Towards Better Adhesive Design – Using Scientific Tools

DMA, the Luth-Burgers Model & DoE

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Afera

7th Afera Technical Seminar

Arizona CHEMICAL

Brussels, 13-15 April 2015

AZC - Our global map

- Production sites
- Sales, trading and representative offices
- Executive offices
- Science and Technology centers

Largest Producer of Pine Chemicals

- **Largest Producer of Pine Chemicals**
  - **Hold 50% global capacity of crude tall oil production at 800,000 tons/year**
- **World class manufacturing facilities and practices**
  - **Favorable carbon footprint balance**
    - **Products range from 50-99% Bio-renewable content**
  - **75% fewer CO2 emissions than oil-based substitutes**
- **Committed to continuous improvement**
  - **ISO 14001**
  - **ISO 9000**
  - **OHSAS 18001**
  - **Responsible Care Program**

Raw materials for Adhesives


Case & Carton Sealing


Non-Wovens


PSA Tape & Labels


Building & Construction

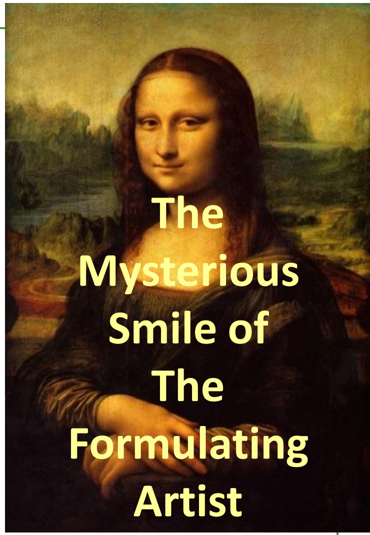

Transportation


Bookbinding


Product Assembly


Wood Assembly

Key Challenges in Adhesive Design



- Current adhesive design is an art
  - Formulations may become *overly complex*
    - Too many "critical" raw materials
  - Development is *time-consuming*
    - With too often a dead-end road taken
  - Depending on the *experience* of a few
    - Not sustainable
  - Inability to adapt (quickly) to new technologies when they appear

Adhesives – improving by using a model

Step 1

- **Creating a model of PSA action**
  - **shows the action(s) of the components**
- **Components *interact***

Step 2

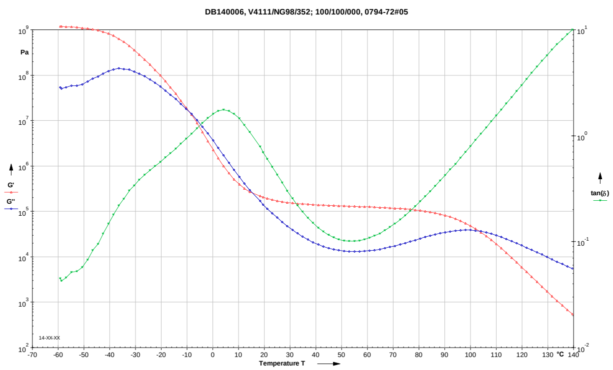
- **Map the *non-linear* interactions: DoE**

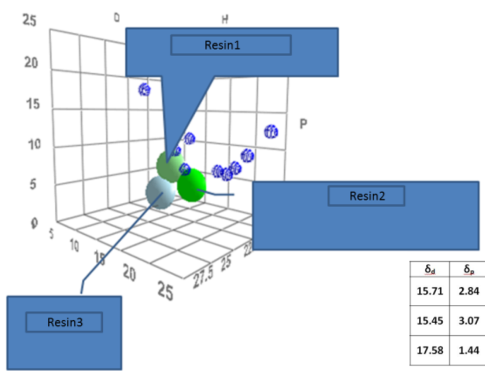
Step 3

- **Create model for formulation**

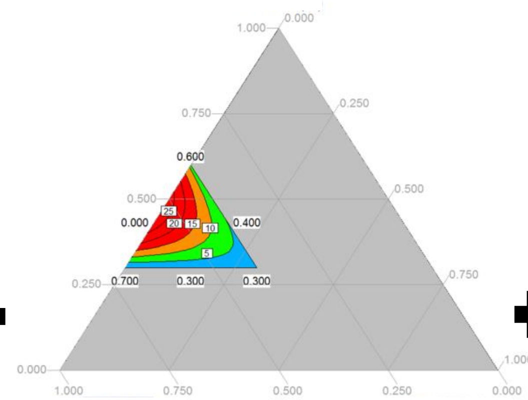
Adhesive Model Building – in pictures

DMA, HSP ➕ **DoE** ➕ **Application Data**

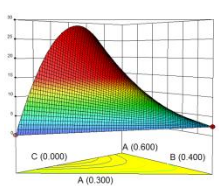


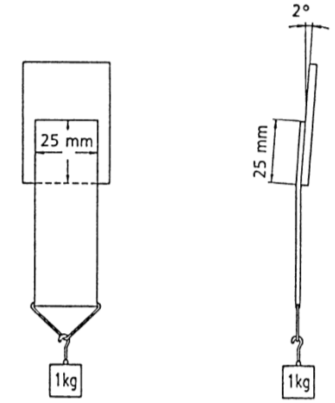


δ_d	δ_p	δ_h	Radius	Resin Type
15.71	2.84	7.89	8.5	Rosin ester
15.45	3.07	8.78	9.5	Terpene phenol
17.58	1.44	3.36	6.5	Polyterpene



180o Peel 20min SS (N)





What is a PSA?

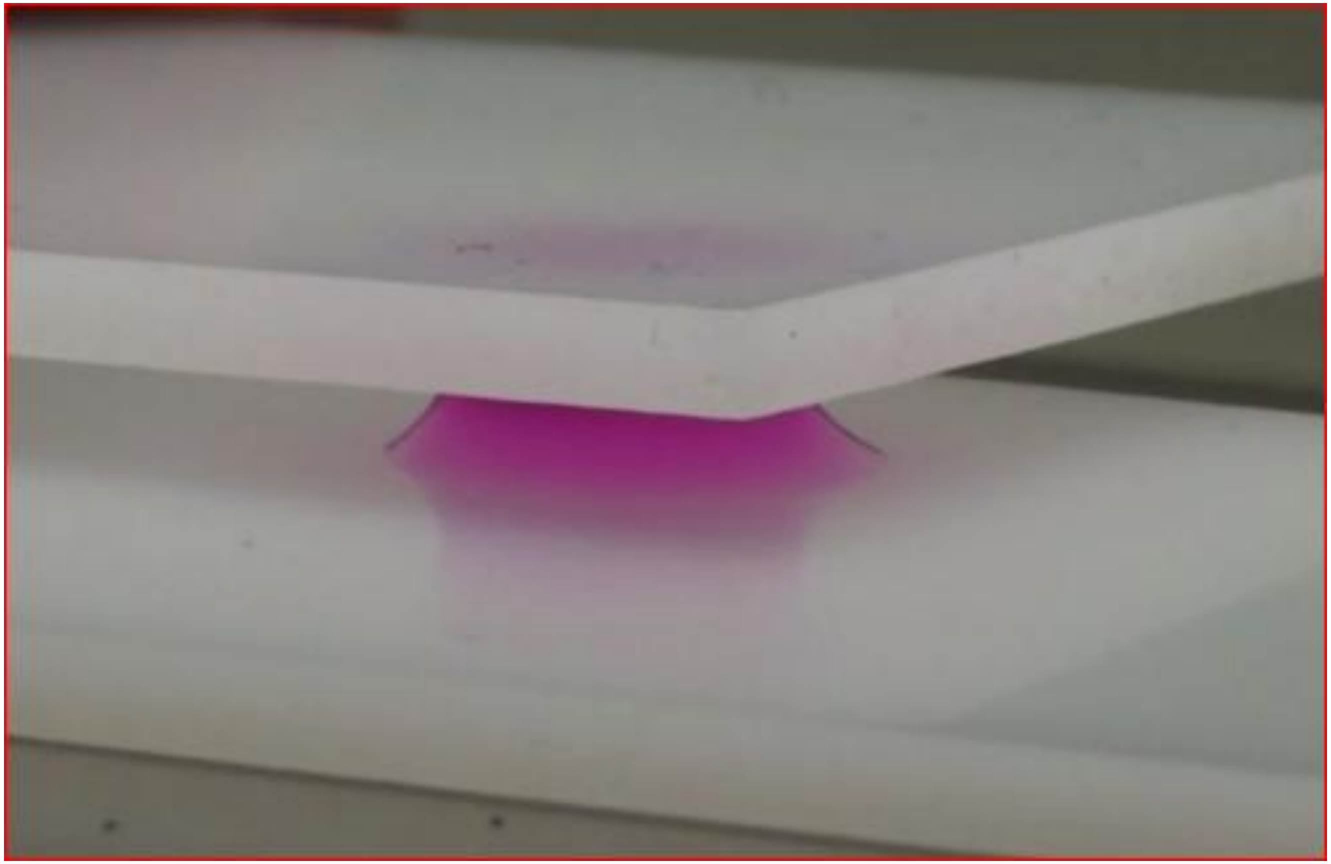
- **PSA's**
  - **are materials that are aggressively and permanently tacky at room temperature and that firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure**

