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

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FORMATIVE FORMULATION

18 March 2019

Maxwell Centre, University of Cambridge

Sugru

Mouldable Glues

Follow Sugru all over the place

About me..

Chemical Engineering studies

Master - Erasmus

PhD in Polymer Chemistry

Formulation Chemist

Senior Formulation Chemist

Formulation Science & Technology

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

We invented Sugru Mouldable Glues to get a new generation fixing, making and improving stuff

Sugru
Mouldable Glues

Mouldable Glue
1-part RTV, highly filled silicone adhesive composite

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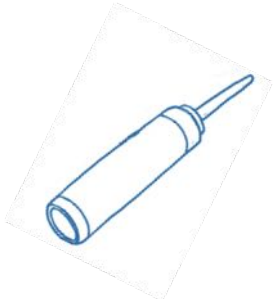
Why RTV-1 silicone adhesive putty?



	Silicone sealants	Silicone putty	Epoxy putty
RTV-1	✓	✓	✗
hand mouldable	✗	✓	✓
flexible	✓	✓	✗
good adhesion	✓	✓	✓
thermal stability	✓	✓	✓

Sugru
Mouldable Glues

Stick It

Sugru sticks permanently to lots of materials like glass, ceramic, wood, metal and plastics*.

Mould It

You have 30 minutes to fix, build and create.

Sets Strong

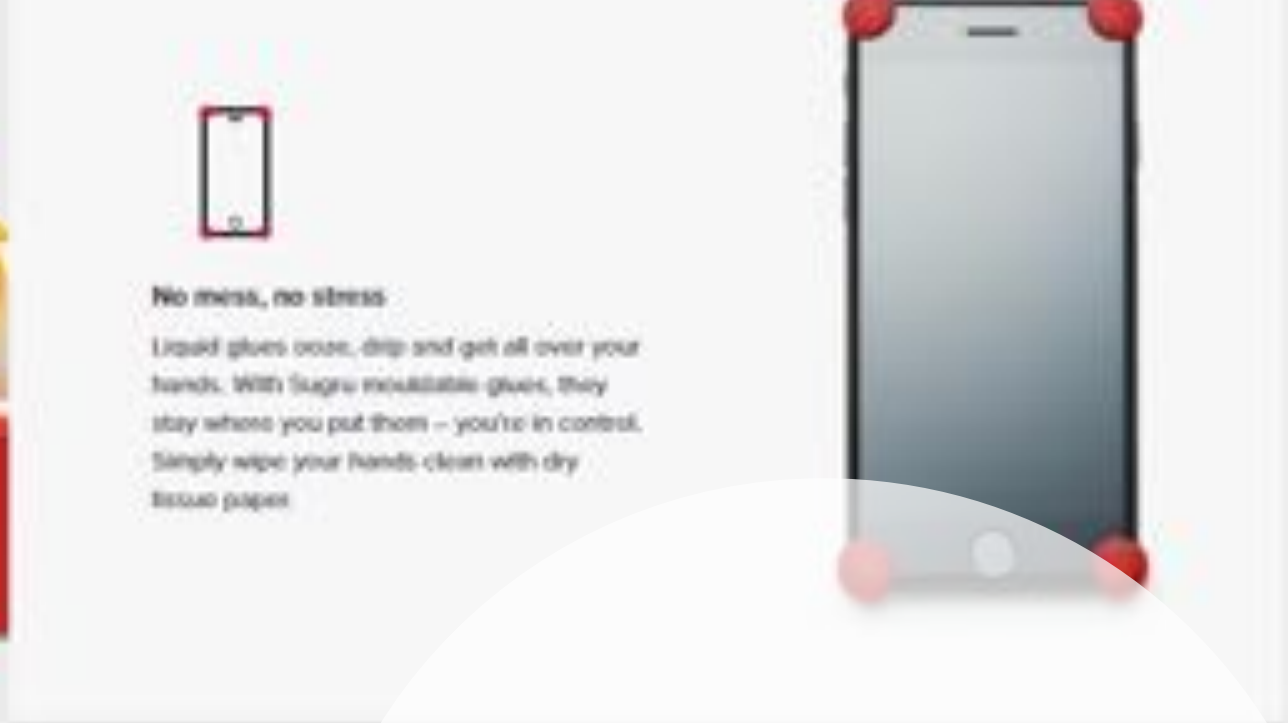
In 24 hours, it turns into a strong and durable silicone rubber that stays stuck.

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 glues, 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 flimsy cables.

So much more than sticking things together

Thanks to their unique properties, users of our mouldable glues 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.

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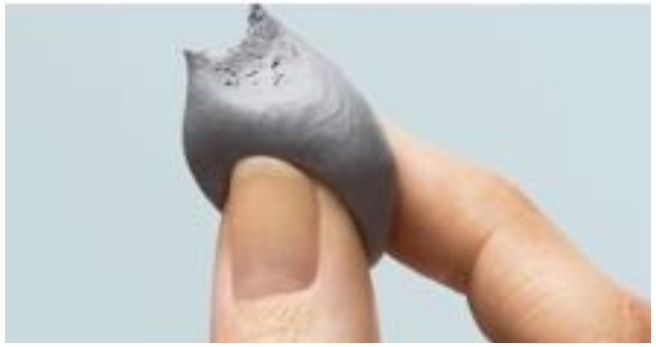
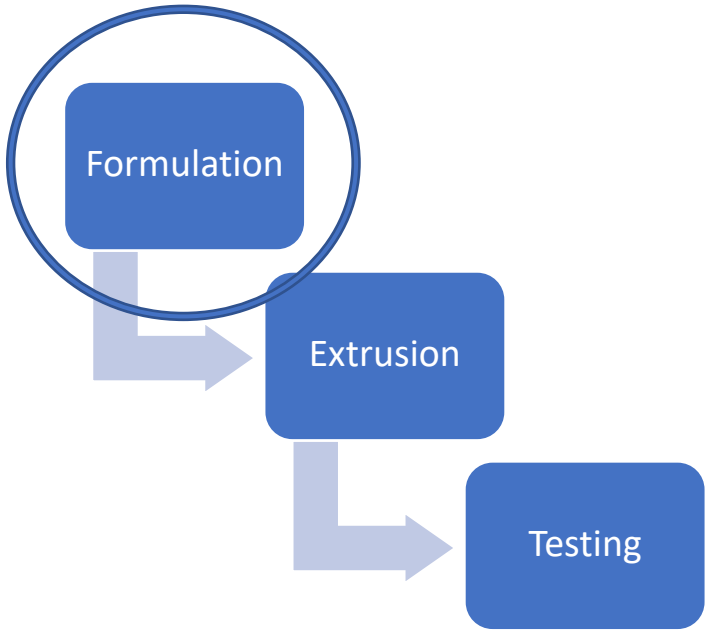
Mouldable Glues

