The Art and Technology of Controlling Alkaline Earth Oxide Thickeners in SMC

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Goals of this Presentation:

• Provide basic overview of SMC formula components
• Discuss importance of rheology during compound and part manufacturing
• How to manage SMC paste viscosity build to achieve desired end results
# Sheet Molding Compound (SMC) Basic Components

<table>
<thead>
<tr>
<th>Required Base Raw Materials</th>
<th>“Other” Raw Materials</th>
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</thead>
<tbody>
<tr>
<td>– Thermosetting resin(s)</td>
<td>– Thickening agent(s)</td>
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<tr>
<td>– Reactive monomer(s)</td>
<td>– Release agent(s)</td>
</tr>
<tr>
<td>– Filler(s) / reinforcement(s)</td>
<td>– thermoplastic resin(s)</td>
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<tr>
<td>– Organic peroxide(s)</td>
<td>– Colorant(s)</td>
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<td></td>
<td>– Inhibitor(s)</td>
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<td></td>
<td>– Processing aid(s)</td>
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<td>– &quot;Special&quot; additive(s)</td>
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Designing a SMC Formula

• An extensive, almost limitless, list of RM choices available for consideration
• Key RM properties regulate / dictate selection, combinations, %’s
• Variation in above choices allow for an infinite number of SMC formulas designed to meet:
  – Specific compound processing parameters
  – Desired final part requirements
ONE Commonality Necessary for ‘Successful’ Compounding and Molding of ALL SMC....

- PREDICTABLE AND RELIABLE VISCOSITY BUILD RESULTING IN A COMPOUNDED MATERIAL WITH A CONSISTENT RHEOLOGY PROFILE!
Why is Repeatable Rheology Profile Necessary?

- Consistent paste delivery through pumps, dams or slit dies
- Wetting of the filler(s) / reinforcement(s)
- Mat weight control
- Stabilization of the liquid phases
- Packaging (saggy rolls, containment of product within carrier film, separation at festoon folds, etc.)
- Preparation and handling of the sheet prior to molding
- Impart a viscoelastic characteristic to carry the filler / reinforcement in a consistent flow pattern during mold fill
- Help to develop a resin rich surface
- Consistent final molded product characteristics
What Causes an Increase in Paste Viscosity?

• Chemical thickeners
  – Alkaline earth (Group IIA metal) oxides and / or hydroxides
    • Magnesium oxides / hydroxides are industry "norm"
  – PG2
    • Proprietary liquid thickener chemistry
    • Similar thickening profile as isocyanates but does not require controlled hydroxyl functionality
  – Polymeric isocyanates
    • Polymeric isocyanates require controlled hydroxyl functionality in the resin, are VERY sensitive to moisture, thicken quickly

• Physical thickeners -- fillers / reinforcements
  – Physical thickening is difficult and appropriate for few types of SMC
How is the SMC Thickening Profile (Viscosity Increase) Controlled?

• To achieve repeatable viscoelastic response batch to batch it is imperative the SMC has:
  – Consistent raw materials
  – Controlled process parameters
  – Stable storage conditions

• Technology developments in industry over last 40 years has resulted in:
  – Advanced manufacturing controls and equipment resulting in tighter tolerances of SMC raw materials
  – Innovative compounding and molding processes and equipment
Why is MgO the Candidate of Choice to Impart a Viscosity Build?

- Meets the basic needs of SMC
- Most widely used chemical thickener in processing of SMC and therefore readily available
- Cost effective
- Potentially can be manipulated and controlled
What is the Mechanism Causing Viscosity Build?

• The resins’ acid functionality and the MgO are the reacting species causing viscosity increase

• Characteristics of each contribute / dictate the viscosity profile
Characteristics of Resins with Acid Functionality Affecting Thickenin Profile:

• Acid value
• Hydroxyl number
• Molecular weight average, distribution, oligomers, etc.
• Distribution of acid groups on polymer chain
• Moisture
Characteristics of MgO Affecting Thickening Profile:

- ????
- No easily tested physical or chemical property of MgO has been identified that correlates to thickening performance
Proposed Mechanism for Thickening Reaction:

- Acid group of resin is chemisorbed to surface anion vacancies of MgO and/or by the basic O2 surface ions.
- Chain extension is by linking polymer chains with "crystals" of MgO not Mg ions.
- Prior mechanism for thickening relied on dissociation of MgO BUT research data does not support this mechanism, i.e.
  - Dead burn / sintered and reagent grades thicken negligibly.
  - Equimolar amounts of Mg(OH)2 and MgO do not thicken equally.
Proposed Mechanism for Thickening Reaction:
SMC Formula Development using MgO Thickeners

