Novel Means to Improving Low Temperature Mechanical Properties in a Silicone Elastomer

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Presented at the Fall 194th Technical Meeting of Rubber Division, ACS Louisville, KY
October 9 – 11, 2018
Paper D10
ISSN: 1547-1977

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Background

• MQ and VMQ silicone elastomers have a broad range of useful temperatures.
  • At about -40°C VMQ silicone elastomers experience a dramatic increase in modulus due to the formation of a semi crystalline state.
  • PVMQ elastomers minimize this semi crystalline state and retain their flexibility to temperatures as low -120°C
• PVMQ is essential for sealing components for low-temperature applications
• Along with the general disruption in silicone rubber markets, PVMQ has experienced a price increase of over 300%

An alternative approach to enhancing low temperature performance was needed
Outline

• PVMQ: Why its needed?
• PVMQ: What is it?
• Alternatives to use of PVMQ Gum
  • Vinyl end-blocked Diphenyl Dimethyl copolymers
  • Other side chain possibilities
• Experimental results
• Discussion
• Q&A
PVMQ: Why its needed?

- VMQ exhibits a doubling of Modulus at about -40°C, 10 times initial modulus at -44°C and by the time it reaches -60°C the modulus is 100 times the starting value.
- Both dynamic and sealing applications are drastically affected by such a large change.
  - Aircraft window seals
  - Aircraft door seals
  - Cryogenic refrigeration seals
  - Regulator diaphragms and valve seals
  - Vibration damping mounts for Rotary equipment
PVMQ: Why its needed?

• The long-term high temperature stability of siloxane polymers is directly impacted by the concentration of phenyl groups
  • The higher concentration of unsaturated aromatic rings provides additional thermal stability
  • Thermal stability ranking;
    • polydimethylsiloxane < poly(dimethylco-methylvinyl)siloxane < low phenyl poly(dimethyl-co-diphenyl) siloxane < high phenyl poly(dimethyl-co-diphenyl) siloxane
      < poly (dimethyl-co-diphenyl-co-methylvinyl)siloxane

• Refractive index matching for clear formulations

There’s more than one way to introduce phenyl groups into an elastomer composition
PVMQ: What is it?

• PVMQ  Silicone rubber having methyl, phenyl and vinyl substituent groups on the polymer chain
  • The important choice here is the location of the vinyl groups
  • The vinyl groups may be pendant or terminal
  • It is suggested that terminal vinyl groups would be best for full incorporation into the polymer with the least impact on mechanical properties

• The choice of methyl phenyl or diphenyl substituent is also important
  • Methyl phenyl polymer synthesis has the potential for the creation of 2,6 Cis phenyl cyclics
  • 2,6-cis-Diphenylhexamethylcyclotetrasiloxane is a known toxicological hazard
PVMQ formulation

• Method for creating PVMQ compounds
  • One method for compounding is to begin with a PVMQ containing base, which already contains treated fillers.
  • A 2nd approach is to combine PVMQ gum with VMQ gum to achieve the desired phenyl content then incorporate reinforcing fillers
  • A third approach is to combine Vinyl endblocked Diphenyl Dimethyl copolymers with VMQ gum either before or after incorporating reinforcing fillers
    • This is the approach followed in our work
Other modification possibilities

• Depending on the property one is seeking to influence, other side chain modifiers are possible

• It has been reported that polymers containing ethyl sidechains also exhibit good low temperature mechanical properties
  • These should not be expected to exhibit the higher thermal stability of phenyl side groups

• Experimental vinyl terminal fluoro methyl dimethyl copolymers have been explored
  • Good low temperature performance and good resistance to oil swelling were observed

• Non-vinyl functional diphenyl dimethyl copolymers can be incorporated to provide controlled surface migration.
PVMQ experimental design

- For reasons of expediency, commercial products available from AB Specialty Silicones were used.

- A fluid compatibility test based on haziness was performed to determine the highest phenyl content that was easily miscible with dimethyl polymer.

- High and low viscosity (molecular weight) copolymers were selected.