Characteristics

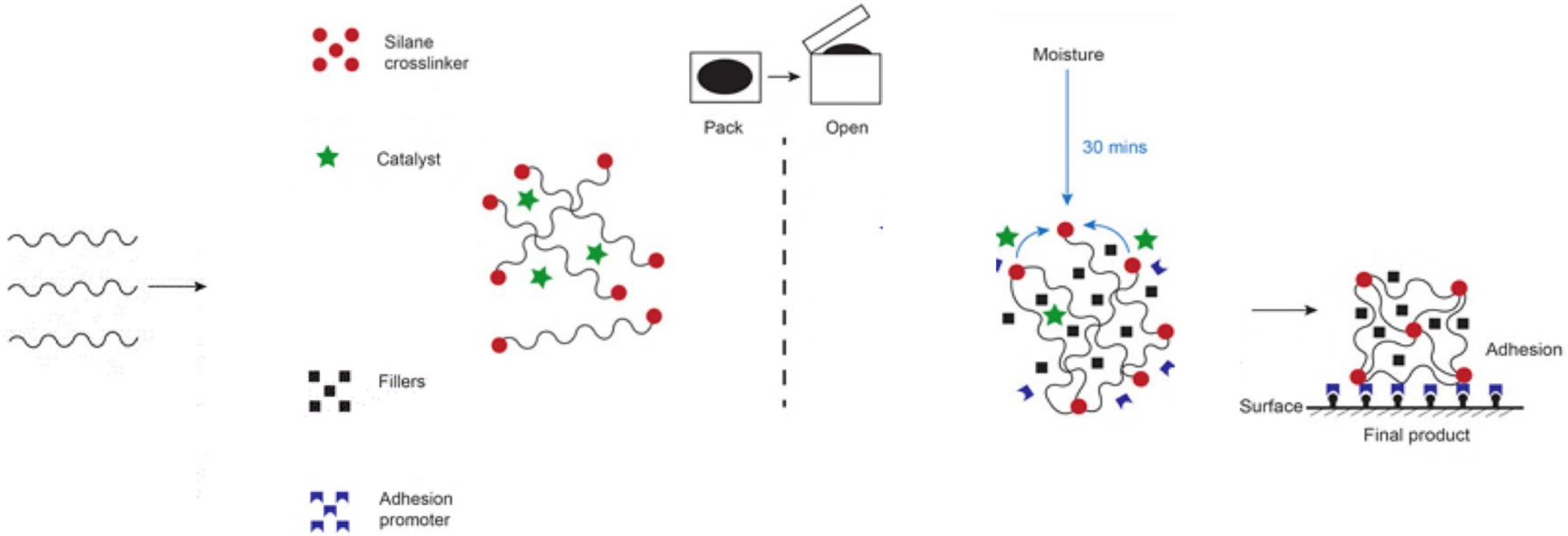


Identify what needs to be tested and why?

Sugru's testing (before rheology)



Formulating an RTV-1 silicone adhesive putty



RSC article: "Freeing a world of fixers: Sugru", September 2014
https://www.chemistryworld.com/news/freeing-a-world-of-fixers/7703.article

Definitions

Sugru
Mouldable Glues

Uncured state

- putty, mouldable
- adhesive, glue

Cured state

- silicone elastomer
- flexible rubber

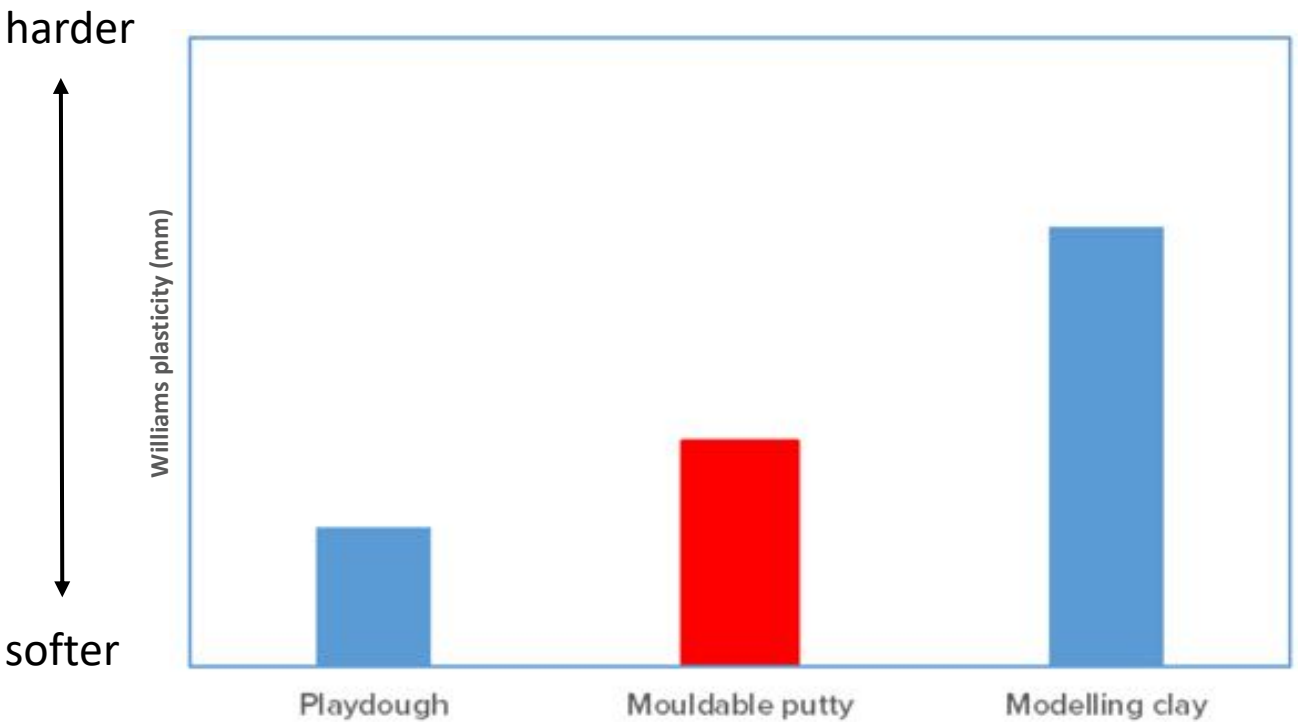
Sugru's first 24 hr testing (before rheology)

