Present Technologies for Devolatilization of High Viscosity Polymers

1. Conventional rubber polymerization process with steam stripping
2. Coagulation/Dewatering process for synthetic rubber
3. Direct devolatilization process for synthetic rubber
   3.1 Experimental results on direct devolatilization
   3.2 Improvement in devolatilization efficiency by stripping agent
   3.3 Devolatilization behavior in an intermeshed twin screw extruder
   3.4 Intermeshed co-rotation twin screw design for devolatilization
   3.5 Devolatilization simulation in an intermeshed twin screw extruder
4. Efficient devolatilization equipment for high viscous polymers

October 22nd, 2015  Tadamoto Sakai, Dr.

Conventional Butyl rubber polymerization process
Coagulation/Dewatering process for synthetic rubber
Coagulation/dewatering extrusion using with long L/D TSE

Experimental results on coagulation/dewatering extrusion for rubber latex

Intermeshed co-rotation twin screw extruder (65mm, L/D=56)

Dewatering extrusion results for rubber crumbs
Intermeshed co-rotational twin screw extruder (65mm, L/D=32.5)

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Initial content wt.-%</th>
<th>Capacity kg/h</th>
<th>Screw speed m/min</th>
<th>Temperature °C</th>
<th>Water in product wt.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR (1)</td>
<td>30-40</td>
<td>115</td>
<td>200</td>
<td>215</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106</td>
<td>250</td>
<td>223</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>179</td>
<td>250</td>
<td>222</td>
<td>0.19</td>
</tr>
<tr>
<td>SBR (2)</td>
<td>40-50</td>
<td>124</td>
<td>155</td>
<td>208</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>146</td>
<td>210</td>
<td>213</td>
<td>0.045</td>
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<tr>
<td></td>
<td></td>
<td>175</td>
<td>300</td>
<td>216</td>
<td>0.050</td>
</tr>
<tr>
<td>NBR</td>
<td>50</td>
<td>125</td>
<td>173</td>
<td>183</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>123</td>
<td>200</td>
<td>189</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>125</td>
<td>258</td>
<td>190</td>
<td>0.15</td>
</tr>
<tr>
<td>ABS</td>
<td>61</td>
<td>230</td>
<td>345</td>
<td>258</td>
<td>≤0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>370</td>
<td>345</td>
<td>244</td>
<td>≤0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>410</td>
<td>343</td>
<td>259</td>
<td>≤0.1</td>
</tr>
</tbody>
</table>

Vaporization Heat and Boiling Point

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point (°C)</th>
<th>Vaporization Heat (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>56.5</td>
<td>500</td>
</tr>
<tr>
<td>CCl₄</td>
<td>76.7</td>
<td>195</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.3</td>
<td>838</td>
</tr>
<tr>
<td>Toluene</td>
<td>110.6</td>
<td>363</td>
</tr>
<tr>
<td>Water</td>
<td>100.0</td>
<td>2,257</td>
</tr>
</tbody>
</table>

Drying processes for heat-sensitive polymers

**Method:**
- Hot air convective drying
- Drying under vacuum
- Microwave drying
- Heat pump drying
- Fluidized bed drying

**Disadvantages:**
- High energy consumption
- Easy thermal degradation
- Easy discoloration
- Poor working atmosphere

Toray ABS polymerization process (Emulsion process)

Mitsui ABS polymerization process (Continuous bulk polymerization)

Direct devolatilization seminars

October 22, 2015

Direct devolatilization process for very high solvent content and very low viscosity solution (Kurimoto) (Kurimoto technical brochure)

Combined process with a thin-film vaporizer & a twin screw kneader

Kneader devolatilization process (List)
Twin screw extruder process
(Coperion, JSW, etc)

Feeding to a twin-screw devolutilizer from a twin-screw flash evaporator

Coperion technical brochure
Technology Characteristics (List Kneader)

- Intensive mixing and kneading
- Large heating/cooling surfaces
- Self-cleaning design
- Long residence time
- Plug flow or back-mixed configuration
- Large free volume reactors
- Residence time largely independent of shaft speed
- Closed design
- Standard construction suitable for hazardous area classifications
- Batch or continuous operation


