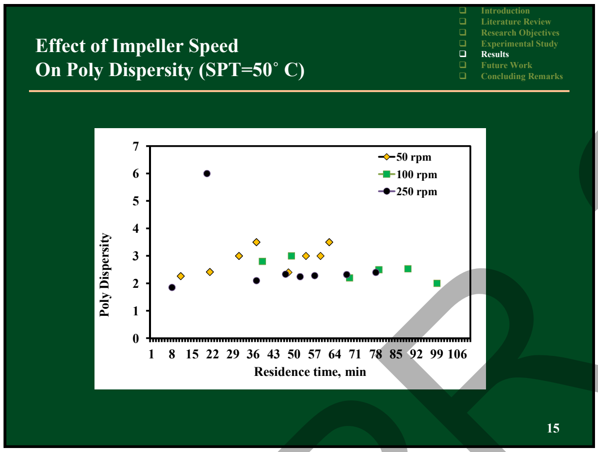

Effect of Impeller Speed
On Poly Dispersity (SPT=50˚ C)

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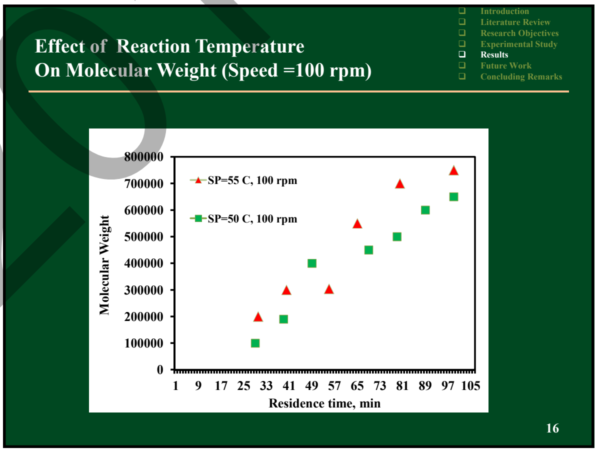

Effect of Reaction Temperature
On Molecular Weight (Speed =100 rpm)

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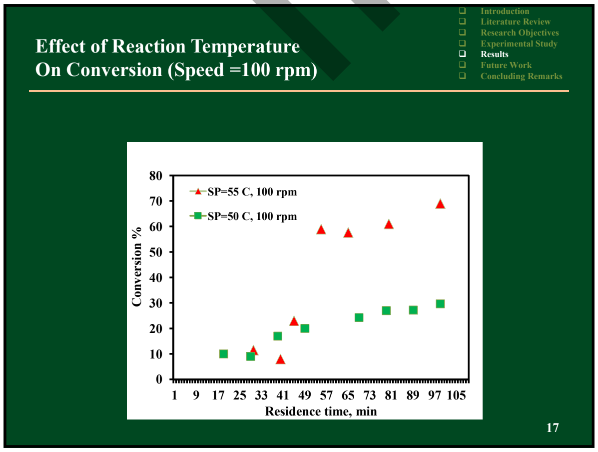

Effect of Reaction Temperature
On Conversion (Speed =100 rpm)

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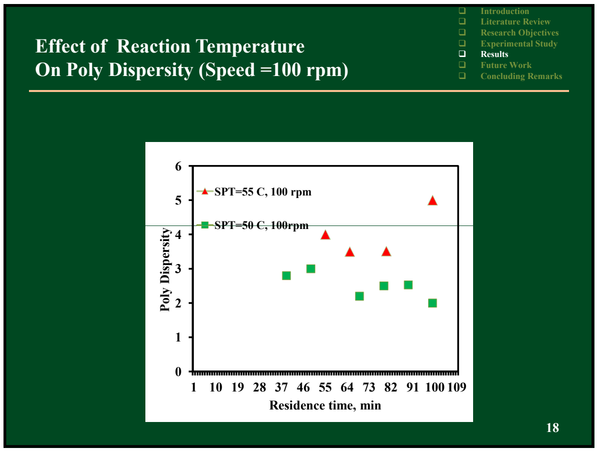

Effect of Reaction Temperature
On Poly Dispersity (Speed =100 rpm)

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Effect of Temperature on PSD
SPT= 50˚C, 100 rpm

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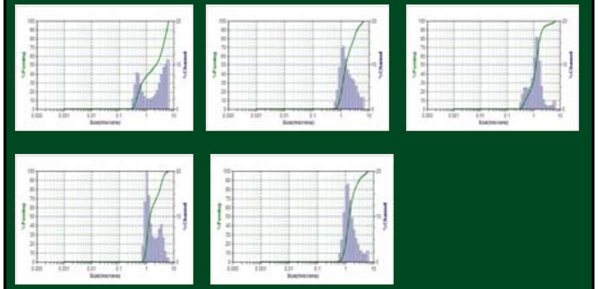

Effect of Temperature on PSD
SPT= 55˚C, 100 rpm

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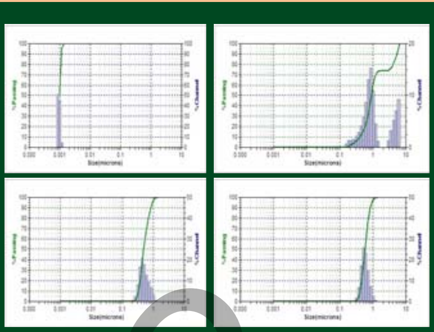

Concluding Remarks

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- **Raising the rate of stirring resulted in higher Mw and conversion at the beginning of reaction, but lower impeller speed had a faster gain at these values as the residence time was enhanced.**
- **Increasing the impeller speed resulted in lower PI.**
- **Raising the reactor temperature enhanced Mw and conversion.**
- **Increasing the reactor temperature produced lower PSD.**

Future Works

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Experimental

- **Continuing experimentation and analyzing PSD data**
- **Study the Effects of Baffles and Rushton turbine on MWD and PSD**
- **Measuring MWD via On line viscometer**
- **Investigating the effect of mixing and flow rate in a semi-batch system**

Modeling

- **Using experimental data to define the mechanism of particle evolution, i.e. nucleation, growth, breakage and coalescence by CFD modelling**

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Acknowledgements:

❑ Supervisors: Dr. Dhib and Dr. Ein Mozaffari
❑ NSERC and Ryerson University for Financial Support
❑ Xerox Research Centre of Canada

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Thanks For Your Attention