- Determine type and concentration by conducting thickening studies
  - Conduct thickening studies at 3 MgO levels; 2 moisture levels
  - Monitor initial, 15', 1hr; and, 1 to 7+ day viscosity
  - Bracket %MgO based on initial study that yields intended viscosity profile required for SMC processing and molding
  - Include a H2O range IF moisture sensitivity of A-paste to thickener is extreme

- If appropriate thickening rate cannot be achieved with initial grade of MgO, as-is moisture or temperature control, then
  - Evaluate different grades / reactivities of MgO
  - Evaluate different types of thickeners
  - Consider adjusting for H2O by moisture scavengers or water addition
Effect of Initial Temperature on A-Paste Viscosity

Increasing initial paste temperature will reduce paste viscosity to assist flow through dam and glass wet-out.
Effect of Initial Temperature on 15’ SMC Paste Viscosity Varying %MgO

Increasing initial paste temperature will reduce paste viscosity to assist flow through dam and glass wet-out

BUT, increasing initial paste temperature will increases thickening rate

Glass wet-out, mat weight, phasing, etc. will be affected
Increased H2O increases sensitivity / viscosity response to % thickener at all levels during initial processing, 15 minutes
At 1 day high moisture paste is still tracking higher than lower moisture pastes
At 1 week viscosities of the high and low moisture pastes SWITCH--the low moisture is as high or higher in viscosity than the high moisture paste
At 2 weeks the low moisture paste is higher in viscosity than all pastes with high moisture
Storing / shipping SMC in extreme hot / cold temperatures can affect thickening rate and ultimately the SMC quality.
Technology Advances in MgO Capabilities

• New SMC applications, environmental concerns, cost containment, etc. have prompted development of new / different chemistries being used in SMC formulating.

• Manufacturers continue to “push the envelope” with raw material and processing changes.
New ‘Tools’ for the Changing SMC World

• Available are various grades of MgO with different thickening reactivity and moisture sensitivity

• Have the potential to “tailor” thickening rate with changing A-side reactivity
Some Comparative Thickening....

- A-side paste was adjusted to three water levels, 0.05, 0.10 and 0.15% BOP H2O
- Four individual grades of MgO were mixed with carrier resin at 40% loading
- A constant loading of each MgO dispersion was mixed with the A-paste to 90F
- Viscosity was monitored by Brookfield
H2O Influence on SMC Paste Thickening rate at 15 and 60 Min. Comparing Four MgO Grades

H2O WILL affect thickening rate and plateau viscosity of MgO containing SMC
H2O% and MgO grade will determine the magnitude of rate change
H2O addition will always increase the 15’ and 60’ thickened viscosity
H2O Influence on SMC Paste Thickening rate at 1 thru 13 Days
Comparing Four MgO Grades

All MgO grades indicate slower thickening rate at low H2O; increasing H2O levels increase thickening rate and ‘usually’ decreases plateau; each MgO grade responds differently to varying moisture levels; adjusting moisture and proper selection of MgO grade are other tools for process adjustment.
Past Control Measures of MgO Dispersions for Use in SMC

• In the beginning....... 
  – Paste can thickening studies were conducted and monitored for 48 or 72 hours usually with Brookfield viscometers 
  – Adequate mixing in cans, temperature control and imparted shear were very difficult to control 
  – Delayed approval or rejection was very costly with respect to time, material, etc. 
  – Limited understanding and few manufacturing controls! yielded variable product 
  – Industry goal - "lights out" molding facility drove understanding and refinement of raw materials, their function and processing
Current Control Measures of MgO Dispersions for Use in SMC at Chromoflo Technologies

• Current practices......
  – Oscillatory chemorheology procedure refined at Chromoflo Technologies is current method for incoming QC of MgO powder and final thickener dispersion
  – Method provides a rapid, repeatable and reliable test (~30 minutes) to characterize reactivity
  – Use of aggressive high speed centrifugal mixer allows consistent mixing to a consistent temperature
  – Comparison of a standard / control lot to the incoming raw material or final product ensures consistency
Chemo-Rheology Slope vs. Brookfield Viscosity

**1 Day Paste Viscosity vs. Slope**

- $R^2 = 0.9675$

**2 Day Paste Viscosity vs. Slope**

- $R^2 = 0.9252$

**3 Day Paste Viscosity vs. Slope**

- $R^2 = 0.8351$

**5 Day Paste Viscosity vs. Slope**

- $R^2 = 0.8586$
Summary

• SMC applications are becoming more demanding
• Regulations have limited the use of some traditional RM’s
• Formulators have to be more creative
• Rheology / viscosity profile more important and more challenging than ever
• Industry understanding of MgO, moisture and temperature affects are imperative to the manufacturing of consistent product
• Advanced testing capabilities allow for predictable, repeatable viscosity build in a variety of SMC chemistries