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



- **Macroscopic** 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

Sugru's first 24 hr testing

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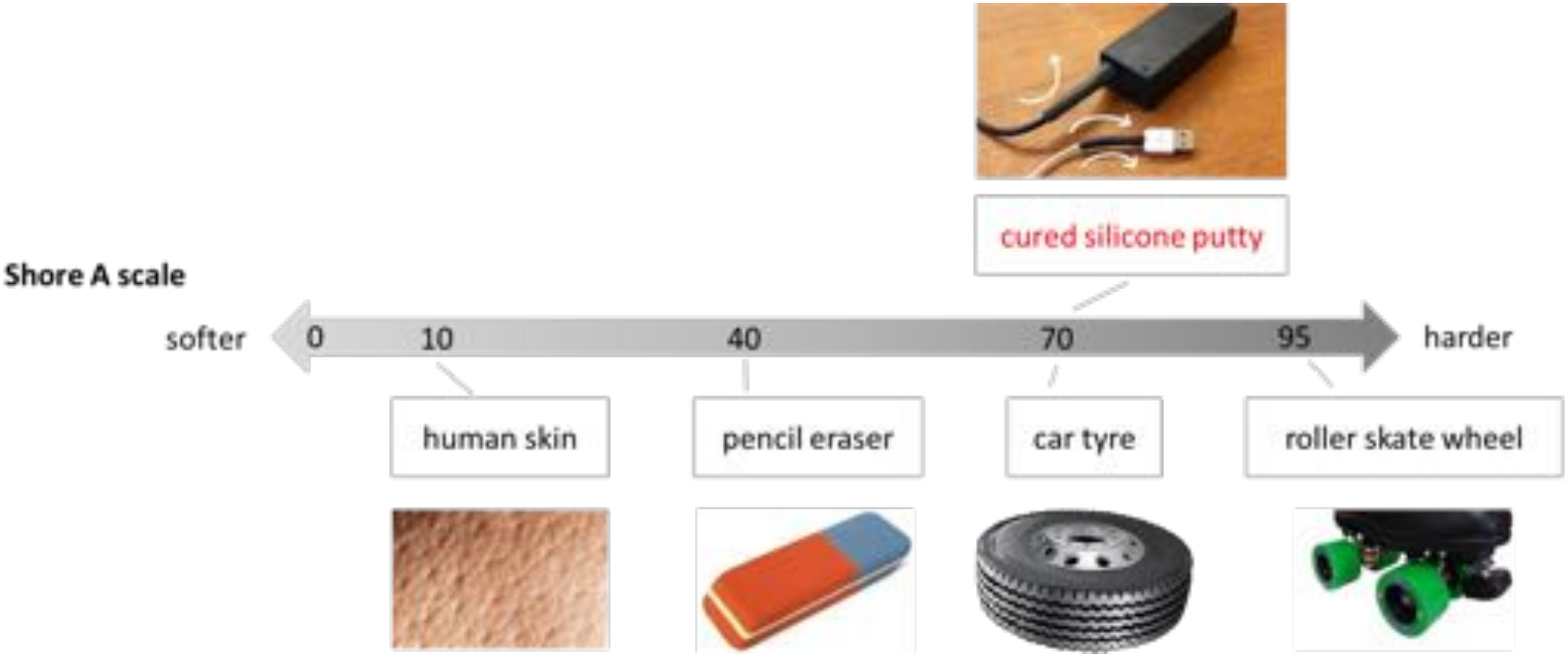
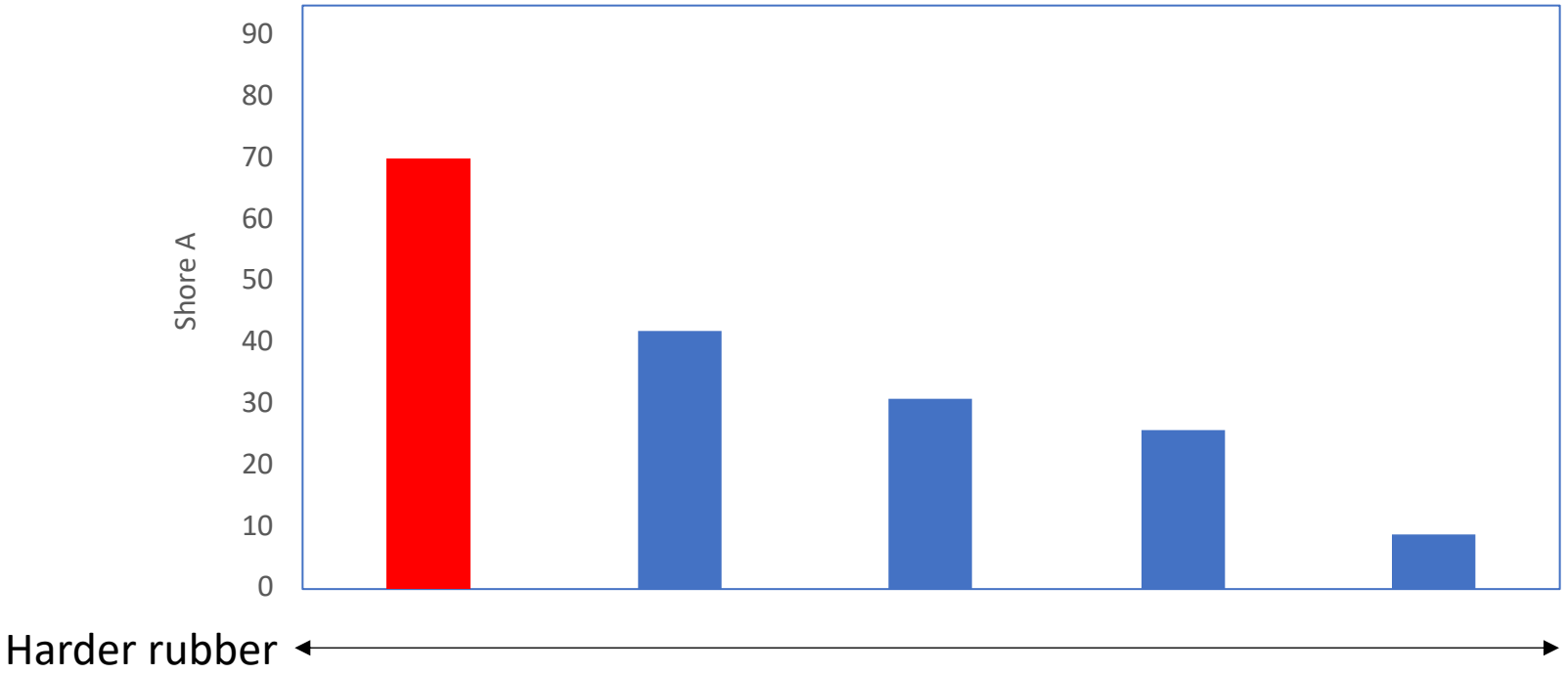
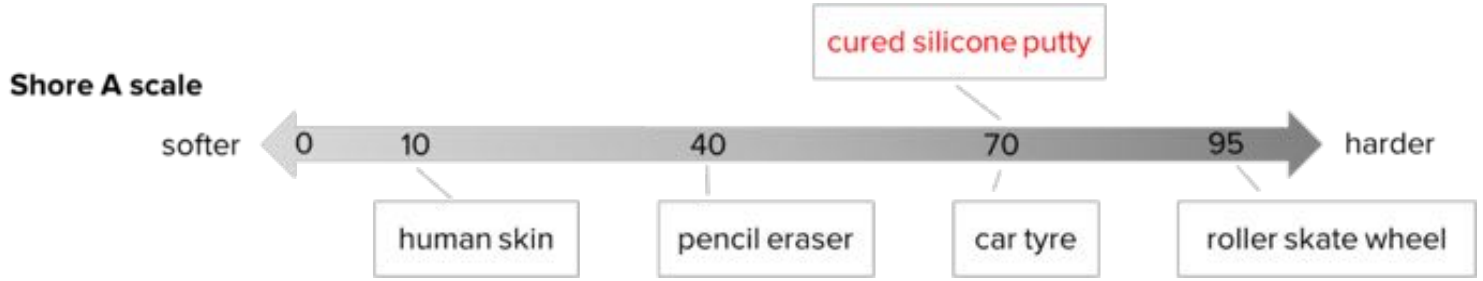
Hardness = resistance to indentation