- **Hypothesis:**

Adhesion is less of a *surface phenomenon,* much more a *bulk material property*

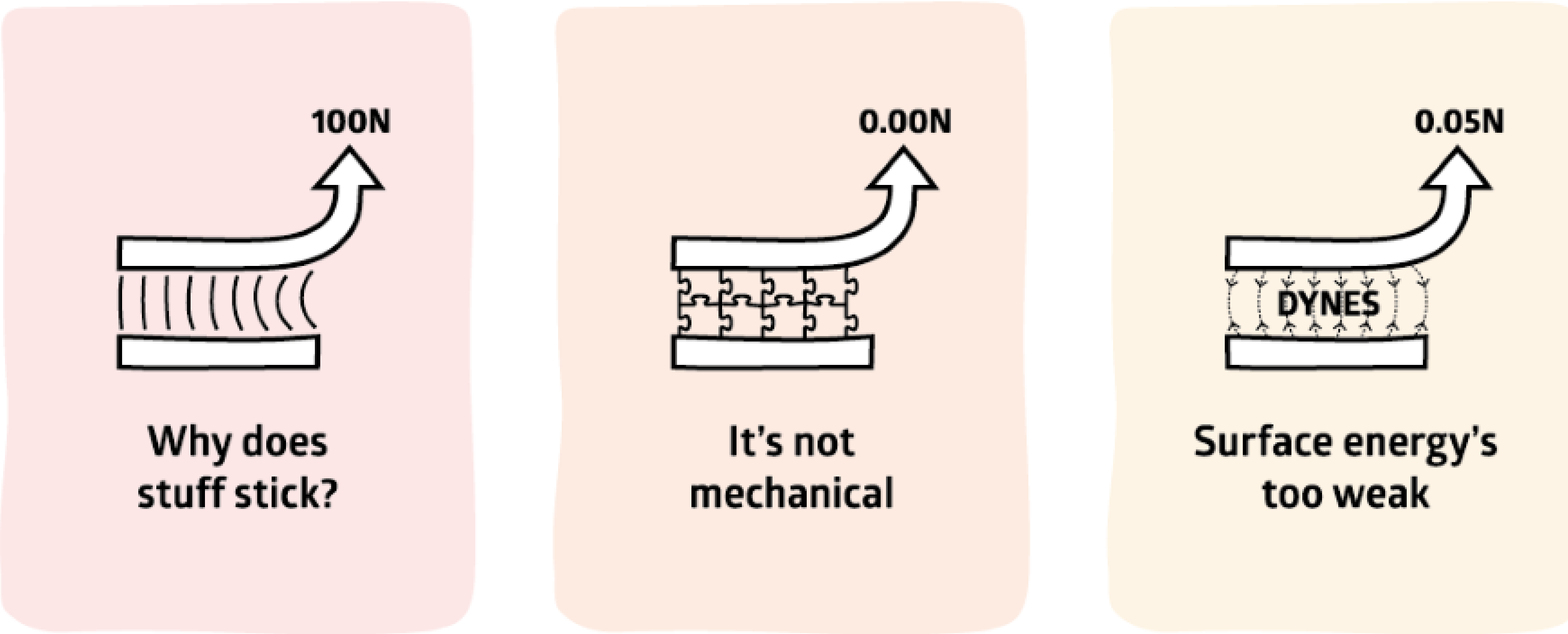
Look what happens:

Reconsidering old truths…



Water will *spontaneously* wet PE ……

Adhering - in pictures



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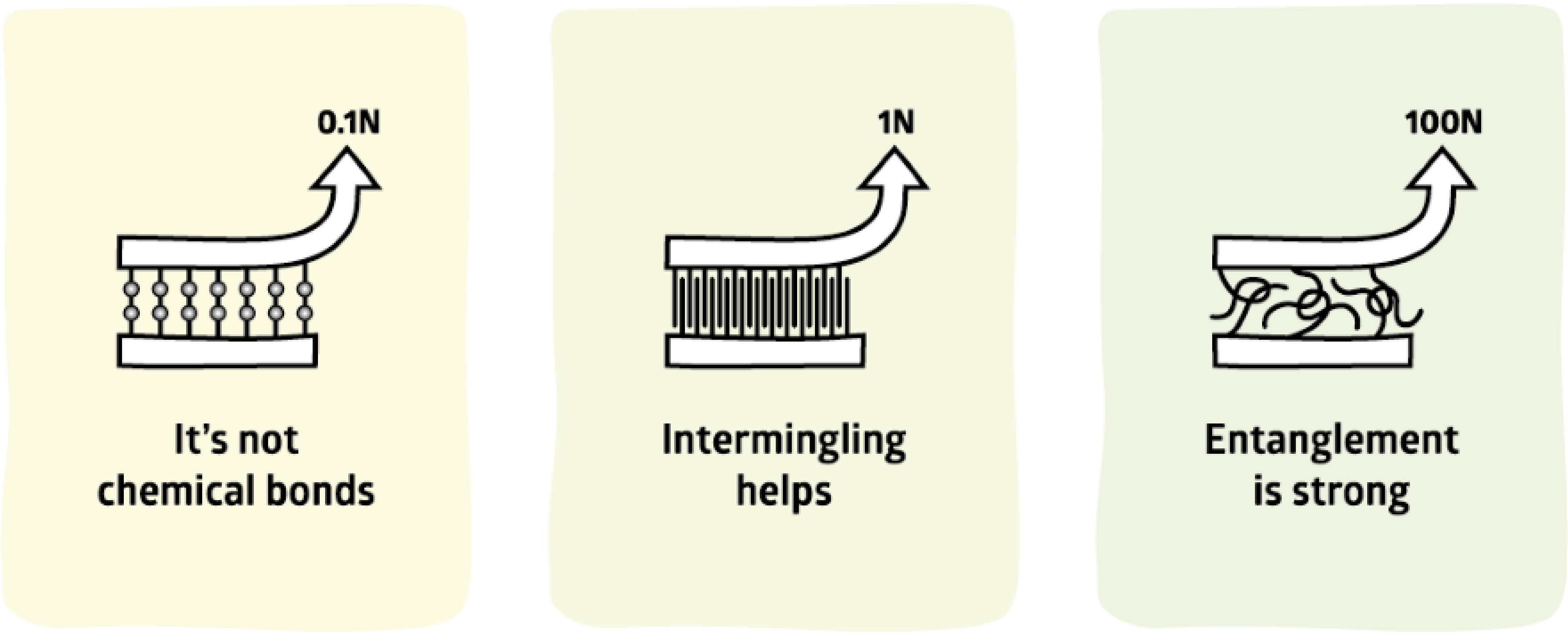
Adhering - in pictures



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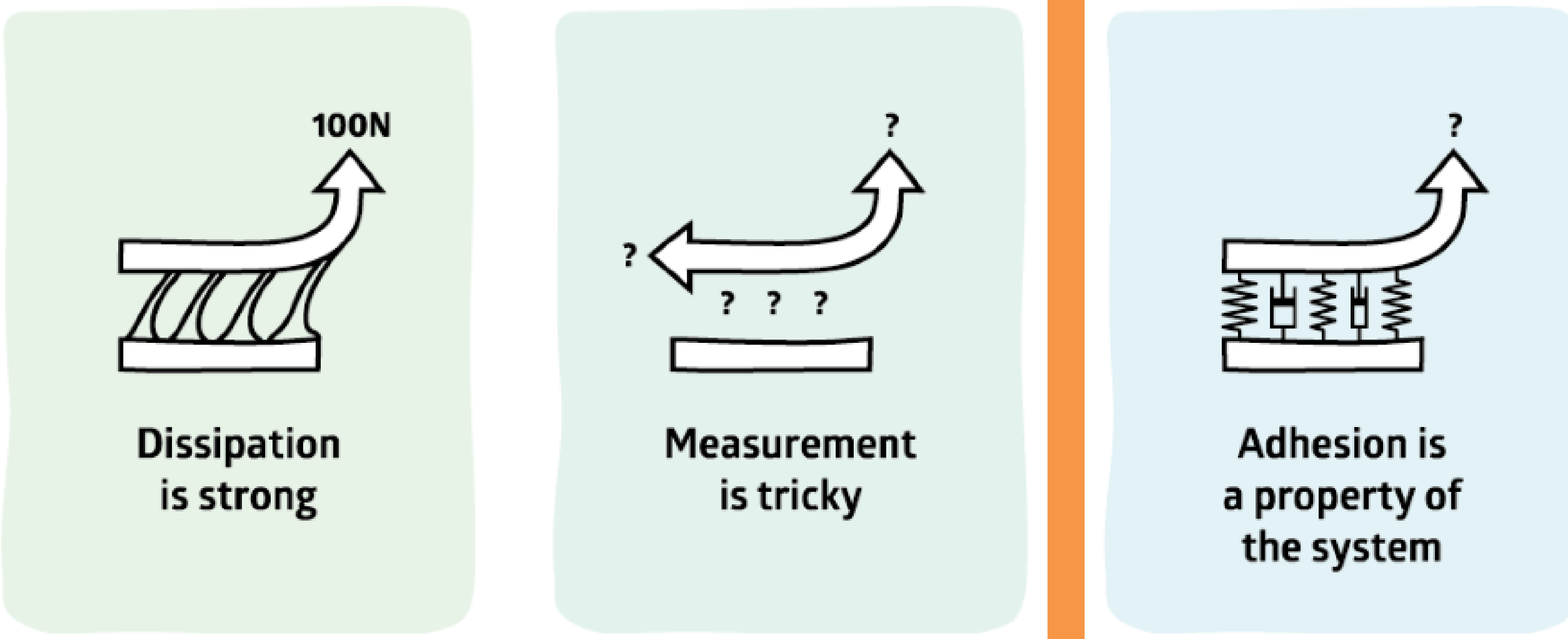
Adhering - in pictures



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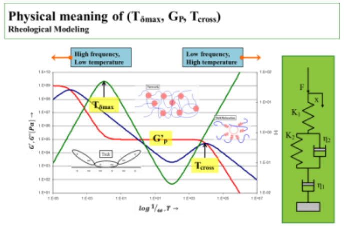
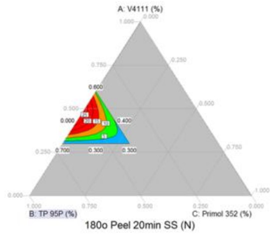
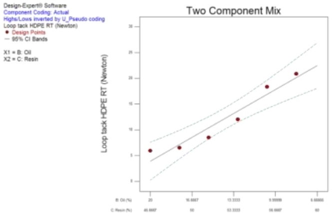
Modelling of Pressure Sensitive Adhesives using DMA

- Old adage “adhesion is a surface phenomenon” is not valid
  - Need to study **bulk** properties as well
- DMA viscoelastic profiles:
  - Study, explain & *predict* PSA behaviour
- *Ultimately: facilitate more intelligent formulation*

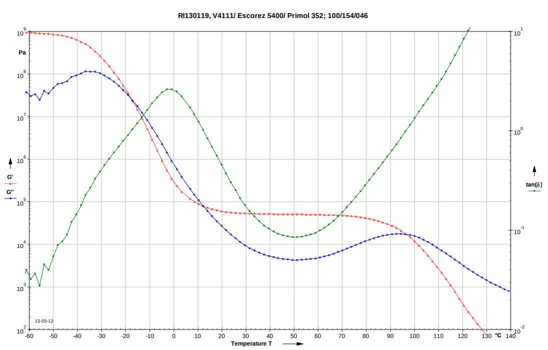


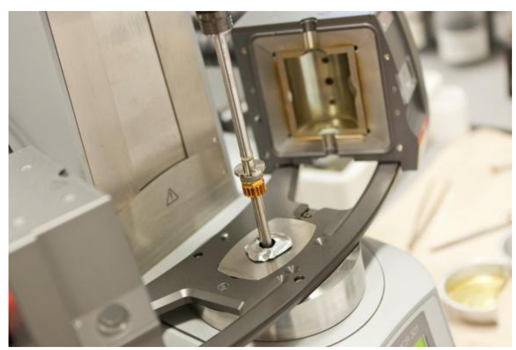




The principle and result
Dynamic Mechanical Analysis

- **What is Dynamic Mechanical Analysis?**
  - **For a start it is:**
- ***"An Accurate Way of Feeling"***

