Rheology and characterisation of Sugru mouldable glues (RTV-1 silicone elastomer putty)

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About me..

Chemical Engineering studies

Master - Erasmus

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Formulation Science & Technology Group

Jan 2019 – Present  •  Committee Member

The Institute of Materials, Minerals and Mining

Dec 2018 – Present  •  Professional Graduate (ProfGradIMMM)
Agenda

- Background info
- Formulation of mouldable adhesives
- Typical characterisation techniques vs. rheology
- Collaborations with Academia and External Partners
- Summary
- Future work
Jane's Story

The invention of Sugru was a happy accident. It landed in the hands of a young woman with dreams for a smarter world.

We invented Sugru Mouldable Glues to get a new generation fixing, making and improving stuff.
Mouldable Glue
1-part RTV, highly filled silicone adhesive composite
Why RTV-1 silicone adhesive putty?

<table>
<thead>
<tr>
<th></th>
<th>Silicone sealants</th>
<th>Silicone putty</th>
<th>Epoxy putty</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTV-1</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>hand mouldable</td>
<td>✗</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>flexible</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>good adhesion</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>thermal stability</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
Easy to use
Applications

**Bond shapes that don't fit**
Unlike conventional glues that require two flat surfaces, you can make strong, flexible joins between all sorts of shapes, uneven surfaces and contrasting materials.

**No mess, no stress**
Liquid glues ooze, drip and get all over your hands. With Sugru mouldable glue, they stay where you put them — you're in control. Simply wipe your hands clean with dry tissue paper.

**Rebuild missing pieces**
When things stop working, it's often because key parts are cracked, worn or even missing. Thanks to its physical bulk and mouldability, Sugru allows you to fill gaps, holes and rebuild parts. It can be used to create 3D parts such as missing rubber feet, replace worn knobs and handles, and add strength and flexibility to fleshy cables.

**So much more than sticking things together**
Thanks to their unique properties, users of our mouldable glue discover all sorts of inventive ways they can help them, far beyond fixing broken things. With a little imagination, all sorts of problems can be solved, indoors and out.
Identify what needs to be tested and why?
Sugru’s testing (before rheology)

- Formulation
- Extrusion
- Testing

**Fresh**
- Plasticity
- 24hrs Hardness
- 24-48hrs Tensile
- 7 days Adhesion

**Month 1**
- Plasticity
- 24-48hrs Tensile

**Month 3**
- Plasticity
- 24-48hrs Tensile

**Month 6**
- Plasticity
- 24-48hrs Tensile

**Month 9**
- Plasticity
- 24-48hrs Tensile

**Month 12**
- Plasticity
- 24-48hrs Tensile
Formulating an RTV-1 silicone adhesive putty

RSC article: “Freeing a world of fixers: Sugru”, September 2014
Definitions

Uncured state
- putty, mouldable
- adhesive, glue

Cured state
- silicone elastomer
- flexible rubber
Sugru’s first 24 hr testing (before rheology)
Plasticity for mouldable glues

Plastometer
Williams plasticity technique – ASTM D926
Quantitative method for mouldability

Higher plasticity → harder to knead consistency
Lower plasticity → softer to knead consistency
Learnings from plasticity

Macrosopic phenomenon - Plasticity

New materials: Effect of filler morphology

Process: Fillers dispersion – overdispersion or agglomeration

User experience: How hard it is to knead

Shelf-life: Increase as product cures in the pack

Bar chart showing Williams plasticity (mm) for Playdough, Mouldable putty, and Modelling clay.
Sugru’s first 24 hr testing

- Formulation
- Extrusion
- Testing

0 hrs
- Plasticity

24 hrs
- Hardness
- Tensile
Hardness = resistance to indentation
Hardness for silicone rubbers

The diagram illustrates the Shore A hardness scale for Silicone rubbers, ranging from 0 to 90. The softer end of the scale is indicated to the left with a red bar, while the harder end is shown to the right with a blue bar.

The Shore A scale is marked with specific values: 0, 10, 40, 70, and 95. These values are associated with different materials:
- 0: Human skin
- 10: Pencil eraser
- 40: Cured silicone putty
- 70: Car tyre
- 95: Roller skate wheel

The image also highlights a transition from harder to softer rubber, with the text 'Harder rubber' on the left and 'Softer rubber' on the right.
Sugru’s first 24 hr testing

- Rheology - 24 hrs Cure profile
  - Plasticity
  - Hardness
  - Tensile

Formulation → Extrusion → Testing
Rheology

What can a rheometer measure in terms of Neo/Sugru?
- Uncured squeeze flow
- Tackiness/pull-off
- Uncured elastic/viscous fingerprint
- Cure rate (ambient, 12h)
- Accelerated cure rate (80°C, 1h)
- Cured material mechanical properties

