Multi-Component Molding of Liquid Silicone Rubber Over Thermoplastics

Eric Bishop  
Shin-Etsu Silicones

David Wolgemuth  
Phillips Plastics
Agenda

• Shin-Etsu Overview
• Properties & Processing
• Select-Hesive™ LIMS
• Applications – Phillips Plastics
• Questions?
Shin-Etsu Chemical

- Largest Chemical company in Japan
- 7th largest by Market Capitalization in the World
- Main business groups:
  - PVC
  - Silicon/Silicone
  - Epoxy overmolds & photoresists
  - Methylcellulose
Shin-Etsu Chemical has an A1 long-term Moody's rating (as of June 30, 2006)

Market Cap. Ranking of Global Chemical Companies

Source: Datastream
Features of Silicone Elastomer

• Thermal Stability (-65F – 400F)
• Non-conductive: Thermal & Electrical
• Naturally Elastomeric (5-80 Shore A)
• High Tear Strength
• Low Hysteresis / Compression Set
• Chemically Inert
• UV Resistant
• Translucent
• Low Surface Energy
• FDA Compliant – Food Contact
• USP Class VI & ISO 10993 Compliant
• Sterilizable: Steam, Gamma, ETO
LIMS Molding Process

Component A
- Methyl Vinyl Polymer
- Platinum Catalyst
- Silica Filler
- Additives

Component B
- Methyl Vinyl Polymer
- Hydride Crosslinker
- Inhibitor
- Silica Filler
- Additives

Static Mixer
- 1:1 Ratio

LIMS Delivery System

Injection Mold
- Heated Mold Cavities
- Cold Runner System

Metering Screw
- Cooled Barrel

Injection Molding Machine
LIMS 2-Component System

Component A
- Methyl Vinyl Polymer
- Platinum Catalyst
- Silica Filler
- Additives

Component B
- Methyl Vinyl Polymer
- Hydride Crosslinker
- Silica Filler
- Additives
- Inhibitor

500M To 2MM CPS Viscosity
1:1 Mixing Ratio
Rheometry  

LIMS  Processing

Monsanto MDR2000E

250°F  350°F

T02 (sec)  29  6
T90 (sec)  47  11
Peak Rate (lb-in/min)  120  129
Max Torque (lb-in)  16  15

T02  Time to 2% Cure  Injection window
T90  Time to 90% Cure  Indicator of Cure Time
Peak Rate  Rate of Cure  Measurement for Cure Speed
Max Torque  Maximum Torque  Complete State of Cure

Shin-Etsu Confidential
Advantages of LIMS

- Clean – No Reaction By-Products
- Contaminant Free – Closed System
- Versatile – Varying Thickness, Undercuts
- Productive – Fast Cure Cycle
- Lean – Flash-Free Parts…No Post Ops
- Stable – Excellent Shelf-Life

Strong History of Silicone Performance
Potential Pitfalls of LIMS

• Low Viscosity → Flash
  – Precise gating, venting, shut-offs, parting lines, and parallelism are essential

• 2-Component System → Improper Mix
  – PM on Pump and Static Mixer are Critical

• Platinum Catalyst → Cure Inhibition
  – Sulfur
  – Phosphorus
  – Nitrogen - Amines
Healthcare LIMS Grades

• KE1950
  – 10-70 Duro

• KEG2000 – Fast Cure
  – 20-75 Duro

• KE2090 & KE2095 – Select-Hesive™
  – 10-70 Duro

• KEG2003 – Low Volatile

• KE2004 – Soft and Tough
  – 5, 10 & 20 Duro

• Anti-Microbial LIMS
Select-Hesive™ LIMS

• KE2090
  – Self-Bond to PC, PBT, PPO
  – 10-70 Duro
  – USP Class VI Compliant
  – ISO 10993 Compliant

• KE2095
  – Self-Bond to PA66, PA6, PPA
  – 40-60 Duro
  – USP Class VI compliant
What are Select-Hesive LIMS?