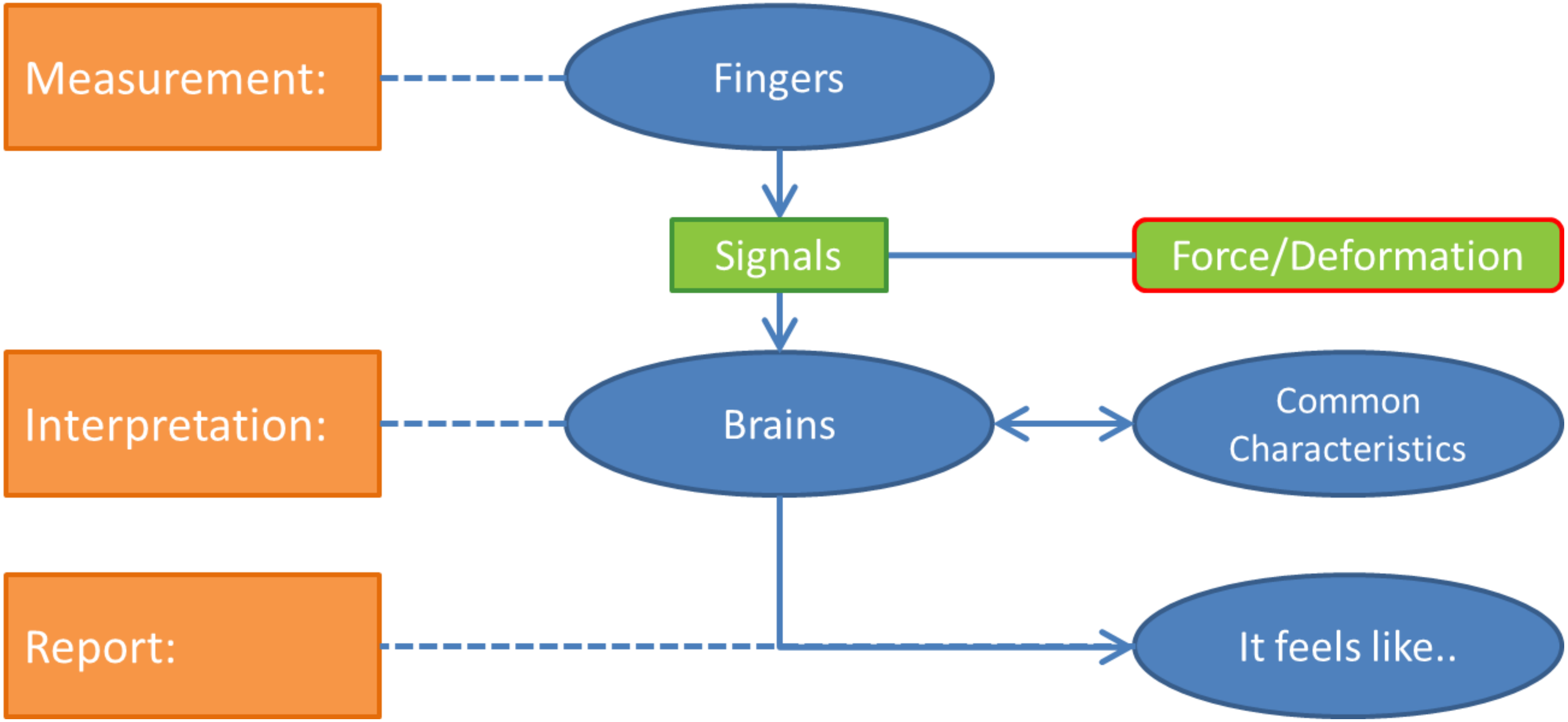




The principle and result

Dynamic Mechanical Analysis

The feeling process



The principle and result

Dynamic Mechanical Analysis

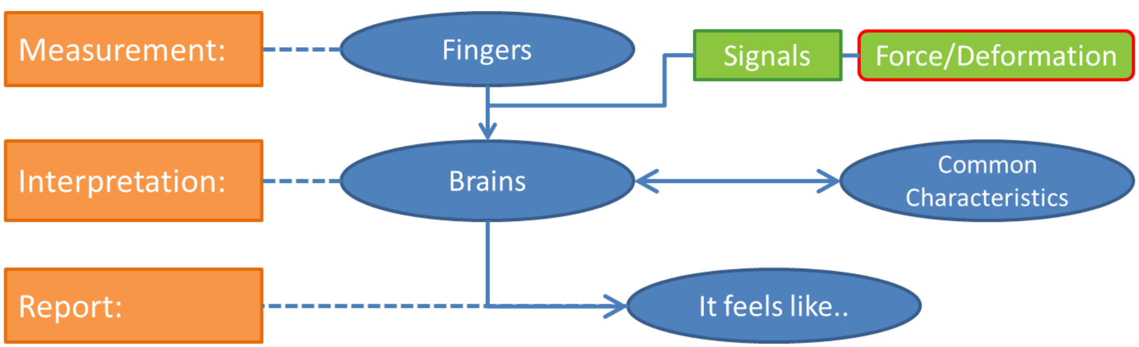
Rheology (definition)

Rheos, (ῥέος) =flow of matter

The study of the relation between forces active in a material and the thereby induced deformations

(includes flow as well).

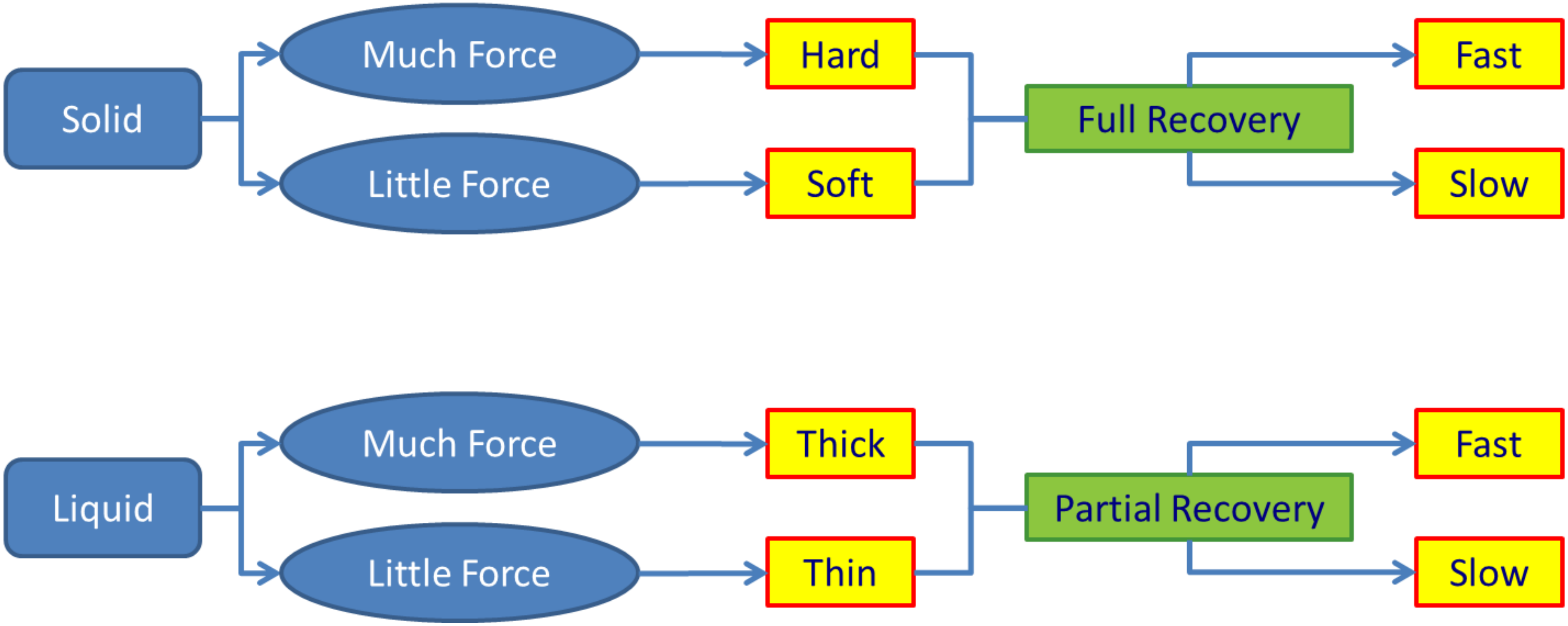
"Feeling is doing Rheology"



