Improved Processing of Highly Filled Calcium Carbonate Compounds

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*Presenter

Presented at the SPE ANTEC 2000
Orlando, FL

Wednesday, May 10, 2000
ABSTRACT

Calcium carbonate treated with an interfacial agent such as stearic acid or a stearate is often used in place of untreated calcium carbonate to take advantage of improved lubricity and wetting characteristics. These characteristics typically lead to lower mixing viscosity, improved filler dispersion and better flow properties. In this paper, the effect of fatty acid derivatives on polypropylene compounds highly filled with calcium carbonate, both treated and untreated, will be discussed. The use of fatty acid derivatives can be effective for lowering extrusion pressure leading to throughput increases. The overall effect on filler addition, viscosity, mixing and processing properties will be shown for one class of fatty acid derivatives.
EFFECT MECHANISMS OF THE ADDITIVES:

- Tribological
  - Adhesives
  - Lubricants
  - Surfactants
- Molecular
EFFECT MECHANISMS OF THE ADDITIVES:

- Tribological
  - Adhesives
    - Increased interfacial forces created by surface attachment
    - Increase energy required to break adhesive bonds causing increased shear
  - Lubricants
    - Function to minimize the frictional forces between moving surfaces
    - Can be divided into internal and external
    - Internal is polymer:polymer, polymer:filler interaction
    - External is polymer:hot metal, filler:hot metal interaction
  - Surfactants
    - Create a surface active film via polar and non-polar ends
    - Polar end absorbs/bonds to a surface
    - Wetting of the filler allows for improved low energy dispersion
    - Similar to lubricants effect
EFFECT MECHANISMS OF THE ADDITIVES:

- Molecular
  - Chemical alteration of molecular weight average and number
  - In polypropylene, addition of peroxide results in chain scission
  - Lower molecular weight results in increased flow rates/low viscosity
TYPICAL PROPERTIES OF HIGHLY FILLED COMPOUNDS:

- Increased:
  - Viscosity (-Negative)
  - Flexural modulus (+Positive)
  - Heat deflection temperature (HDT) (+Positive)
  - Dimensional stability (+Positive)

- Decreased:
  - Izod Impact (-Negative)
  - Mold shrinkage (+Positive)
  - Thermal expansion (+Positive)
  - Part cost (+Positive)
MATERIALS USED IN THIS PROGRAM:

- Montell Homopolymer Polypropylene ProFax 6323 (12 MFI)
- Amoco Polypropylene 1016 (5 MFI)
- Calcium Carbonate
  - Omyacarb F (Untreated)
  - Omyacarb FT (Treated)
- Struktol ZB30A
  - Fatty acid derivative
- Struktol ZB30B
  - Fatty acid derivative
- Struktol ZB31/1
  - Fatty acid derivative
## FORMULATIONS:

<table>
<thead>
<tr>
<th>Material</th>
<th>Treated</th>
<th>Untreated</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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<td>60</td>
<td>59.6</td>
<td>59.4</td>
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<td>59.6</td>
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<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
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<tr>
<td>ZB30A</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td></td>
<td></td>
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<td>ZB30B</td>
<td></td>
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<tr>
<td>ZB31/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
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<tr>
<td>TOTAL</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<td></td>
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<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**NOTE:** All formulations with additives use untreated CaCO₃
LABORATORY EXPERIMENT:

Data generated is based on compounding on a Brabender PL2000 torque rheometer using the bowl mixer equipped with cam blades at 180°C and 70 rpm. The total time of the mixing cycle was 800 seconds.

Capillary rheometer testing was performed on a Shimadzu CFT-500C equipped with a 10 mm by 1 mm diameter die and set at 200°C. A variety of shear rates were used to give a complete viscosity picture.

Physical property data was generated using injection molded test specimens prepared on a Cincinnati Milacron 33 ton lab molding machine:

Color measurements were taken on injection molded specimens using a Minolta Spectrophotometer.