1) Bonds aggressively to Plastics without adhering to Metal tooling
2) Adhesion is obtained during short curing time - < 1 minute

<table>
<thead>
<tr>
<th></th>
<th>Metals</th>
<th>Plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSR</td>
<td>NG</td>
<td>NG</td>
</tr>
<tr>
<td>Silicone Adhesive</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Select-Hesive LIMS</td>
<td>NG</td>
<td>Good</td>
</tr>
</tbody>
</table>

Insert Injection Molding
Two-Shot Injection Molding
Mechanism for Selective Adhesion

- Mold
- Silicone Rubber
- Thermoplastic
- Weak Interaction
- Special Adhesion Promoter
- Interfacial Compatibility
- Chemical Interaction
  (Hydrogen Bonding...)
Adhesive Strength Test Method

**Molding Conditions**
- Injection Time: 7 sec
- Injection Pressure: 200 kgf/cm²
- Mold Temperature: 120°C, 165°C
- Curing Time: 1-3 min

**Silicone Injection**
- Mold (Metal) t=2mm
- Insert 50 mm/min

**Shear Strength of Adhesion**
- Silicone Rubber t=2 mm
- Area=2.5 cm²
- 50 mm/min
Adhesive Test by Insert Injection Molding

Curing Condition: 1min @165°C (*3min@120°C)
**Adhesion Durability for PC**

KE2090-50

KE2095-50
Adhesion Durability for PA

Shear Ts (MPa) vs Time (hr)

- **PA66 165C/1min**
- **PPA 165C/1min**

Temperature Ranges:
- 120C
- -35C
- -40 to 120C
- 85C/85%RH

Time (hr) Range: 0, 100, 300

**KE2095-50**

Shin-Etsu Confidential
Molding Condition Effect on Adhesive Properties

**Temperature Effect/ PA66**

- 130°C/1'
- 140°C/1'
- 150°C/1'
- 160°C/1'
- 168°C/1'

**Time Effect/ PA66**

- 168°C/1'
- 168°C/30s
- 168°C/15s

**Evaluation Criteria**

- 5 Excellent
- 5 Very Good
- 5 Good
- 5 Marginal
- 1 No good
2-Shot Molding Drivers

- Eliminate Assembly
- Reduce Inventory
  - Minimize Work in Progress
- Reduce Equipment & Floor Space Needs
- Improve Quality
- Increase Throughput
- Eliminate Outsourcing

Process Productivity Reduces Hidden Factory Costs
Co-Injection Molding Model

Molding Condition
Mold Temperature: PA66 (120C/248F)
LIMS (168C/334F)
Curing Time: 15sec/60sec

Injection (Plastic @ 280C)
Injection (Silicone @ R.T.)

Mold open
Mold Temperature
120C (248F)

Mold Temperature
120-168C (248-334F)

Coaster
Silicone t=0.1mm

8cm
6cm

Plastic (Polyamide)
t=2mm

Shin-Etsu Confidential
Select-Hesive LIMS

Video
Applications

• Needle-Free Valves
• Respiratory Masks
• Handles / Grips
• Connectors
• Gaskets / Seals
• Straps
Phillips Plastics » Overview

- Founded in 1964
- Annual sales over $260 million
- Annual Volume: 3 million
- Focused factories – 718,000 square feet
- 1500 people
- 254 presses – 0.44 to 935 tons
- One of the top 30 custom injection molders in North America
Phillips Plastics » Value-Added Proposition

- Total solutions provider
- Early involvement
- Engineering resources
- Project management
- Supply chain management
- Turnkey supplier
- Skilled workforce
- Diverse market base
- State-of-the-art technology
- Offshore/global capabilities
- Strategic alliances
Multi-Material Molding
Tech Brief
Process » Molding

- Two part LSR pumped, mixed, and injected into heated side of tool
- Thermoplastic gravity fed, heated, and injected into cold side of tool
- Additional color or additives in third and/or fourth stream for LSR
Process » Tooling Concepts
Materials » Compatibility