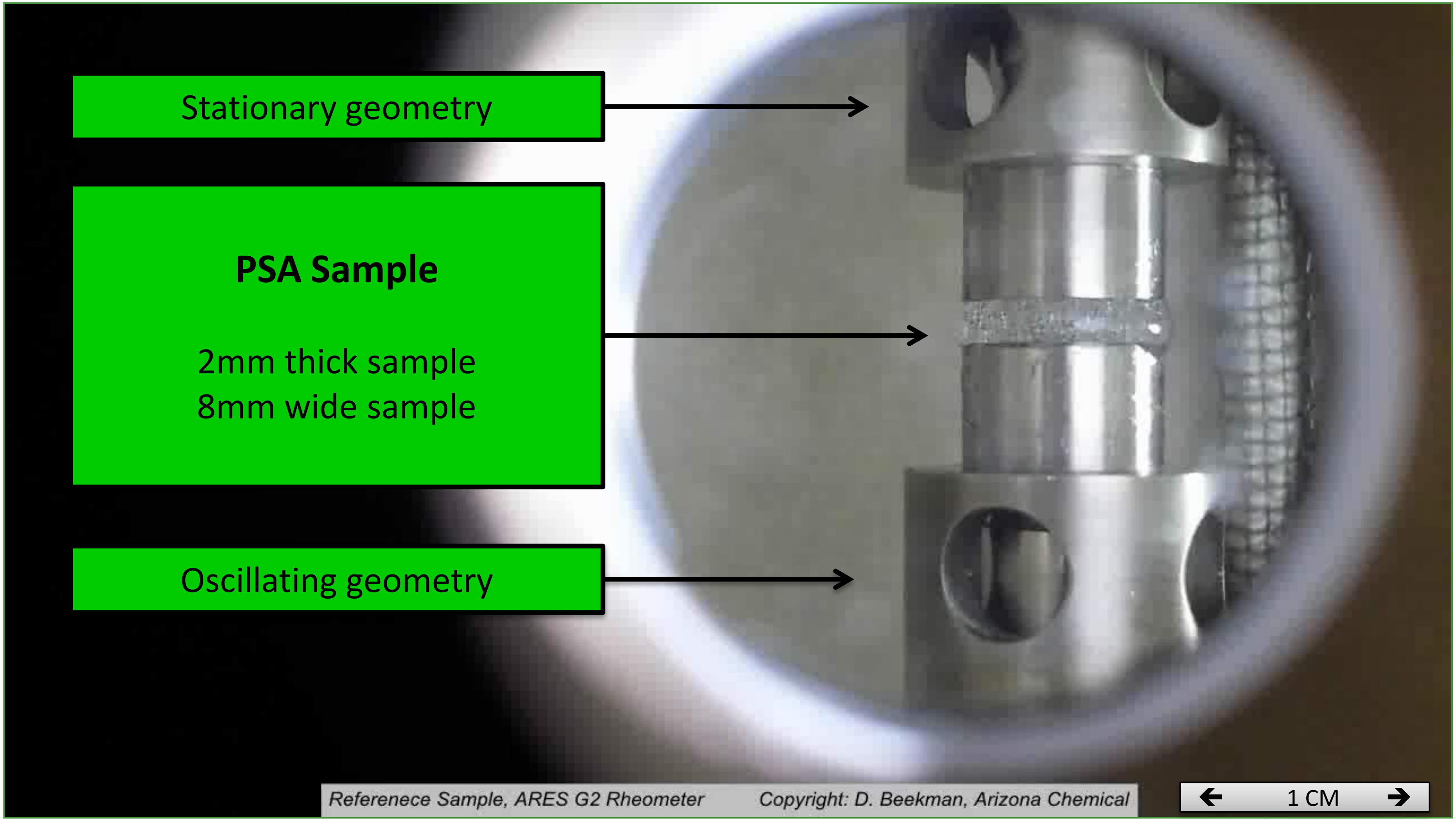
The principle and result

Dynamic Mechanical Analysis

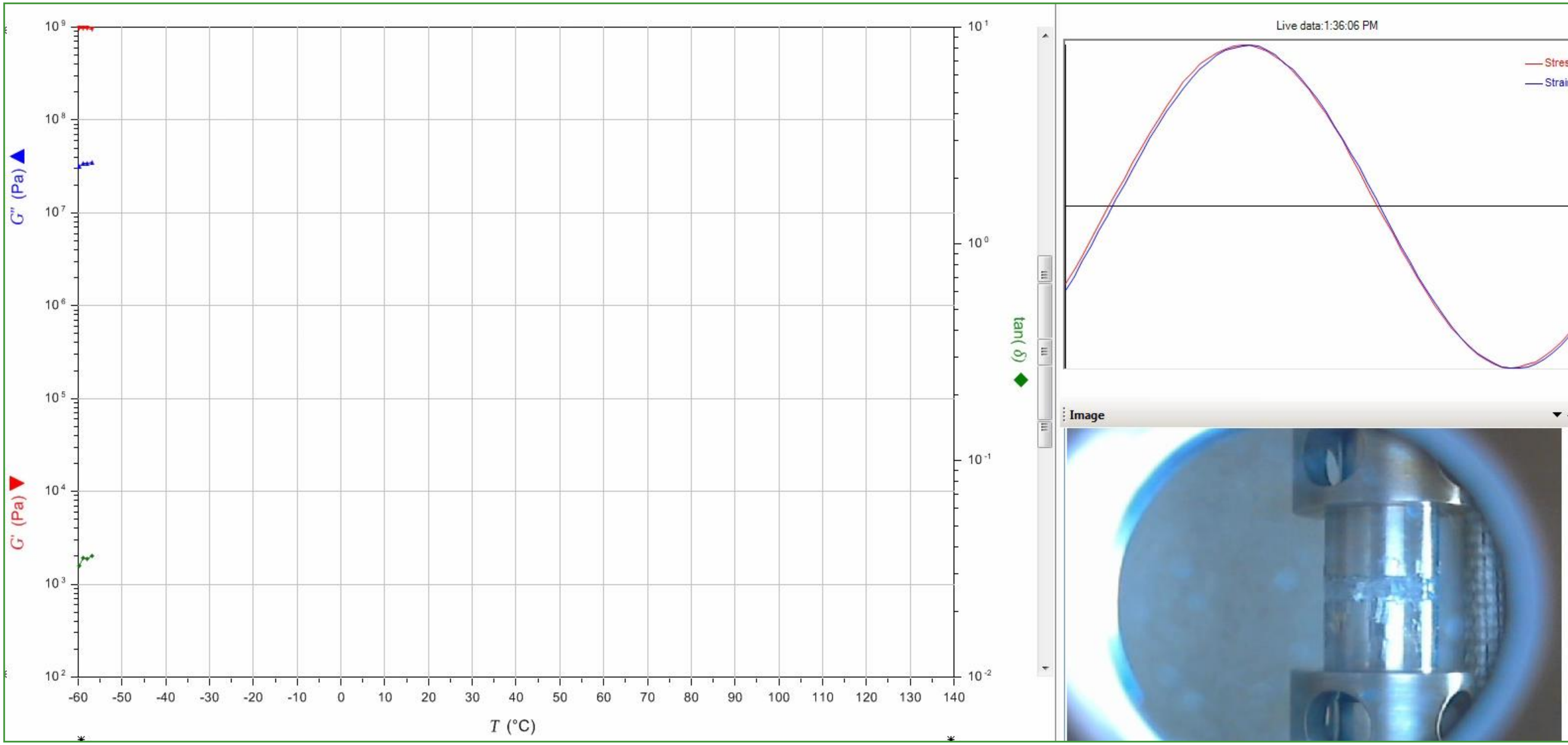
Distinctions by feeling



DMA – how does the machine *feel* ?



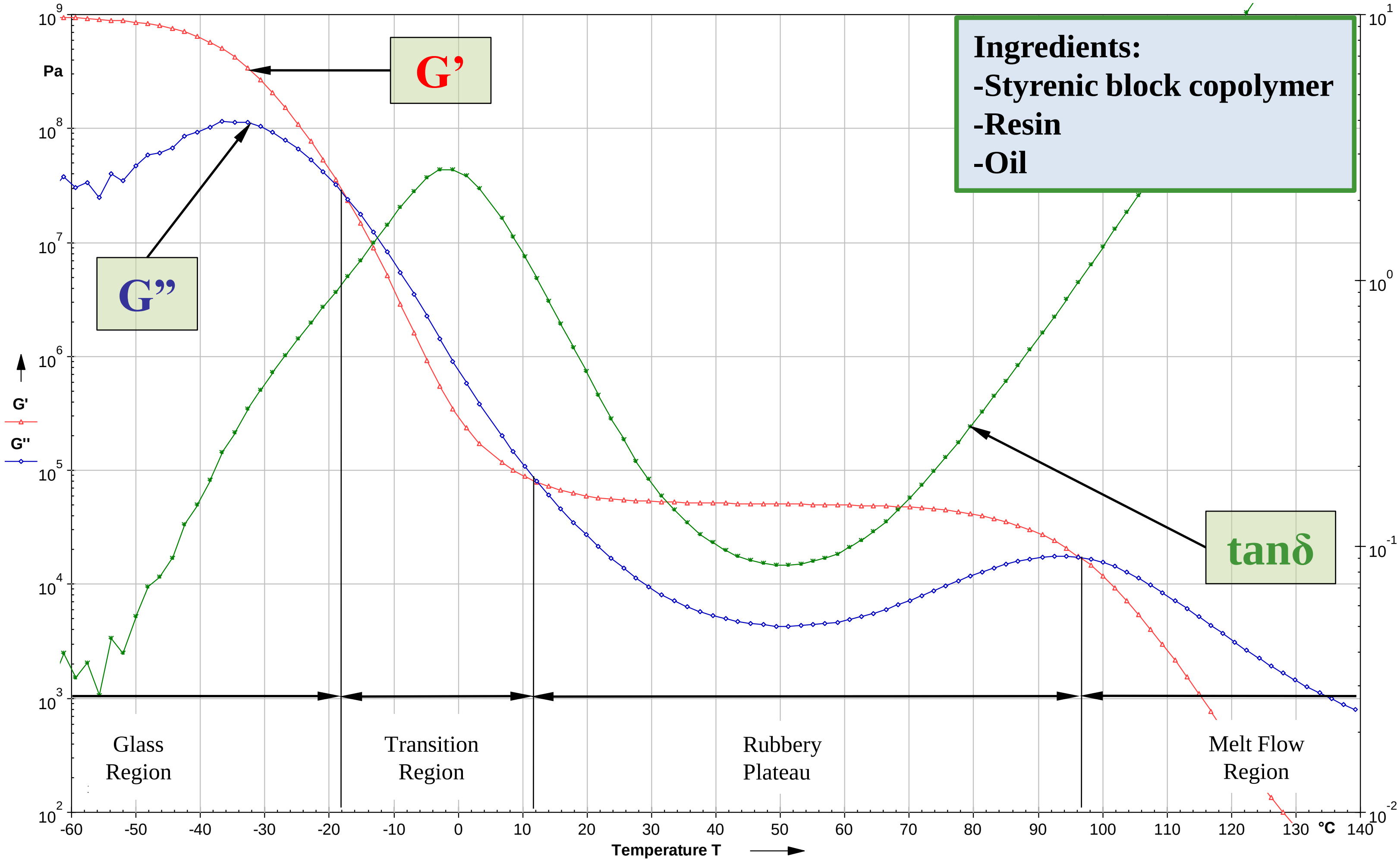
DMA – Measurement (50x real time)