Thermal stability measurements were made on a Mettler Toledo DSC at 10°C/min.
MIXING CURVES FOR 40% CaCO₃ FILLED COMPOUNDS

ProFax 6323

Torque, Nm

Time, sec

Untreated

Treated
ZB30A-1%
ZB30B-1%
ZB31/1-1%

Quality Additives for Performance
MIXING CURVES FOR 40% CaCO₃ FILLED COMPOUNDS

Amoco 1016

Time, sec

Torque, Nm

Untreated

Treated

ZB30A-2%

ZB30B-2%

ZB31/1-2%
MIXING PROPERTY RESULTS:

- Untreated CaCO$_3$ with no additives showed higher torques throughout the mixing cycle and the resulting compound displayed poor dispersion with residue CaCO$_3$ left in the bowl.

- The treated CaCO$_3$ showed improved wetting characteristics resulting in lower torques throughout the mixing cycle. The resulting compound displayed good dispersion and color.

- The untreated CaCO$_3$ with fatty acid derivatives added showed wetting and mixing characteristics typical of treated CaCO$_3$. The resulting compound displayed good dispersion and color.
VISCOSITY AND SHEAR STRESS AT 200°C
ProFax 6323 Compounds

Graph showing the apparent viscosity and shear stress at 200°C for different compounds. The graph compares untreated and treated samples, as well as ZB30A-1%, ZB30B-1%, and ZB31/1-1%.

Quality Additives for Performance
VISCOSITY AND SHEAR STRESS AT 200°C

Amoco 1016 Compounds

- Untreated
- Treated
- ZB30A-2%
- ZB30B-2%
- ZB31/1-2%

Shear Stress, Pa

Apparent Viscosity, Pa.s

Quality Additives for Performance
VISCOSITY TESTING RESULTS:

- Untreated CaCO₃ with no additives had higher melt viscosities across the shear range when compared to treated CaCO₃.

- The untreated CaCO₃ with fatty acid derivatives added had melt viscosities comparable to treated CaCO₃ across the shear range.
## SPECTROPHOTOMETER DATA, D65/10°

<table>
<thead>
<tr>
<th>Description</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h</th>
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<tbody>
<tr>
<td>ProFax 6323</td>
<td></td>
<td></td>
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<tr>
<td>Untreated</td>
<td>85.2</td>
<td>0.6</td>
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<td>Treated</td>
<td>87.2</td>
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<td>94.3</td>
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<td>ZB30A - 1%</td>
<td>88.1</td>
<td>-0.3</td>
<td>3.5</td>
<td>3.5</td>
<td>95.0</td>
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<td>ZB30B - 1%</td>
<td>87.8</td>
<td>-0.3</td>
<td>3.6</td>
<td>3.6</td>
<td>94.0</td>
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<tr>
<td>ZB31/1 - 1%</td>
<td>88.3</td>
<td>-0.3</td>
<td>3.3</td>
<td>3.3</td>
<td>95.0</td>
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<tr>
<td>ZB30A - 1.5%</td>
<td>88.2</td>
<td>-0.3</td>
<td>3.3</td>
<td>3.3</td>
<td>95.6</td>
</tr>
<tr>
<td>ZB30B - 1.5%</td>
<td>88.1</td>
<td>-0.3</td>
<td>3.4</td>
<td>3.4</td>
<td>95.0</td>
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<tr>
<td>ZB31/1 - 1.5%</td>
<td>88.2</td>
<td>-0.3</td>
<td>3.4</td>
<td>3.4</td>
<td>95.1</td>
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<td>6.5</td>
<td>84.2</td>
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<td>Treated</td>
<td>86.4</td>
<td>-0.5</td>
<td>5.2</td>
<td>5.2</td>
<td>96.0</td>
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<tr>
<td>ZB30A - 1.5%</td>
<td>87.6</td>
<td>-0.6</td>
<td>5.5</td>
<td>5.5</td>
<td>96.5</td>
</tr>
<tr>
<td>ZB30B - 1.5%</td>
<td>88.0</td>
<td>-0.4</td>
<td>5.0</td>
<td>5.0</td>
<td>95.1</td>
</tr>
<tr>
<td>ZB31/1 - 1.5%</td>
<td>87.7</td>
<td>-0.5</td>
<td>4.7</td>
<td>4.7</td>
<td>96.1</td>
</tr>
</tbody>
</table>
REFLECTANCE BY SPECTROPHOTOMETER FOR ProFax 6323 COMPOUNDS, D65/10 degree

Wavelength, nm

Reflectance, %

- Untreated
- Treated
- ZB30A-1%
- ZB30B-1%
- ZB31/1-1%

Quality Additives for Performance
REFLECTANCE BY SPECTROPHOTOMETER FOR AMOCO 1016 COMPOUNDS
D65/10 degree

Reflectance, %

Wavelength, nm

Untreated
Treated
ZB30A-2%
ZB30B-2%
ZB31/1-2%

Quality Additives for Performance
COLOR TESTING RESULTS:

- Untreated CaCO$_3$ with no additives gives a more yellow/grey compound when compared to treated CaCO$_3$.