- Thermoplastics
- Chemical bonding if adhesion is required
  - Nylon bonding and PC, PC/ABS bonding
  - Immediate cure bonding vs. post molding bonding
- Heat compatibility
  - Glass transition temperature to withstand LSR cure temperature and time
  - 300 to 400 degrees F, for 5 to 60 seconds
  - Depends on amount and location of LSR
## Materials » Thermoplastic Compatibility

<table>
<thead>
<tr>
<th>Typical Thermoplastic Types</th>
<th>Typical Manufacture Name</th>
<th>Anticipated Bond Y/N</th>
<th>Anticipated Heat Compatibility Y/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Cycolac/Lustran</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Acetal(POM)</td>
<td>Celcon/Delrin</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Acrylic(PMMA)</td>
<td>Acrylite/Plexiglas</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>ASA</td>
<td>Gelyo</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>LCP</td>
<td>Vectra</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Crystalline Nylon</td>
<td>Zytel/Celenese</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Amorphous Nylon</td>
<td>Grilamid</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Polycarbonate(PC)</td>
<td>Lexan/Makrolon</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PC/ABS</td>
<td>Xenoy</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PBT</td>
<td>Valox/Celenex/Pocan</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PEEK</td>
<td>Victrex</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PE</td>
<td>Rexene/Marlex</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>PET</td>
<td>Rynite/Ektar</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PPO</td>
<td>Noryl</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PP</td>
<td>Norchem/Profax/Tenite</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>PS</td>
<td>Styron/Lustrex/K-resin</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>Udel/Mindel/Amodel</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Texin/Estane</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>PVC</td>
<td>Vista/Geon</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>SAN</td>
<td>Tyril/Starex</td>
<td>Y</td>
<td>N</td>
</tr>
</tbody>
</table>
# Materials » Compatibility

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Bonding Excel/Good/Poor/None</th>
<th>Failure Type Adhesive/Cohesive</th>
<th>Heat Compatibility No affect/part specific/Too low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lexan 121-111 PW Clear</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Makrolon 2405-1000 Clear</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lexan 141 Trans White</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xenoxy 5220U Yellow</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Cyclosil MC1300</td>
<td>Poor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond ABS 7401 Natural</td>
<td>None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crastin SK602 White 15% Glass</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Crastin ST620 White</td>
<td>Excel</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Valox V3901WX GY80301 Light Grey</td>
<td>Excel</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Celanex 3300 Natural</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Celanex 2002 Natural</td>
<td>Excel</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Zytel 101 Natural</td>
<td>Good</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Noryl GF42 Black</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Fortron 1140L4 Natural</td>
<td>None</td>
<td>Adhesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Vectra A130 Natural</td>
<td>Good</td>
<td>Adhesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Amodel AS-1133 Black</td>
<td>Poor</td>
<td>Adhesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Amodel ET-1000 Natural</td>
<td>Poor</td>
<td>Adhesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Grilamid TR90 Natural</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Grilamid TR60 Clear</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Terblend N MM-11 White</td>
<td>Good</td>
<td>Adhesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Zytel 103H6L Natural</td>
<td>Good</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Zytel 801H6S Natural</td>
<td>Good</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Zytel 330 NOC10 Natural</td>
<td>Good</td>
<td>Adhesive</td>
<td>Part Specific</td>
</tr>
<tr>
<td>Radel R Gray</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Udel P1700 Clear</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Grilamid Grivory GV-4H</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Noryl HNA055 Grey</td>
<td>Excel</td>
<td>Cohesive</td>
<td>No Affect</td>
</tr>
<tr>
<td>Lexan HP51 Natural</td>
<td>Good</td>
<td>Cohesive</td>
<td>Part Specific</td>
</tr>
</tbody>
</table>

Phillips Plastics Corporation
Tubular Contact Tip
Tubular Contact Tip

- Device:
  - Tissue ablation device requiring contact with body for cavity inflation during procedure
Tubular Contact Tip

- Component Problem:
  - Previously molded out of ABS
  - Did not seal against body as needed
  - Resulted in gas leakage
Tubular Contact Tip » Material Selection