Experimental results on devolatilization for stripping agent addition & multi-venting
Acceptable volatile content for polymers with high melt viscosity

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymerization</th>
<th>Volatile Substance</th>
<th>Residual Volatile Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Bulk</td>
<td>Styrene</td>
<td>≤ 150 to 300 ppm</td>
</tr>
<tr>
<td>L-LDPE</td>
<td>Solution</td>
<td>C₆, C₈, etc.</td>
<td>≤ 500 ppm</td>
</tr>
<tr>
<td>ABS</td>
<td>Emulsion</td>
<td>AN, styrene</td>
<td>≤ 500 ppm</td>
</tr>
<tr>
<td>AS</td>
<td>Bulk</td>
<td>AN, styrene</td>
<td>≤ 500 ppm</td>
</tr>
<tr>
<td>PC</td>
<td>Condensation</td>
<td>Methylene chloride, etc.</td>
<td>≤ 20 to 50 ppm</td>
</tr>
<tr>
<td>EPDM</td>
<td>Solution</td>
<td>C₆, etc.</td>
<td>≤ 500 ppm</td>
</tr>
<tr>
<td>PMMA</td>
<td>Bulk</td>
<td>MMA</td>
<td>≤ 1000 to 2000 ppm</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>Emulsion</td>
<td>Water</td>
<td>≤ 1000 to 2000 ppm</td>
</tr>
<tr>
<td>PET</td>
<td>(Condensation)</td>
<td>Water</td>
<td>≤ 20 to 40 ppm</td>
</tr>
<tr>
<td>AS</td>
<td>Suspension</td>
<td>AN, styrene</td>
<td>≤ 500 ppm</td>
</tr>
</tbody>
</table>

Experimental set-up for devolatilization operation

Devolatilization extrusion for high content solvent

Chloroprene Rubber + CCl₄ (58 wt%)

Solvent residue (wt %)

Vent port number

Screw dia.: 65mm
Screw rpm: 125rpm
Output: 30 kg/h
Total L/D: 40

Effect of water addition on LLDPE devolatilization

LLDPE + C₆-C₈ solvent (10 wt %)

Initial conc.: 10 wt %

Screw: 65 mm
Output: 110 kg/h
 Polymer temp: 270°C
The improvement in devolatilization efficiency by the addition of stripping agent
Parameters related to devolatilization effects

Machine design and operational conditions:
1. Longer residence time under vent holes
2. Higher surface area of molten polymers
   - Rolling film effects, screw geometry, screw speed, etc.
3. Better surface renewal under vent holes
   - Rolling melt pools, screw geometry, screw speed, etc.
4. Bubbling from molten polymers
   - Stripping agent injection, foaming, rupture, etc.
5. Lower vacuum level under vent holes
6. Higher de-pressurization at the inlet of vent holes
   - From high pressure zone to low pressure zone

Materials with low fluidity:
1. Higher diffusion coefficient,
2. Lower equilibrium concentration
3. Higher polymer temperature & lower initial concentration

Devolatilization calculation
Effect of water addition

\[
\log \left( \frac{C_0 - C_k}{C_L - C_k} \right) = K \cdot S \cdot L \cdot N^{1/2} / W
\]

Latinen’s equation

C: concentration, K: constant, L: screw length, N: screw speed,
W: Output, \( \frac{C_0 - C_k}{C_L - C_k} \): Devolatilization efficiency

No addition Water addition
Visualization of foaming behavior

Experimental apparatus

- View Cell
- CCD Camera
- Digital Video Recorder
- Video Monitor
- Computer
- Optical Rail
- Cold Light
- Temperature Controller
- Cartridge Heater
- Thermocouples
- Buffer Tank
- Heater
- Pressure Transducer
- Pressure Indicator
- Pressure Release Valve
- Valve Controller
- Valve Function Generator
- High Pressure Pump
- CO₂ Cylinder

Visualization of foaming behavior

Still images of PP samples before and after the rapid (average value 0.8 MPa/s) depressurization, SC-CO$_2$ solubilization condition: 160 °C, 20 MPa.