<table>
<thead>
<tr>
<th>Phenyl Mol %</th>
<th>Viscosity cSt. (MW)</th>
<th>Target Phenyl level %</th>
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<tr>
<td></td>
<td>L 1000</td>
<td>H 10000</td>
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<tr>
<td>3</td>
<td>SF 1421</td>
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</tr>
<tr>
<td>7</td>
<td>SF 1721</td>
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<tr>
<td>13</td>
<td>SF 2430 SF 9530</td>
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Experiment variables - Base

• Cure system selection
  • Non-vinyl-specific (NVS) peroxide, Di(2,4-dichlorobenzoyl) Peroxide (DCBP)
  • Vinyl-specific (VS) peroxide, Dicumyl Peroxide (DCP)

• Filler treatment
  • No treatment of fumed silica – cold mix
  • Insitu treatment of fumed silica with vinyl silane – hot mix

• Phenyl group concentration
  • 1 mol % & 3 mol % bases were mixed using 3 levels of phenyl content and 2 levels of polymer viscosity in the diphenyl dimethyl siloxane fluid selection

• Post cure (1 hour at 204°C)
High Phenyl set 3% loading

Tensile
Elong
Duro

Low MW
High Vinyl

High MW

Vinyl Specific
Non-Vinyl Specific
Experimental results - Base

• Cure system selection
  • NVS peroxide produced higher tensile strength with 1 mol % phenyl groups
  • VS peroxide produced higher duro and tensile strength and lower elongation and tear strength with 3 mol % phenyl groups
  • VS peroxide increased duro substantially in the low viscosity, vinyl-terminated phenyl silicone fluid iterations, which contain about 10 times more vinyl groups by weight
  • Using a dual catalyst combining NVS & VS peroxide produced even higher physical properties than either option on its own

• Filler treatment
  • Hot mixing with in situ filler treatment produced considerably higher tensile strength and lower ultimate elongation

• Phenyl group concentration
  • 1 mol % produced higher physical properties than corresponding 3 mol % iterations

• Post cure
  • This was introduced to ensure adequate state of cure after witnessing apparent low state of cure results with the low viscosity fluids and higher fluid loading levels
Discussion – Base

• Selection of variables for testing in final compound for low temperature extruded gasket
  • Use high viscosity, high phenyl content fluid at 3 mol % - Andisil SF 9530
  • Hot mix with insitu vinyl silane filler treatment
  • Use tri-catalyst cure system
    • NVS peroxides – DCBP and di-(2-tert-butylperoxyisopropyl) benzene (VCP or Vulcup)
    • VS peroxide – DCP

• Optimize base ratio of PVMQ:VMQ (i.e. 100:0, 70:30, 50:50, & 30:70)
  • Physical Properties
  • Heat Aged Properties – 70 hours at 232°C
  • Compression Set – 22 hours at 177°C
  • Cold Flexibility – 24 hours at -86°C
Experimental results - Compound

- Controls using commercially available PVMQ gum
  - Existing 100:0 PVMQ:VMQ peroxide-cured compound – J6230-1 WHT
  - Existing 30:70 PVMQ:VMQ platinum-cured compound – J6240-P WHT

- Physical Properties
  - Improvement observed as PVMQ base level was reduced
  - 30:70 iteration produced higher overall properties than J6230-1 WHT and higher tensile but lower elongation and tear strength than J6240-P WHT

- Heat Aged Properties
  - Improvement observed as PVMQ base level increased
  - 30:70 iteration produced comparable results to the Controls

- Compression Set
  - Improvement observed as PVMQ base level was reduced
  - 30:70 iteration produced substantially lower compression set than the Controls

- Cold Flexibility
  - All tri-catalyst iterations passed
Discussion – Compound

• Optimized base ratio at 30:70 PVMQ:VMQ using 3 mol % PVMQ Base
  • Good Physical Properties
  • Good Heat Aged Properties
  • Excellent Compression Set
  • Flexible at -86°C
  • Good availability of ingredients
  • Lower Cost than Control compounds
Future directions

• Commercialization of the finished formulation

• Evaluate the impact of high vinyl dimethyl copolymers on mechanical properties
  • Andisil VDM
    • Modulus increase
    • Modify tear

• Andisil experimental vinyl fluoro dimethyl copolymers
  • Surface property modification
  • Low-temperature property modification
Questions?
ABSS Rubber Product line

Products

Andigum BASE - General Purpose VMQ Silicone Base in 40 and 70 durometer
Andigum - Vinyl containing silicone polymers
Andifil AS 200 - 200 m²/g fumed silicas
Andisil® OH 30 & OH 40 - Silica process aids
Andisil® XL Crosslinkers - Silicone Hydride crosslinkers
Andisil® CE Chain Extenders - Terminal hydride chain Extenders
Andisil® VS - Vinyl polymer modifiers
Andisil® SF - Plasticizers and additives
Platinum Catalyst - High-quality Johnson Matthey catalyst dispersed in Andisil® VS for convenient handling