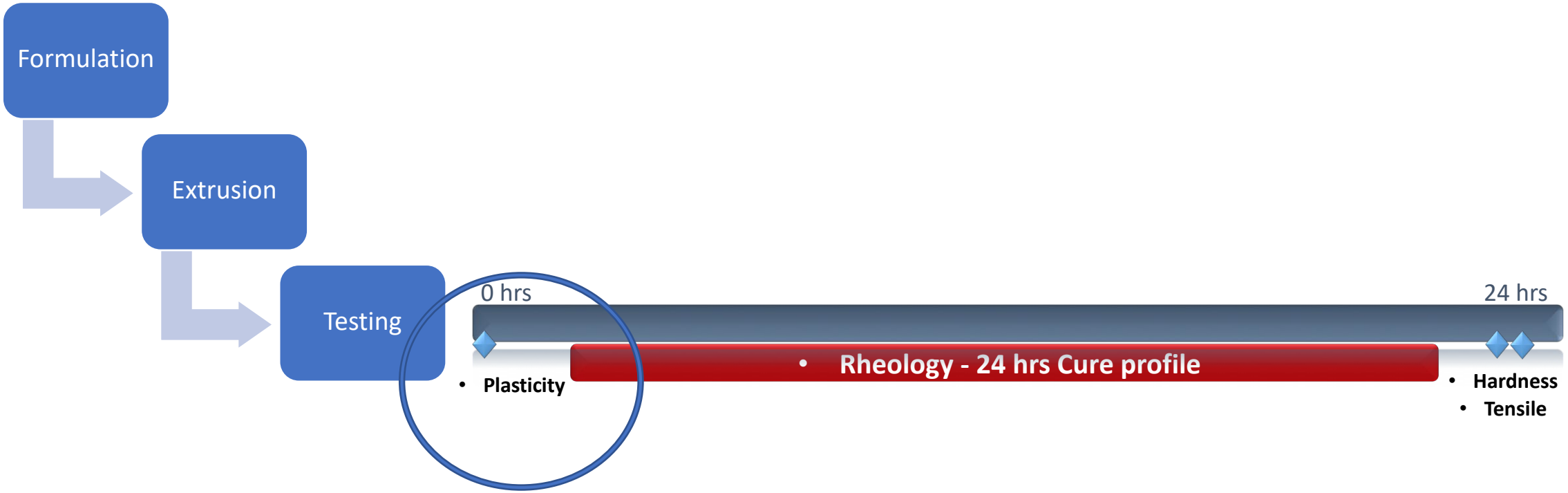


Hardness for silicone rubbers





Sugru's first 24 hr testing



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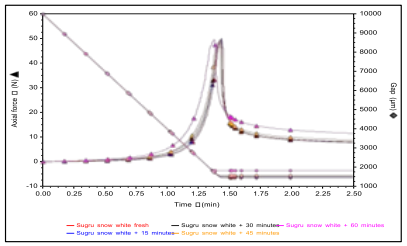
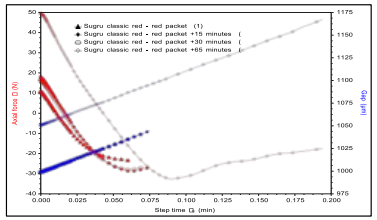


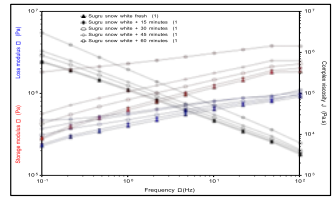
Uncured squeeze flow

- axial

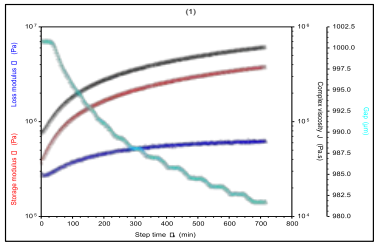


Tackiness/ pull-off

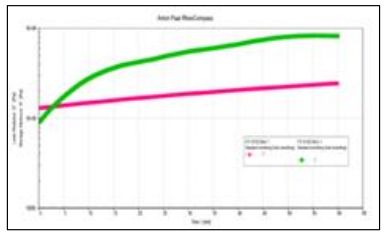
- axial



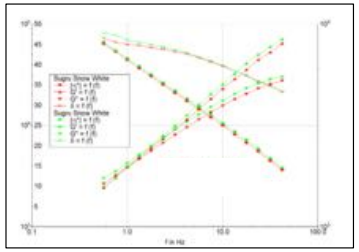
Uncured elastic/viscous fingerprint



Cure rate (ambient, 12h)



Accelerated cure rate (80C, 1h)



Cured material mechanical properties

Rheology

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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