Connection to Reality

Dynamic Mechanical Analysis

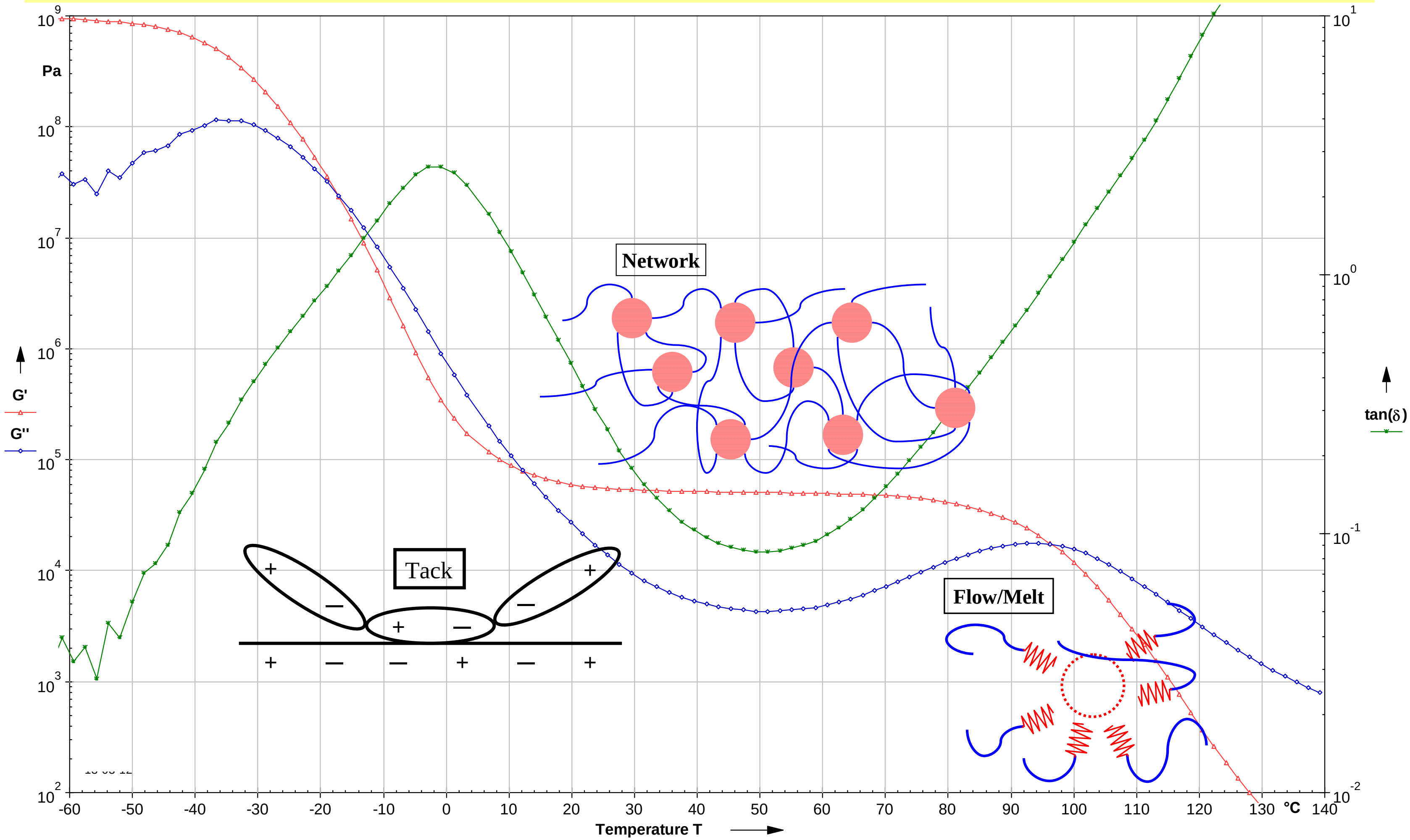
Typical viscoelastic response of a "real Hot Melt Pressure Sensitive Adhesive system"



Connection to Reality

Dynamic Mechanical Analysis

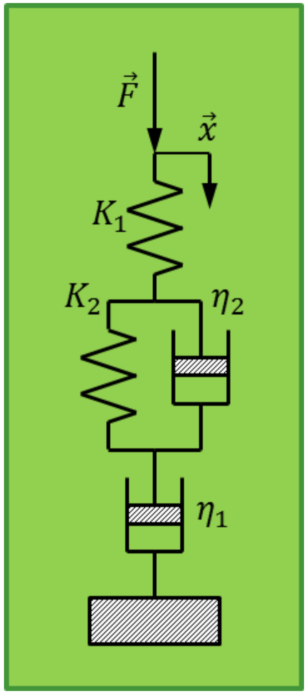
Typical areas related to HMPSA characteristics

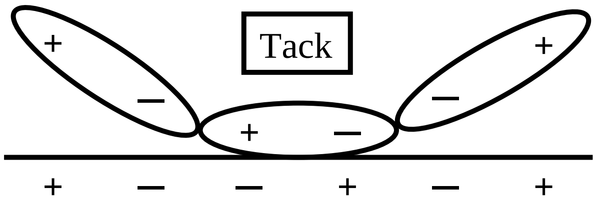


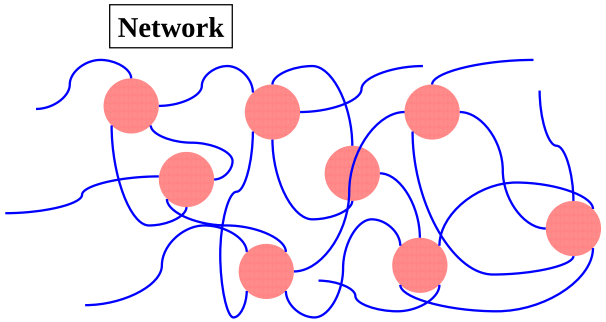
Ideal (HM)PSA / Key Parameters

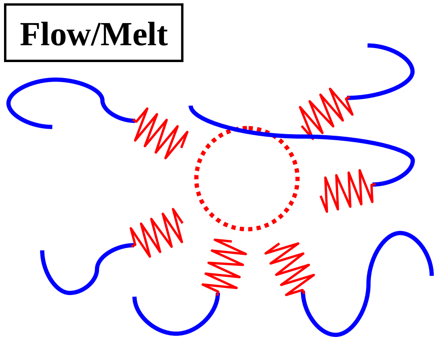
Dynamic Mechanical Analysis

- **An SIS/Resin/Oil blend.**
  - **Hard Styrenic domains connected by elastic isoprenic midblocks; K_2**
  - **Local resin has temperature dependent damping effect on movement K_2; η_2//K_2**
  - **Free flow at high temperature; η_1**
  - **Glassy at very low temp.; K_1**
- **Model is known as the "Burgers model"**



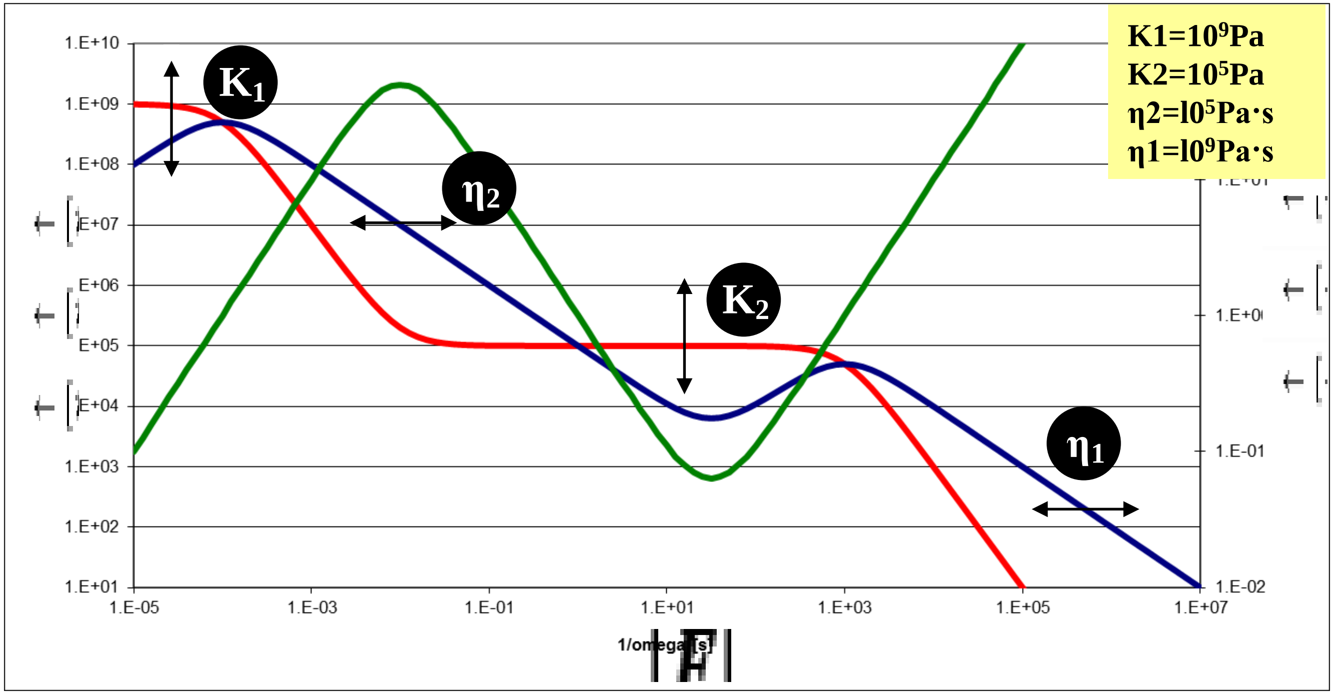


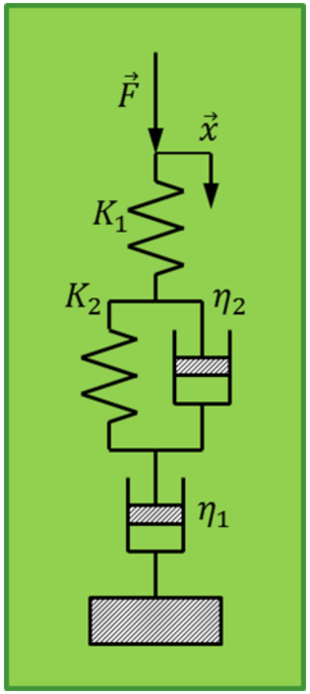




Ideal HMPSA / Key Parameters

The Luth-Burgers PSA Model





$$\frac{F}{x} = 1/\left(\frac{1}{K_1} + \frac{1}{K_2 + j\omega\eta_2} + \frac{1}{j\omega\eta_1}\right) =$$

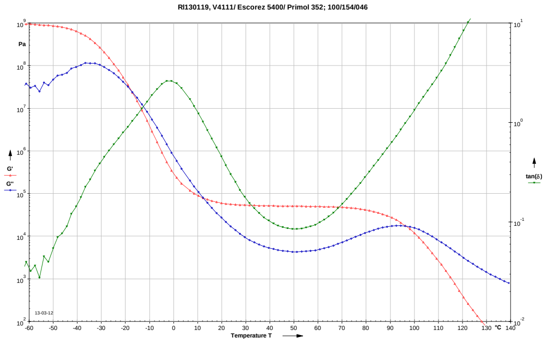
$$\frac{-\omega^2\eta_2\eta_1K_1 + j\omega\eta_1K_1K_2}{(K_1K_2 - \omega^2\eta_1\eta_2) + j\omega(\eta_1(K_1+K_2) + \eta_2K_1)} =$$

$$\frac{A + jB}{C + jD} = \left(\frac{AC + BD}{C^2 + D^2}\right) + j\left(\frac{-AD + BC}{C^2 + D^2}\right) = G' + jG''$$

Facts:

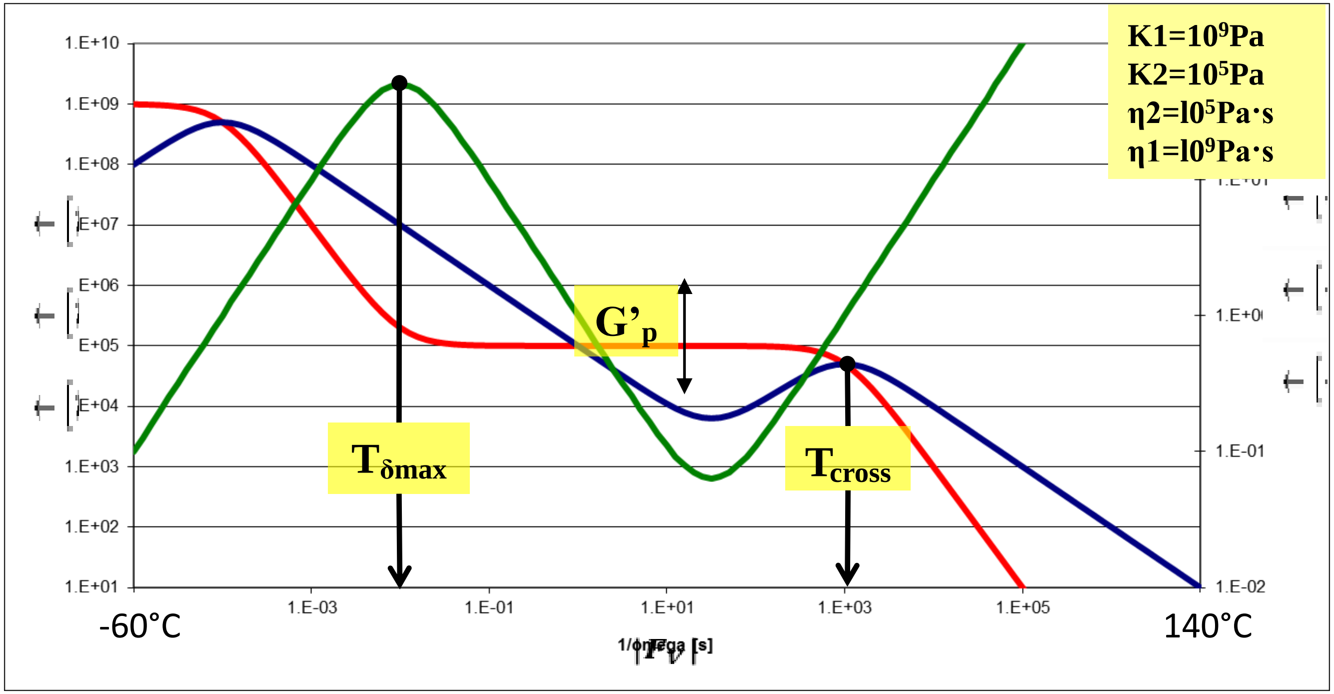
Fixed values for K_1, K_2, η_1, η_2, represent an unique viscoelastic profile.

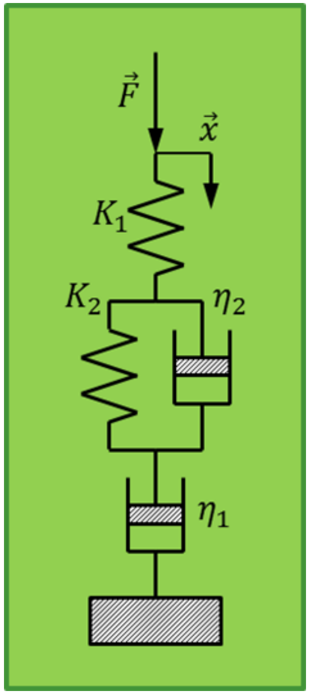
G'(ω) and G" (ω) @ T=const.;
Introducing temperature dependent dashpots will result in G'(T) and G"(T)



Ideal HMPSA / Key Parameters

The Luth-Burgers PSA Model





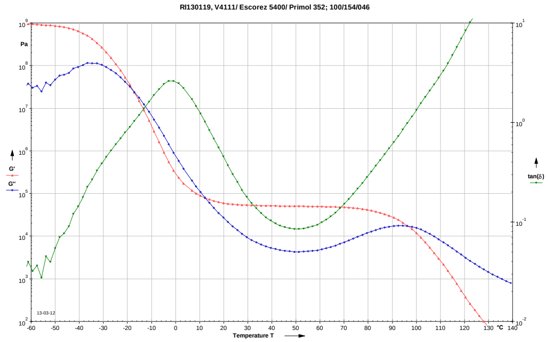
$$\frac{F}{x} = 1/\left(\frac{1}{K_1} + \frac{1}{K_2 + j\omega\eta_2} + \frac{1}{j\omega\eta_1}\right) =$$

$$\frac{-\omega^2\eta_2\eta_1K_1 + j\omega\eta_1K_1K_2}{(K_1K_2 - \omega^2\eta_1\eta_2) + j\omega(\eta_1(K_1+K_2) + \eta_2K_1)} =$$

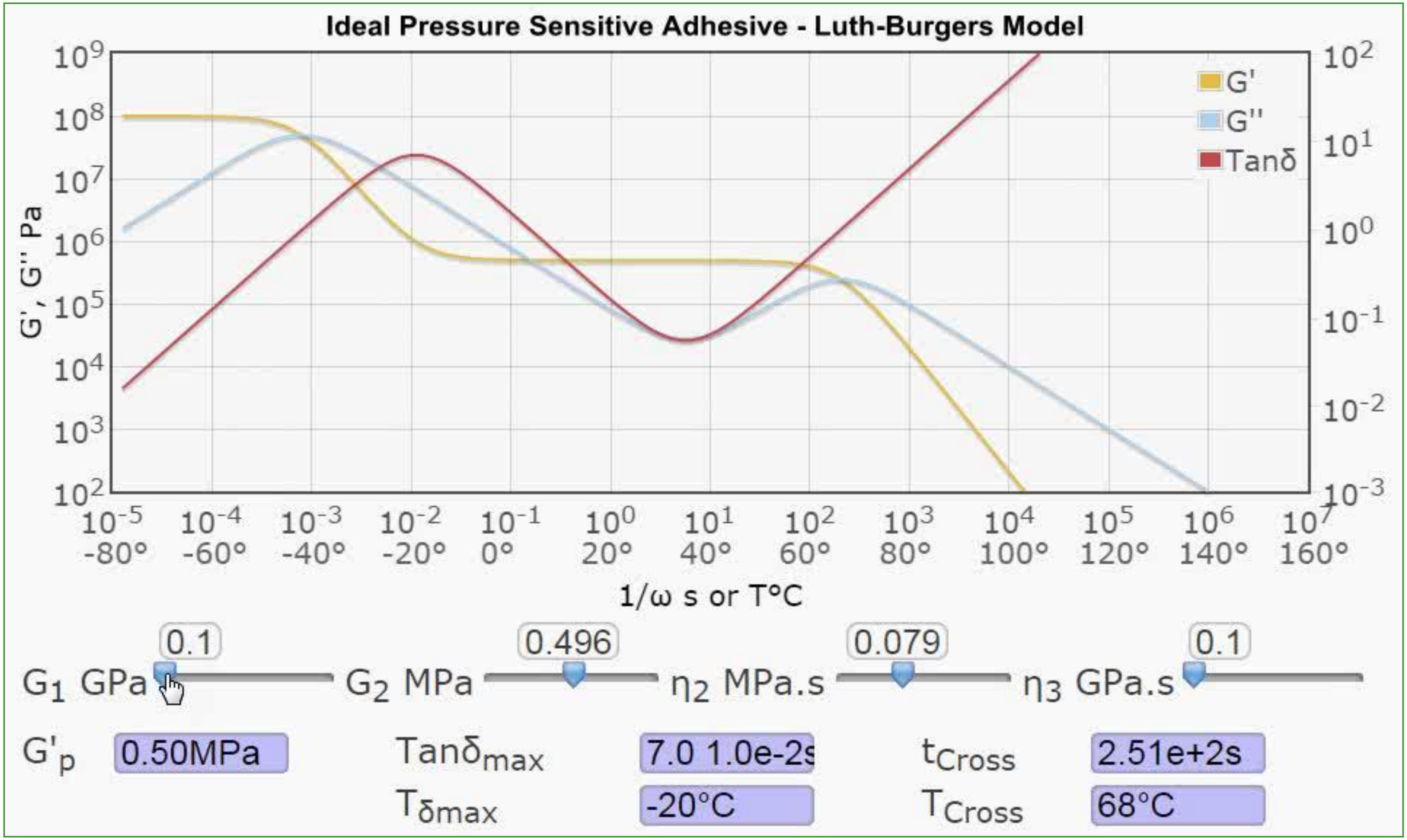
$$\frac{A + jB}{C + jD} = \left(\frac{AC + BD}{C^2 + D^2}\right) + j\left(\frac{-AD + BC}{C^2 + D^2}\right) = G' + jG''$$

Facts:

{(-), $T_{\delta max}$, G'_p, T_{cross}}; {(K1), K2, η1, η2}
Temp. sweep; η(T) η=$\eta_0$exp{-A(T-T_{ref})}.
i.e varying "log1/ω" or "T" will result, apart from a scaling factor, in a similar viscoelastic profile {WLF TTS}.



Interactive version of the
Luth-Burgers PSA model (Now available on the internet!)



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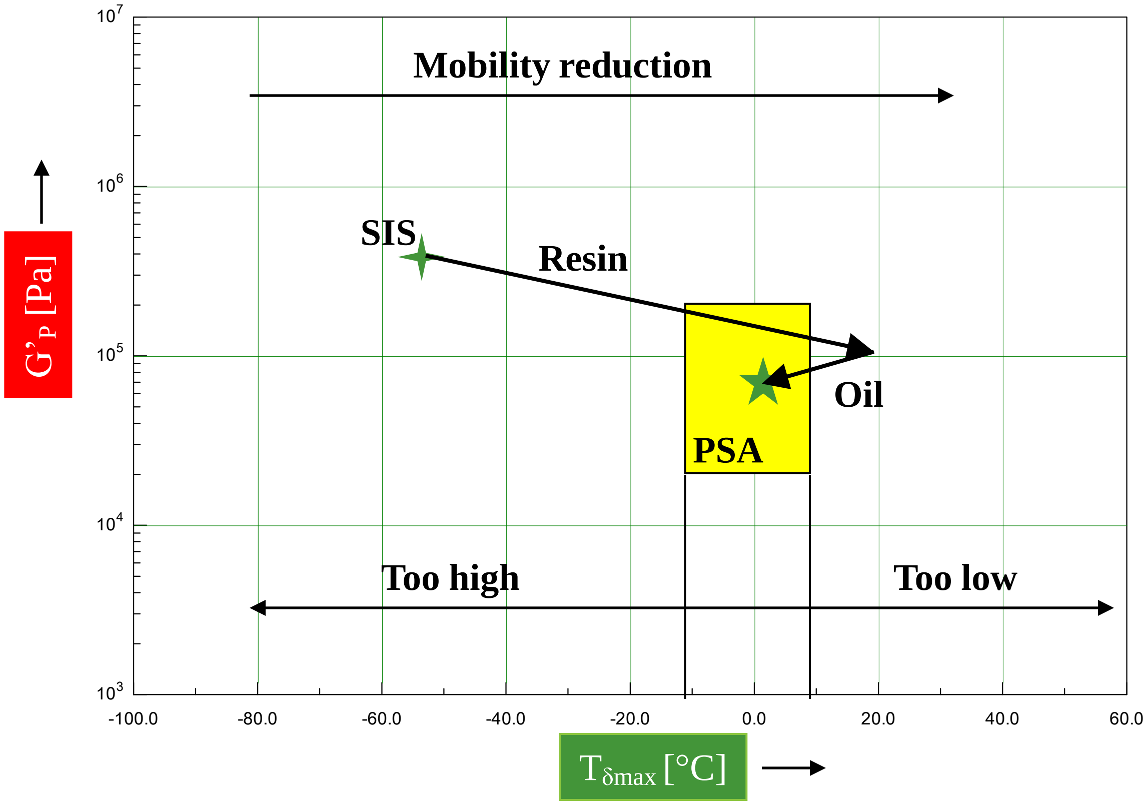
Ideal HMPSA/ Key Parameters

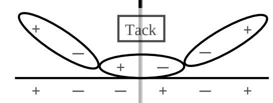
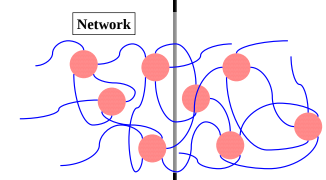
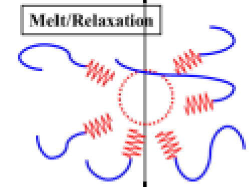
Dynamic Mechanical Analysis

Dahlquist !