SC-CO$_2$ Injection under high pressure, high temperature

SC-CO$_2$ bubble nucleation and growth when depressurized


Bubble nucleation and growth rate

(Saturation temperature and Pressure: 433 K, 25MPa; Pressure release rate: 0.64 MPa/s)

Devolutilization behavior in an intermeshed twin screw extruder

Flow behavior in a co-rotational twin screw extruder

Flow behavior in a counter-rotational twin screw extruder

Flow behavior of molten polymer in a twin screw extruder

Comparison of devolatilization effects between co-rotational and counter-rotational twin screw extruders


Intermeshed counter-rotational twin screw extruder for devolatilization
(Screw diameter: 305mm)

Intermeshed twin screw extruder design for direct devolatilization

Self-wiping effect of an intermeshed co-rotation twin screw extruder
Progress of an intermeshed twin screw design

W. Wiedmann, Corotating twin screw extruder (Hanser)

**Deeper screw channel depth**
**Higher screw rotational speed**
**Longer screw/barrel length (L/D)**
**Sophisticated screw mixing elements**

1956: 1st generation
\[ \frac{D_o}{d} = 1.22, \quad M_o a^2 = 3.7 \text{ Nm/cm}^2, \quad n = 150 \text{ min}^{-1} \]

1979: 2-flight
\[ \frac{D_o}{d} = 1.44, \quad M_o a^2 = 5.6 \text{ Nm/cm}^2, \quad n = 300 \text{ min}^{-1} \]

1983: SC
\[ \frac{D_o}{d} = 1.55, \quad M_o a^2 = 8.7 \text{ Nm/cm}^2, \quad n = 600 \text{ min}^{-1} \]

1995: Mc
\[ \frac{D_o}{d} = 1.55, \quad M_o a^2 = 11.3 \text{ Nm/cm}^2, \quad n = 1200 \text{ min}^{-1} \]

2004: Mc PLUS
\[ \frac{D_o}{d} = 1.55, \quad M_o a^2 = 13.6 \text{ Nm/cm}^2, \quad n = 1200 \text{ min}^{-1} \]

1972: Continua
\[ \frac{D_o}{d} = 1.71, \quad M_o a^2 = 4.3 \text{ Nm/cm}^2, \quad n = 300 \text{ min}^{-1} \]

2001: Mv
\[ \frac{D_o}{d} = 1.80, \quad M_o a^2 = 8.7 \text{ Nm/cm}^2, \quad n = 1800 \text{ min}^{-1} \]

**JSW**: 250mm Intermeshed co-rotation twin screw extruder with six vent holes

**Multi-venting extruder for high content solvent/monomer**

Sakai, 「高分子・複合材料の成形加工」 豊山サイテック出版 (1992)
Intermeshed co-rotational twin screw extruder for devolatilization
(Screw diameter: 450mm)
Devolatilization simulation in an intermeshed twin screw extruder

Devolatilization extrusion for synthetic rubber solution
Various parameters on devolatilization

- **Polymer related data**
  Initial volatile content, Diffusion coefficient, Polymer feeding temperature, etc.

- **Volatile/solvent related data**
  Density, Specific heat, Latent heat, Evaporation diagram, etc.

- **Devolatilizing device data**
  Barrel diameter, Screw geometry (channel depth, pitch, length, etc.), Vent-port geometry, Barrel heat transfer, etc.

- **Operational condition data**
  Barrel heating/cooling, Vacuum conditions, Screw speed, Feeding rate, Stripping agent, Vent-port number

\[
\frac{c_{in} - c_{out}}{c_{in} - c_{GG}} = 2 \cdot \rho \cdot \sqrt{\frac{\frac{A_{SF}}{t_{SF}} + \frac{A_{cyl,free}}{t_{Cyl}} + \frac{A_{S,free}}{t_S}}{G}} 
\]

- $c_{in}$: Input concentration of volatile components
- $c_{out}$: Output concentration of volatile components
- $c_{GG}$: Equilibrium concentration of a volatile component
- $\rho$: Melt density of the polymer
- $D$: Diffusion coefficient
- $A_{SF}$: Free surface of a thrust flank
- $A_{cyl,free}$: Free internal cylinder surface of an eight-fold hole
- $A_{S,free}$: Free surface of a rear screw flank
- $t_{SF}$: Renewal time of the phase interface on the thrust flank
- $t_{Cyl}$: Renewal time of the phase interface on the inner cylinder
- $t_S$: Renewal time of the rear screw flank phase interface
- $G$: Throughput
Devolatilization simulation for LDPE-Hexane mixture(1)

Material data, screw/barrel data, operating conditions

Viscosity data, screw performance

Flash calculation

Calculation on pressure, filling, residence time, etc.