- Requirement:
  - Elastomer in a 20 or 30 durometer
- TPE vs. LSR
  - TPE is a lower cost for material and process
  - TPE is not easily found in durometer lower than 50 shore A, which is FDA approved
  - LSR is class 6 and sterilizable
- Selection:
  - Medical grade Makrolon with PC
  - 30 Durometer PC bonding LSR
Tubular Contact Tip » Process / Tooling

- Solution:
  - Two barrel two-shot press used with thermoplastic and silicone
  - Mold first shot then overmold LSR
Tubular Contact Tip » Overview

• Why MS LSR?:
  - Biocompatible elastomer with clean material transitions and permanent adhesion to substrate

• Program Timing:
  - 4 week tool design
  - 10 week tool build
  - 6 week sample and validation

• Annual Volume: 500,000

• Program Results:
  - New NRE was required
  - Increased performance leading to increase in product use and sales growth
Small Diaphragm Seal
Small Diaphragm Seal

- Device:
  - Wearable, disposable drug dosing device with sealed exit port for needle and cannula
Small Diaphragm Seal

- Component Problem:
  - Formerly a rigid disk with assembled silicone diaphragm
  - Due to extreme small size, assembly was useful in development stage but not viable for high volume production
Small Diaphragm Seal » Material Selection

- Requirement:
  - Design for silicone to be molded directly into the rigid part
  - Rigid frame for assembly in unit and low durometer LSR for sealing during use and for shelf line
Small Diaphragm Seal » Material Selection

- Selection:
  - Rigid material: Grilamid TR60 for toughness, chemical resistance, and compatibility with chosen LSR
  - LSR: nylon bonding 10 shore A durometer
Small Diaphragm Seal » Process / Tooling

• Solution:
  - LSR in b-barrel for smallest screw size possible
  - Valve gate was placed to insure heat into part
  - Sequential valve gate system was used for dosing of LSR
Small Diaphragm Seal » Overview

- Why MS LSR?:
  - Very small part, assembly not viable for production

- Program Timing:
  - 5 week tool design
  - 11 week tool build
  - 8 week sample and validation

- Annual Volume: 3 million

- Program Results:
  - Part price reduced with NRE pay back within one year
  - Allowed for high volume production with designed performance
Manifold Emergency Valve
Manifold Emergency Valve

- Device:
  - Fluidic/gaseous dispensing unit
    for patient treatment
Manifold Emergency Valve

- Component Problem:
  - Rigid frame and die cut assembled seal
  - Assembly must be cleanable and autoclavable for reuse
  - Die cut seal was difficult to place consistently and separation occurred after repeated disassembly, cleaning, and autoclave of the unit
Manifold Emergency Valve » Material Selection

- Requirement:
  - Chemical resistance, autoclavability, and excellent chemical adhesion of materials

- Selection:
  - Autoclavable Polysulfone in custom color 30 durometer self-adhesive LSR
  - Material adhesion was tested for initial bonding and after autoclave
Manifold Emergency Valve » Process / Tooling

- Solution:
  - Two barrel, two-shot press using modular mold base
  - Valve gate to center of part in cavity/core set
  - Rigid frame was designed to have seal molded in and seal was redesigned with functional surface geometry
  - Tool is a rotary platen design with valve gate on the silicone
Manifold Emergency Valve » Overview

- Why MS LSR?:
  - Assembly was difficult and design was failing for the performance requirements

- Program Timing:
  - 2 week tool design
  - 4 week tool build
  - 2 week validation

- Annual Volume: 5,000

- Program Results:
  - Total part price reduced with NRE pay back in six months
  - Eliminated quality issues and field failures
MS LSR Applications

- Medical MS LSR Applications:
  - Patient care
  - Wound drain systems
  - Masks and skin contact diagnostics
  - Valving
  - Diaphragms and pumps
  - Drug dispensing and monitoring devices
  - Infant care
  - Feeding and pacification/toys
  - Skin contact for care provider
MS LSR Applications

- Other MS LSR Applications:
  - Silicone and silicone
  - Silicone on thixotropic molded magnesium
  - Silicone on ceramic and metal injection molded parts
Questions and Answers...