Tack and Cohesion / Adhesion balance

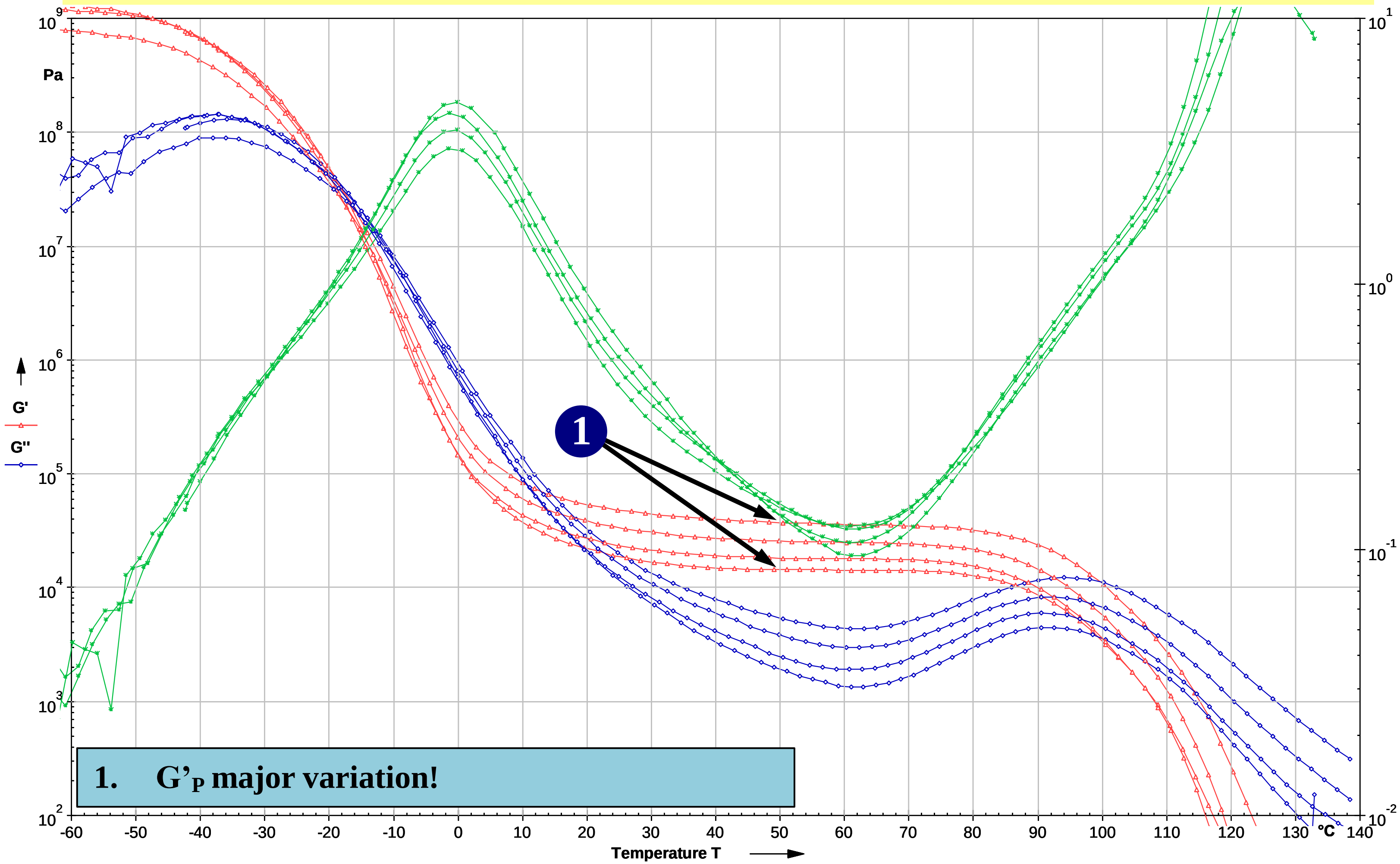


Summary: Ideal HMPSA/ Key Parameters
The Luth-Burgers PSA Model

	Adhesive property	"Burgers model"	"DMA control"
Glassy	Glassy	$K_1 \cong 10^9\ Pa$	$Const.$
Mobility/Fast processes	Tack/ Recovery	η_2 	$T_{\delta max}^{(*)}$
Strength/ Hardness	Cohesion/Adhesion balance	K_2 	$G'_P{}^{(*)}$
Melt Viscosity	Creep/ Relaxation/ Melting temp.	η_1 	T_{cross}