Mouldable Glues
Filled system

- Tackiness – Pull-off test method
- Working time – Monitor changes in tackiness
- Cure depth – Different environmental conditions

Unfilled system

- Quality Control – Polymer grade
- Reactivity of the system - Cure time profile, Modulus increase
- Stability of the system - Proof of end-capping polysiloxanes
- Physical properties – chain polymer length

Rheological case studies
Rheological case studies

**Filled system**
- Tackiness – Pull-off test method
- Working time – Monitor changes in tackiness
- Cure depth – Different environmental conditions

**Unfilled system**
- Quality Control – Polymer grade
- Reactivity of the system - Cure time profile, Modulus increase
- Stability of the system - Proof of end-capping polysiloxanes
- Physical properties – chain polymer length
Cure time profile

- Gel point or Modulus increase
- Reactivity of silanes
- Stability - ageing
Gel test

End-capped polymer + catalyst

- No instant gelation
- Remained fluid
- Good cross-linking density

Not protected end-groups polymer + catalyst

- Instant gelation
- Slow relaxation
- Poor cross-linking density
Gel test

- A linear chain extension of chains involved by formation of catalyst’s ligand groups and polymer bonds.
- Decrease in functionality to 2 (from 3 or more)
- Polymer-catalyst bonds not stable with time.
- Polymer-catalyst bonds highly sensitive to hydrolysis. [1]

Gel test

No-protected end-groups polymer + catalyst

End-capped polymer + catalyst
Simple viscosity measurements

- Rearrangement of the polymer chains
- Higher viscosity
  - Risk of incomplete functionalisation of the polymer
  - Risk of lumps and difficulty during discharge due to very thick mixture
- Lower viscosity
  - Chain scission
  - Risk of the batch being low plasticity, sticky to handle
Simple viscosity measurements

- Rearrangement of the polymer chains
- Higher viscosity
  - Risk of incomplete functionalisation of the polymer
  - Risk of lumps and difficulty during discharge due to very thick mixture
- Lower viscosity
  - Chain scission [2]
  - Risk of the batch being low plasticity, sticky to handle

Pull-off test

- Tack is the ability of a material to adhere instantaneously to a solid surface when brought into contact by a very light pressure.

- Working Time: the amount of time from when the adhesive has set, to the time it will no longer bond.
Pull-off test
Pull-off test

SUBJECTIVE LABORATORY TEST

QUANTIFY THE TACK OR “STICKINESS” OF A FORMULATION

MONITOR THE NORMAL FORCES

MONITOR WORKING TIME

REFLECTED TACK BETWEEN THE SAMPLE AND THE MATERIAL OF THE TOP GEOMETRY

NOT MUCH INSIGHT INTO THE MECHANISMS THAT CONTROL TACK BEHAVIOR
Sugru’s first 24 hr testing

Unfilled system
- Quality Control – Polymer grade
- Reactivity of the system – Cure time profile, Modulus increase
- Stability of the system – Proof of end-capping polysiloxanes
- Physical properties – chain polymer length

Filled system
- Tackiness – Pull-off test method (still under development - need help – rolling ball)
- Working time – Monitor changes in tackiness
- Cure depth – Different environmental conditions
Sugru’s testing

Formulation

Extrusion

Testing

Fresh

Month 1

Month 3

Month 6

Month 9

Month 12

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Adhesion methods

- Lap Shear (ASTM D1002)
- Cleavage (ASTM D1062)
- Tensile (ASTM D2095)
Entanglement gives strong adhesion [3]

• Short-chain polymers and some specific types of polymers even with long chains have no tangles
  • Very easy to “open up” via abrasion (or with a bit of solvent) - so particles are easily removed

• Long-chain polymers are intrinsically tangled
  • It is very hard to open them up because trying to move one part of a chain is resisted by the tangles

[3] https://www.stevenabbott.co.uk/practical-adhesion/
Lap shear method

- Adhesive strength – Lap Shear (ASTM D1002)
External collaborations
Summary

**Unique properties and applications of silicone adhesive formulations**
- Soft consistency, hand mouldable, no sagging, retains its shape while curing
- Filling gaps, complex irregular shapes
- No drilling, controlled texture/finish applications
- Non corrosive by-product, customised hardness, chemical, temperature and weathering resistant
- Shock absorbing, flexible joints

**Basic tests**
- Characterisation methods for end-user applications of silicone glues.

**Rheology**
- Reactivity of the system
- Stability of the system
- Chain polymer length
- Tackiness
- Working time
- Cure depth

**Adhesion**
- Important property for new formulations.
- Adhesion & Cohesion Start with Tangles
- Sugru - Excellent bonding to various organic and inorganic substrates
Future work in FormFormForm R&D

FormFormForm R&D Projects

- New Technologies
- Formulation Development
- Process Development
- Application Development

- Performance
- Safety
- Shelf-life
Thanks for listening!

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