- The untreated CaCO$_3$ with fatty acid derivatives gives a much whiter compound comparable with and in some cases better than the treated CaCO$_3$.

- In the 5 MFI PP compound, reflectance data shows a much whiter compound in the untreated CaCO$_3$ with fatty acid derivatives.
FLEXURAL PROPERTIES AND IZOD IMPACT STRENGTH:

<table>
<thead>
<tr>
<th></th>
<th>Flex Strength, MPa</th>
<th>Flex Modulus, MPa</th>
<th>Notched Impact, J/m</th>
<th>Unnotched Impact, J/m</th>
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<tbody>
<tr>
<td><strong>ProFax 6323</strong></td>
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<tr>
<td>Untreated CaCO₃</td>
<td>44.1</td>
<td>2191</td>
<td>75</td>
<td>641</td>
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<tr>
<td>Treated CaCO₃</td>
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<td>150</td>
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<td>ZB30A - 1%</td>
<td>45.7</td>
<td>2274</td>
<td>171</td>
<td>No Break</td>
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<td>ZB30B - 1%</td>
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<td>2640</td>
<td>171</td>
<td>No Break</td>
</tr>
<tr>
<td>ZB31/1 - 1%</td>
<td>45.9</td>
<td>2265</td>
<td>176</td>
<td>No Break</td>
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### MELT TEMPERATURE AND DEGRADATION BY DSC:

<table>
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<th>$T_m$, °C</th>
<th>$T_{\text{deg}}$, °C</th>
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<tbody>
<tr>
<td>Unfilled ProFax 6323</td>
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<td>246</td>
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<tr>
<td>Untreated CaCO$_3$</td>
<td>168</td>
<td>237</td>
</tr>
<tr>
<td>Treated CaCO$_3$</td>
<td>166</td>
<td>231</td>
</tr>
<tr>
<td>ZB30A - 1%</td>
<td>167</td>
<td>248</td>
</tr>
<tr>
<td>ZB30B - 1%</td>
<td>167</td>
<td>248</td>
</tr>
<tr>
<td>ZB31/1 - 1%</td>
<td>168</td>
<td>247</td>
</tr>
</tbody>
</table>
OVEN AGING DEGRADATION (158 hrs. AT 150°C):

- ProFax 6323 + Untreated CaCO$_3$ (40%)
- ProFax 6323 + Treated CaCO$_3$ (40%)
- ProFax 6323 + Untreated CaCO$_3$ (40%) + Fatty Acid Derivative (0.4%)
ECONOMICS:

- Price estimations used:
  - Untreated, F Grade CaCO$_3$ = $0.093$/lb.
  - Treated, F Grade CaCO$_3$ = $0.122$/lb.
  - Untreated, UF Grade CaCO$_3$ = $0.134$/lb.
  - Treated, UF Grade CaCO$_3$ = $0.180$/lb.
  - Polypropylene, generic = $0.400$/lb.
  - Fatty Acid Additive analyzed at $1.25$, $1.00$ and $0.80$/lb.

- Compound costs based on the formulations used in this study
- No change in output rates or other production costs
COST SAVINGS REALIZED USING FATTY ACID DERIVATIVES
VS. TREATED CONTROL
1 MM LB. PRODUCTION RUN

Estimated Annual Cost Savings Based on F Grade CaCO3
Estimated Annual Cost Savings based on UF Grade CaCO3

FA = $1.25/lb.
FA = $1.00/lb.
FA = $0.75/lb.
COST SAVINGS REALIZED USING FATTY ACID DERIVATIVES VS. TREATED CONTROL
10 MM LB. PRODUCTION RUN

Estimated Annual Cost Savings Based on F Grade CaCO3
Estimated Annual Cost Savings based on UF Grade CaCO3

FA = $1.25/lb.  
FA = $1.00/lb.  
FA = $0.75/lb.