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Filled system

- Tackiness – Pull-off test method
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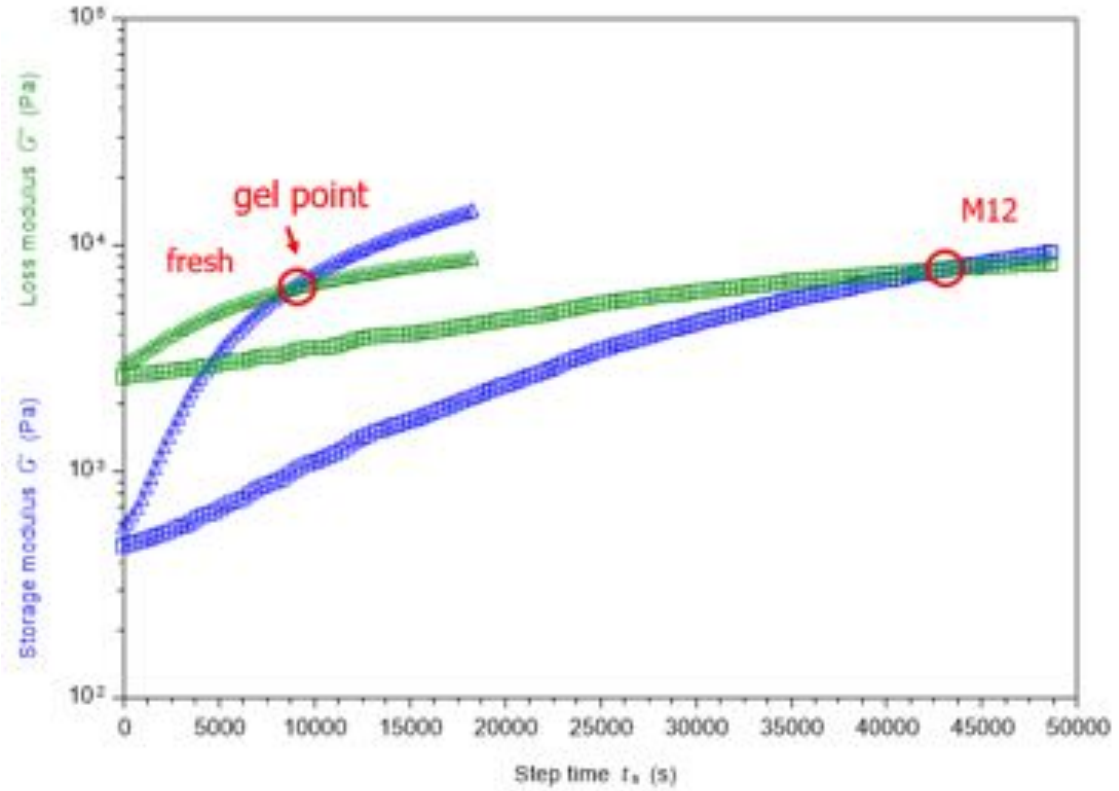
Rheological case studies

Cure time profile



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

Gel test

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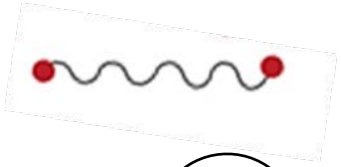


End-capped polymer + catalyst

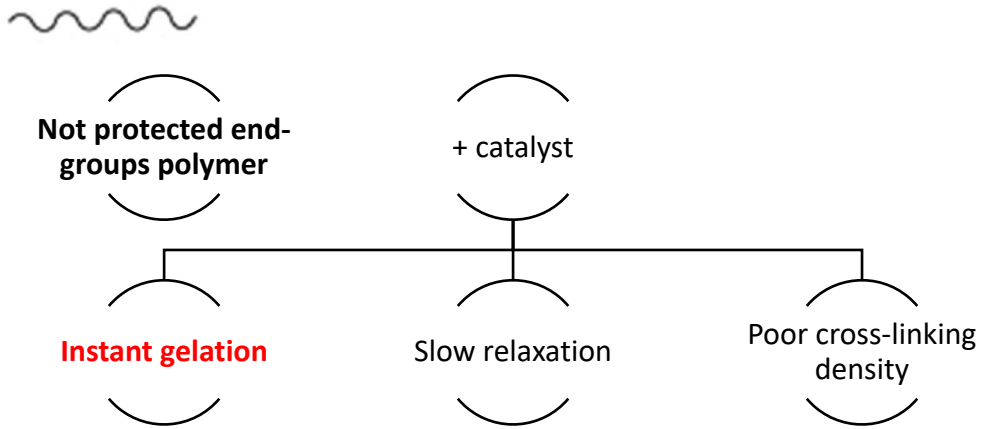
- **No instant gelation**
- Remained fluid
- Good cross-linking density

Not protected end-groups polymer + catalyst

- **Instant gelation**
- Slow relaxation
- Poor cross-linking density

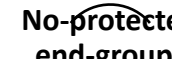
Gel test

- ***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]***



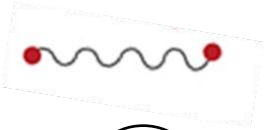
[1] Laura Comaills-Autin, Philippe Cassagnau, Anne Seggio, Aurélie Mondière, Roger Spitz, Vincent Monteil, Investigations on interactions between titanium alkoxides and α,ω-dihydroxy PDMS by a combination of rheology and spectroscopy, European Polymer Journal, Volume 57, 2014, Pages 37-46

