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 into 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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>55- 65°C</td>
</tr>
<tr>
<td>Residence time</td>
<td>30- 150 min</td>
</tr>
<tr>
<td>Impeller Speed</td>
<td>0- 600 RPM</td>
</tr>
<tr>
<td>Baffles</td>
<td>Yes/No</td>
</tr>
<tr>
<td>Surfactant Concentration</td>
<td>4- 8 g/L</td>
</tr>
</tbody>
</table>

Figure 1: Schematic Diagram of the Polymer Reactor System
References


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May 2nd, 2012
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Introduction

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

Outline
- Introduction
- Literature Review
- Research Objective
- Experimental Study
- Results
- Concluding Remarks
- Future Works

Experimental Previous Studies

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

Lack of Information

Effects of process parameters (mixing, temperature, and ...) on particle nucleation, growth, agglomeration and breakage are not clear.
Exploring the effects of mixing and other operational parameters on molecular weight and particle size distribution of the product.
Effect of Impeller Speed
On Molecular Weight (SPT=50°C)

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Concluding Remarks

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

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

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

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

Effect of Reaction Temperature
On Poly Dispersity (Speed =100 rpm)
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Effect of Temperature on PSD
SPT= 50 °C, 100 rpm

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

Concluding Remarks

- 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

Experimental
- Continuing experimentation and analyzing PSD data
- Study the Effects of Ralffles 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

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

Thanks For Your Attention