Bubble generation/growth

Surface renewal calculation

Calculation on temperature, power, viscous heating

Devolatilization calculation scheme
Residence time
Filling ratio
Polymer temperature
Polymer pressure
Dispersion
Distributive
Volatile concentration
Simulation results used with TEX-FAN


Intermeshed co-rotation twin screw extruder (Fully filled condition)

Flow behavior of molten polymer calculated by particle tracing
(Ishikawa, Kajiwara, Funatsu, et al)
H. Tomiyama, JSPP Annual Meeting (Tokyo), 2010

Intermeshed co-rotation twin screw extruder (Partially filled condition)

Filling simulation used with particle tracing method for devolatilization process

Efficient devolatilizing equipment for highly viscous polymers
Requirements for efficient devolatilizing equipment used for highly viscous polymers

1. High performance of separation and devolatilization
   Corresponding to wide viscosity and raw material grades
2. High energy efficiency
   Corresponding to better energy balance in separation
3. Low thermal degradation and contamination
   Corresponding to less stagnation and low temperature
4. Low environmental burden
   Corresponding to least emission and closed loop system
5. High operational stability
   Corresponding stable quality, cleanliness and easy maintenance
6. High safety and reliability
   Corresponding to explosion and working atmosphere
7. Automated control, operation and monitoring
8. Compact layout area
9. High mechanical stability for high viscous rubber

Venting-up trouble shooting

Causes
* Conveying capacity shortage for molten polymer
* High filling ratio at the venting zone
* Molten polymer adhesion with the vent wall
* Poor vapor discharge
* Precipitation of volatiles at the wall

<table>
<thead>
<tr>
<th>ZL-type</th>
<th>C-type</th>
<th>ZH-type</th>
<th>CZH-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly viscous</td>
<td>High volatile</td>
<td>Small clumps or</td>
<td>Small clumps and</td>
</tr>
<tr>
<td>High viscosity</td>
<td>concentration</td>
<td>crumb at vent</td>
<td>easy entrainment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>holes</td>
<td></td>
</tr>
</tbody>
</table>

Highly viscous polymer tends to form small clumps or crumbs at the vent holes, which can lead to blockage and poor discharge. High volatile concentration can also cause issues with easy entrainment.
## Comparison of performance on devolatilization operation

<table>
<thead>
<tr>
<th></th>
<th>LIST Kneader</th>
<th>Twin screw extruder</th>
<th>Thin layer devolatilizer</th>
<th>Steam stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-wiping effect</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>Low uniform shear rate</td>
<td>good</td>
<td>no good</td>
<td>no good</td>
<td>no good</td>
</tr>
<tr>
<td>Large venting area</td>
<td>good</td>
<td>no good</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>High viscosity flexibility</td>
<td>good</td>
<td>good</td>
<td>no good</td>
<td>good</td>
</tr>
<tr>
<td>Liquid mixing capability</td>
<td>good</td>
<td>good</td>
<td>limited</td>
<td>no good</td>
</tr>
<tr>
<td>Heat addition capability</td>
<td>good</td>
<td>good</td>
<td>limited</td>
<td>no good</td>
</tr>
<tr>
<td>Heat removal capability</td>
<td>good</td>
<td>no good</td>
<td>good</td>
<td>-</td>
</tr>
<tr>
<td>High turn-down ratio</td>
<td>good</td>
<td>no good</td>
<td>no good</td>
<td>no good</td>
</tr>
<tr>
<td>Flexibility to polymer grades</td>
<td>good</td>
<td>no good</td>
<td>no good</td>
<td>-</td>
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<tr>
<td>Energy efficiency</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>no good</td>
</tr>
<tr>
<td>Environmental containment</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>no good</td>
</tr>
<tr>
<td>Residence time controllability</td>
<td>good</td>
<td>no good</td>
<td>no good</td>
<td>good</td>
</tr>
</tbody>
</table>

Thank you for your attention

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