Gel test



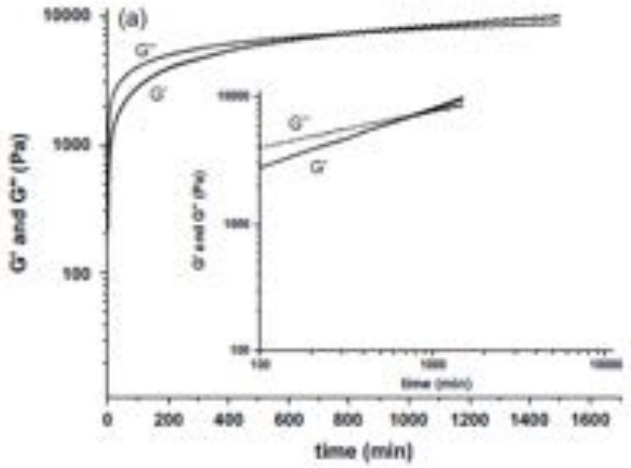
No-protected end-groups polymer

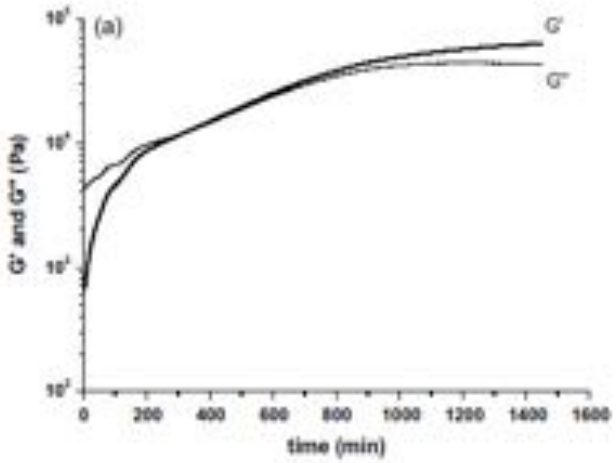
+ catalyst



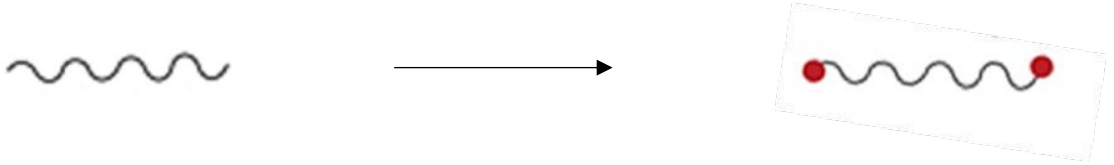
End-capped polymer

+ catalyst



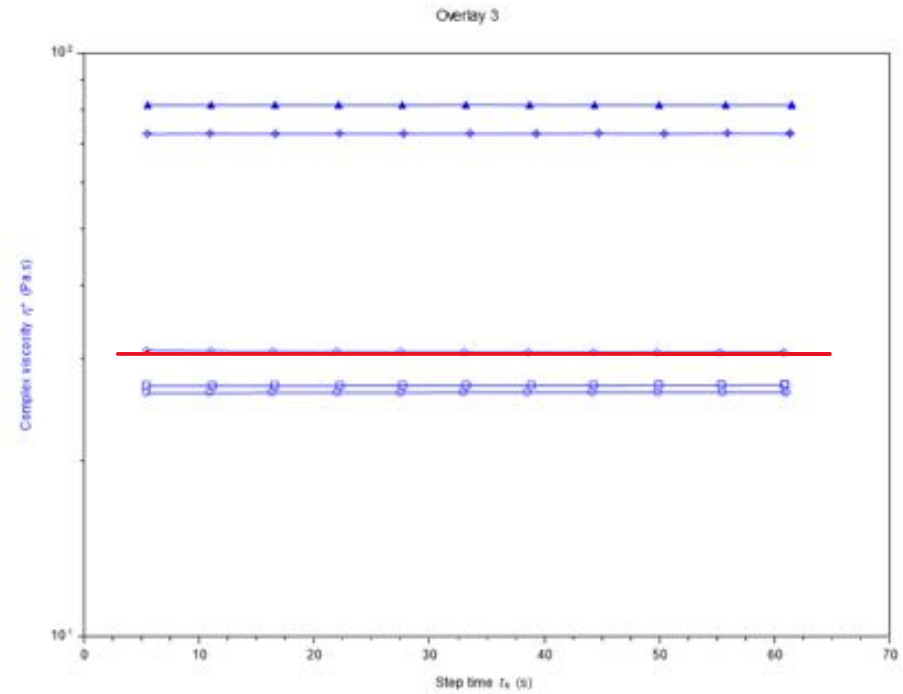


Simple viscosity measurements



- 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



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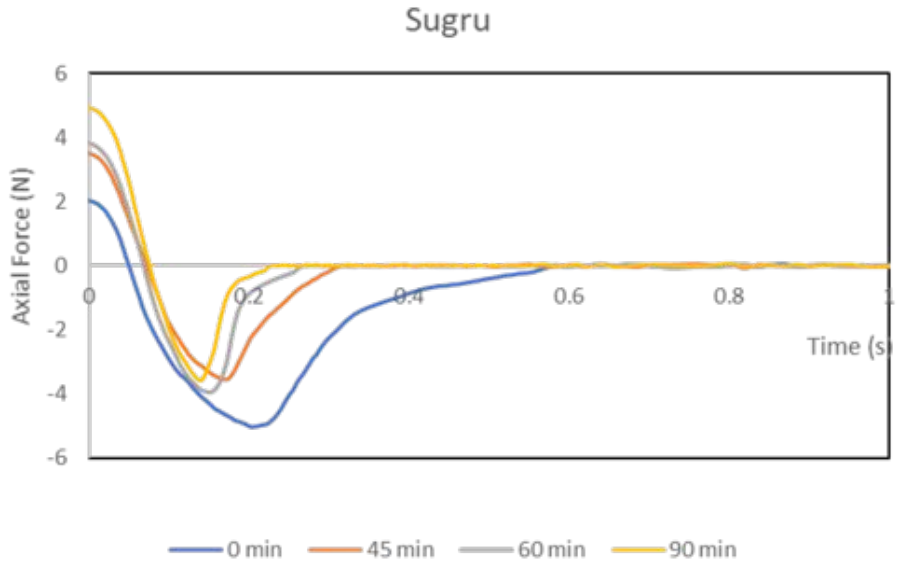
[2] Delor-Jestin, Florence et al. "Durability of crosslinked polydimethylsyloxanes: the case of composite insulators" Science and technology of advanced materials vol. 9,2 024406. 24 Jul. 2008

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

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SUBJECTIVE LABORATORY TEST

QUANTIFY THE TACK OR “STICKINESS” OF A FORMULATION

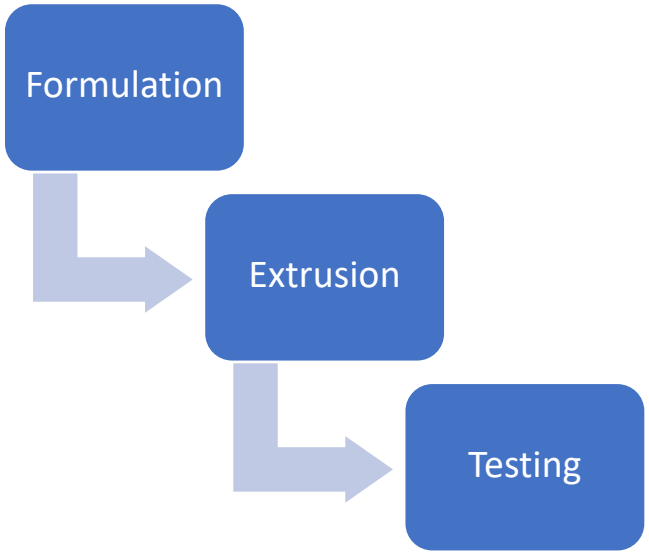
MONITOR THE NORMAL FORCES

MONITOR WORKING TIME

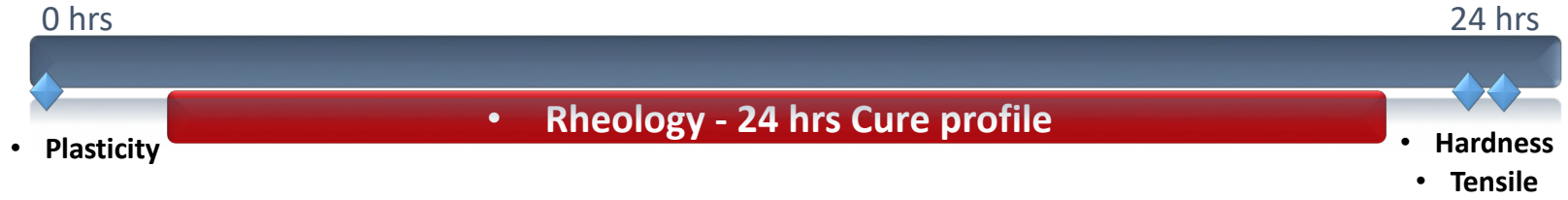
REFLECTED TACK BETWEEN THE SAMPLE AND THE MATERIAL OF THE TOP GEOMETRY

NOT MUCH INSIGHT INTO THE MECHANISMS THAT CONTROL TACK BEHAVIOR

Sugru's first 24 hr testing

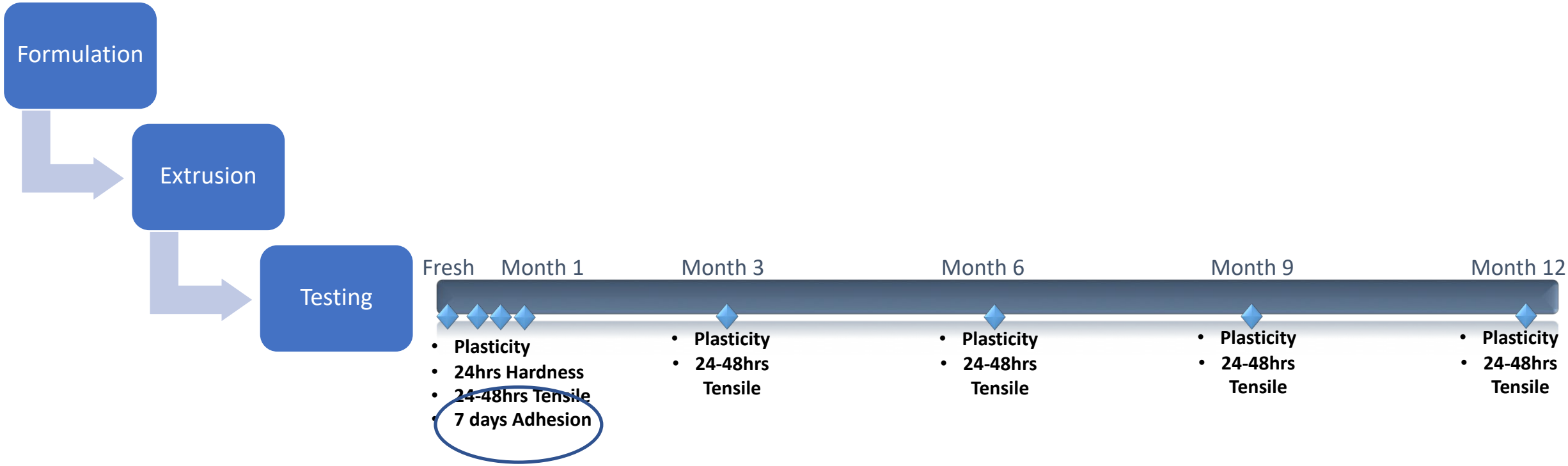


Unfilled system
Quality Control – Polymer grade
Reactivity of the system - Cure time profile, Modulus increase
Stability of the system - Proof of end-capping polysiloxanes
Physical properties – chain polymer length



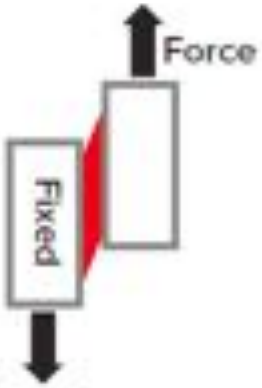
Filled system
Tackiness – Pull-off test method (still under development - need help – rolling ball)
Working time – Monitor changes in tackiness
Cure depth – Different environmental conditions

Sugru's testing



Adhesion methods

- **Lap Shear (ASTM D1002)**



- **Cleavage (ASTM D1062)**

- **Tensile (ASTM D2095)**

Entanglement gives strong adhesion [3]

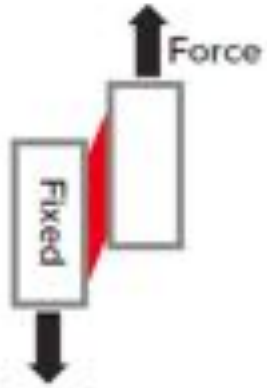
- Short-chain polymers and some specific types of polymers even with long chains have no tangles
  - Very easy to “open up” via abrasion (or with a bit of solvent) - so particles are easily removed

- 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

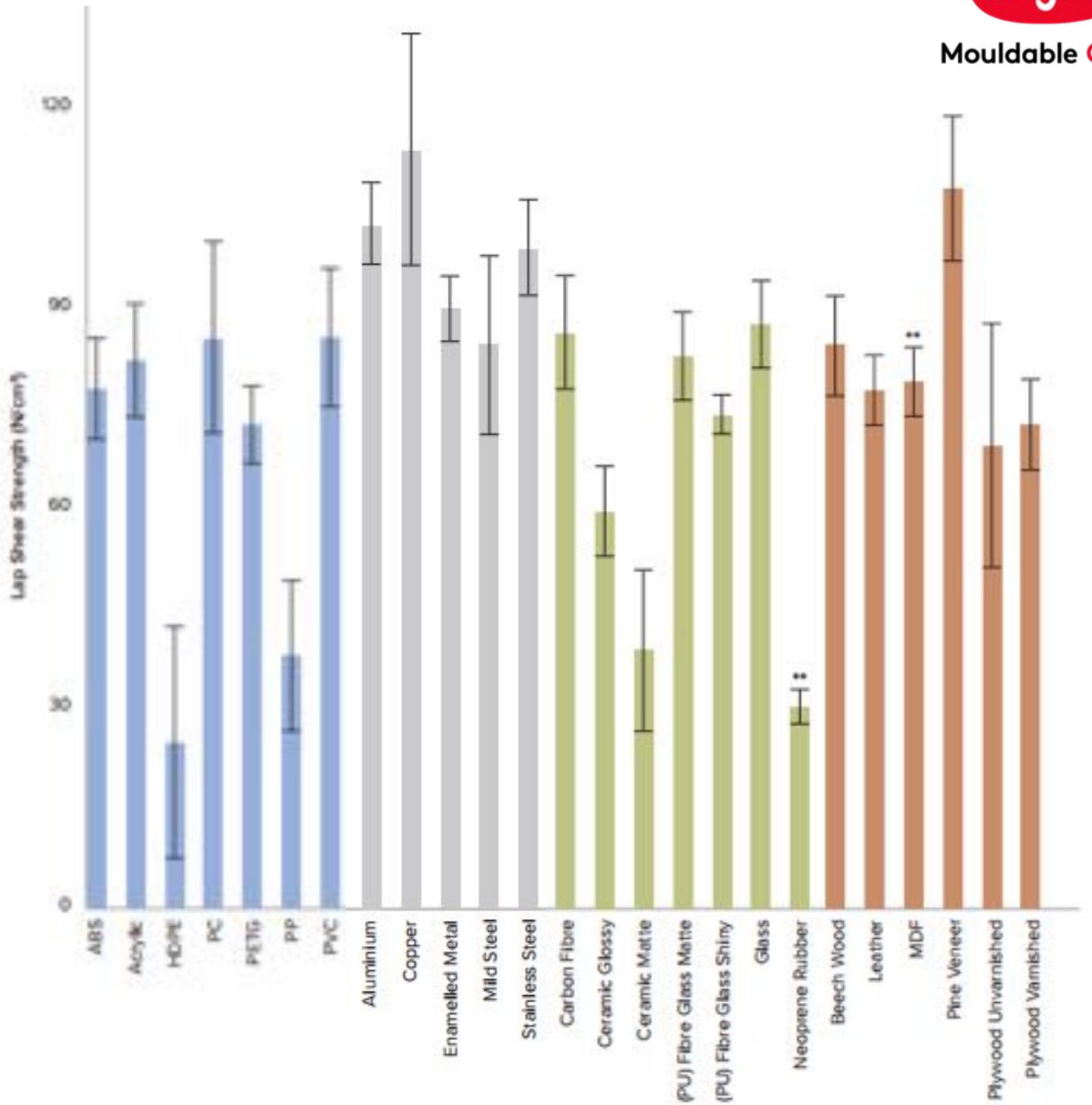
[3] https://www.stevenabbott.co.uk/practical-adhesion/

Lap shear method

- **Adhesive strength – Lap Shear (ASTM D1002)**



Plastic
Metal
Household
Organic



Queen Mary University of London

Rubber Consultants
TESTING • INNOVATION • SOLUTIONS
since 1984

Sugru
Mouldable Glues

BUREAU VERITAS 1828
BUREAU VERITAS

WMG
THE UNIVERSITY OF WARWICK

The University of Nottingham

intertek

External collaborations

Sugru
Mouldable Glues

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.

Plasticity

Hardness

Tensile strength

Rheology

Reactivity of the system

Stability of the system

Chain polymer length

Tackiness

Working time

Cure depth

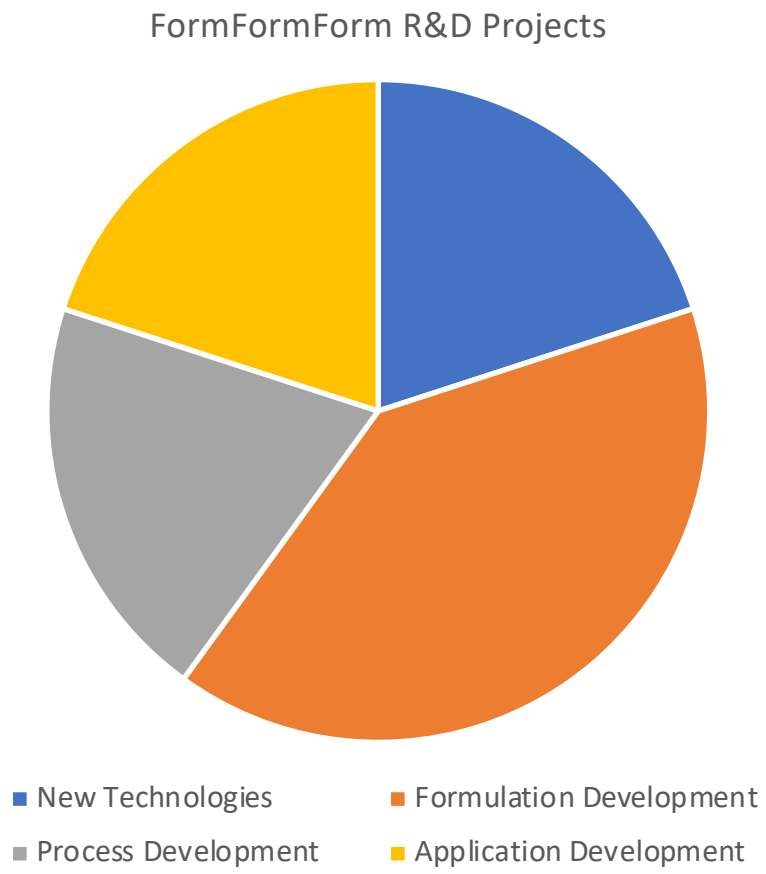
Adhesion

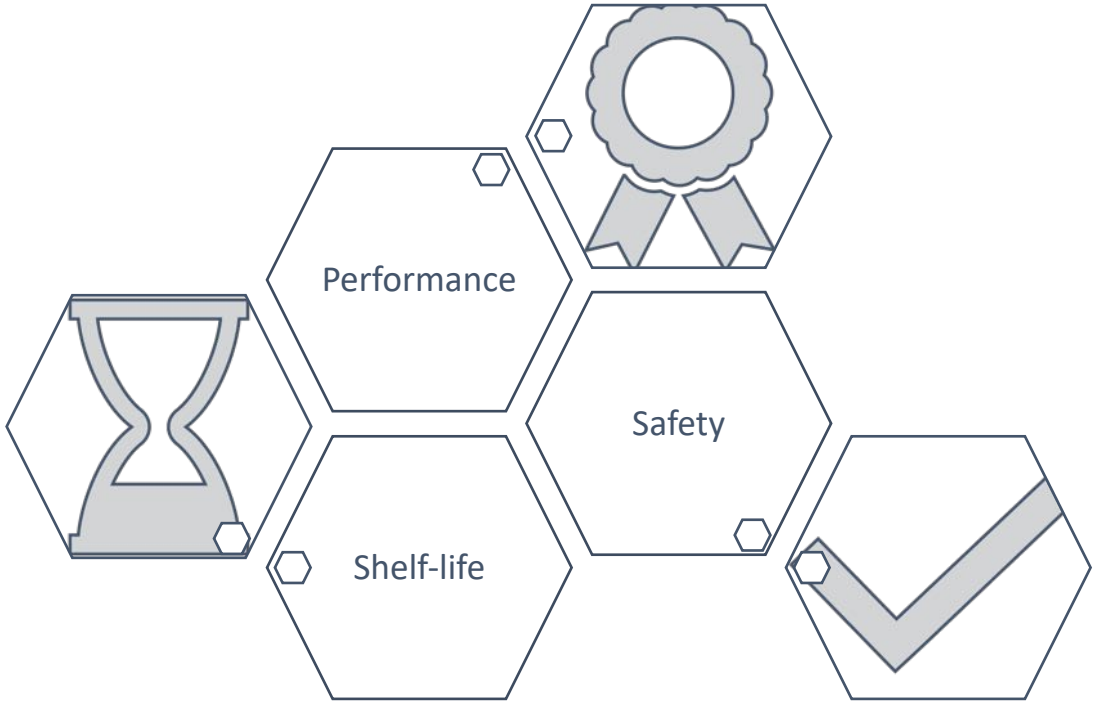
Important property for new formulations.

Adhesion & Cohesion Start with Tangles

Sugru - Excellent bonding to various organic and inorganic substrates

Future work in FormFormForm R&D





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Thanks for listening!

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Senior Formulation Chemist

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