Example A: varying (just) G'$_P$

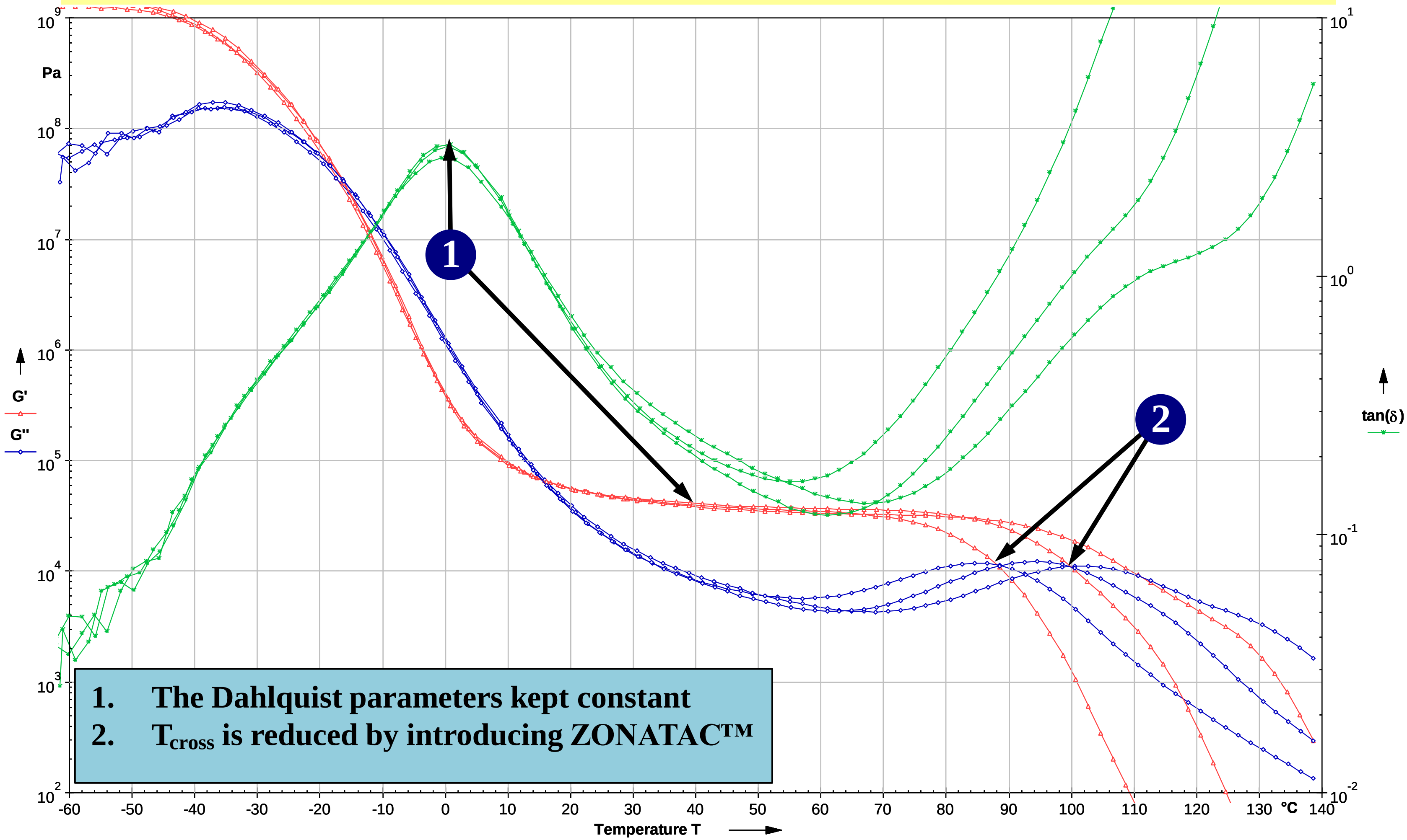
SIS/SYLVAGUM™ TR 90 /ZONATAC™ NG98 /Oil



1. G'$_P$ major variation!

Example B: varying (just) T_{cross}

SIS/SYLVAGUM™ TR 90 /ZONATAC™ NG98 /Oil

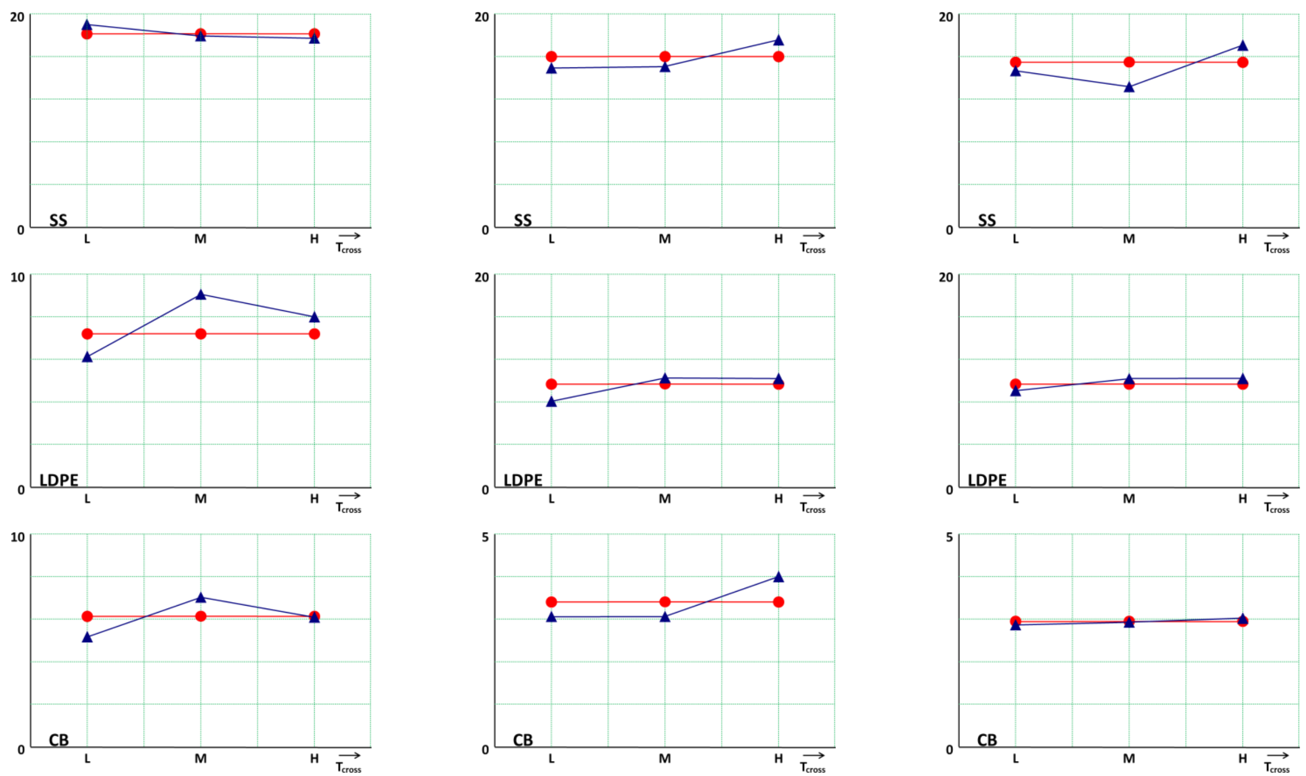


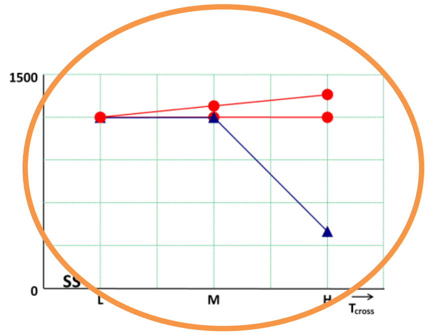
1. The Dahlquist parameters kept constant
2. T_{cross} is reduced by introducing ZONATAC™

Relating model expectations to actual values

“Outliers” well identified - deeper study

Looptack | **Peel 180° / 20 min** | **Peel 180° / 24hr** | **Shear @ 23°C**





Expected trend from Model

Actual Data

Tcross controls slow processes;
Loop tack and Peel constant
Shear: no decrease

Taking to the next level

Why measuring everything on all samples was outdated in 1920.

"Early in the 20th century it was proven that changing one factor at a time does not necessarily provide information about the optimum conditions"(1).

Let's take a smarter path, limiting the amount of experiments and using smart tools to get the most valuable data.

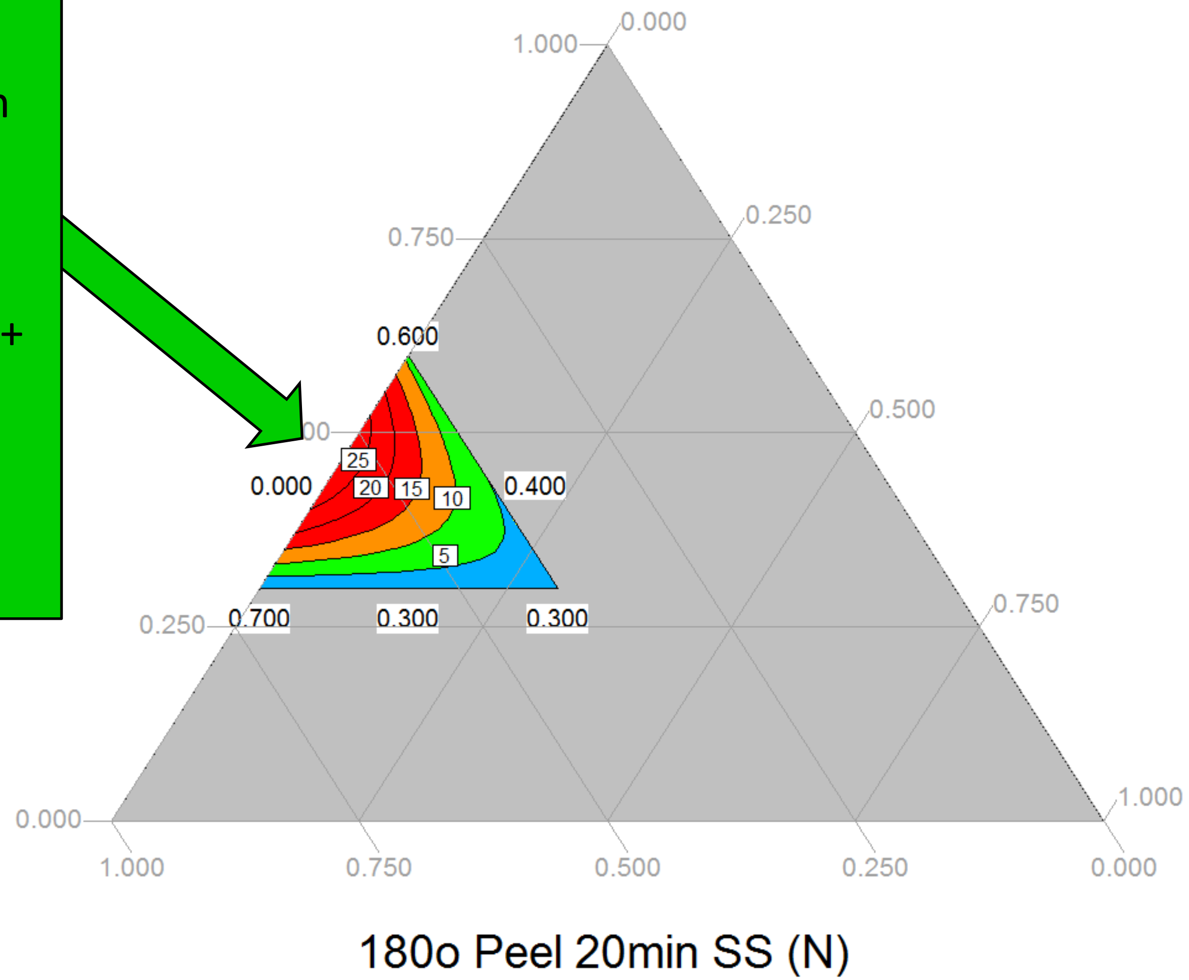
(1). Design of Experiments Principles and application – Page 3 – UMETRICS ACADEMY - 2008

Formulation influence: adhesive properties

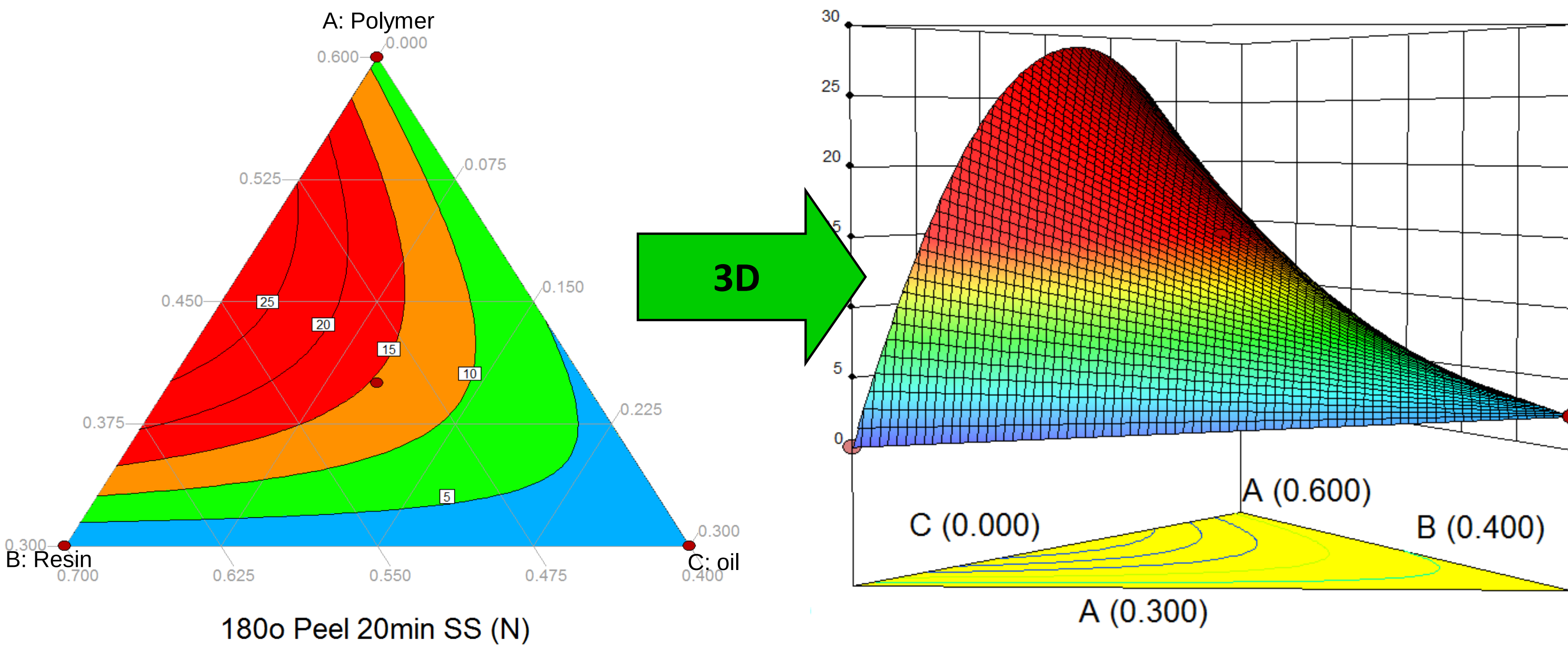
Focus area

Real application data on formulations

- Loop Tack SS
- 180° Peel SS (20min + 24hr)
- ….

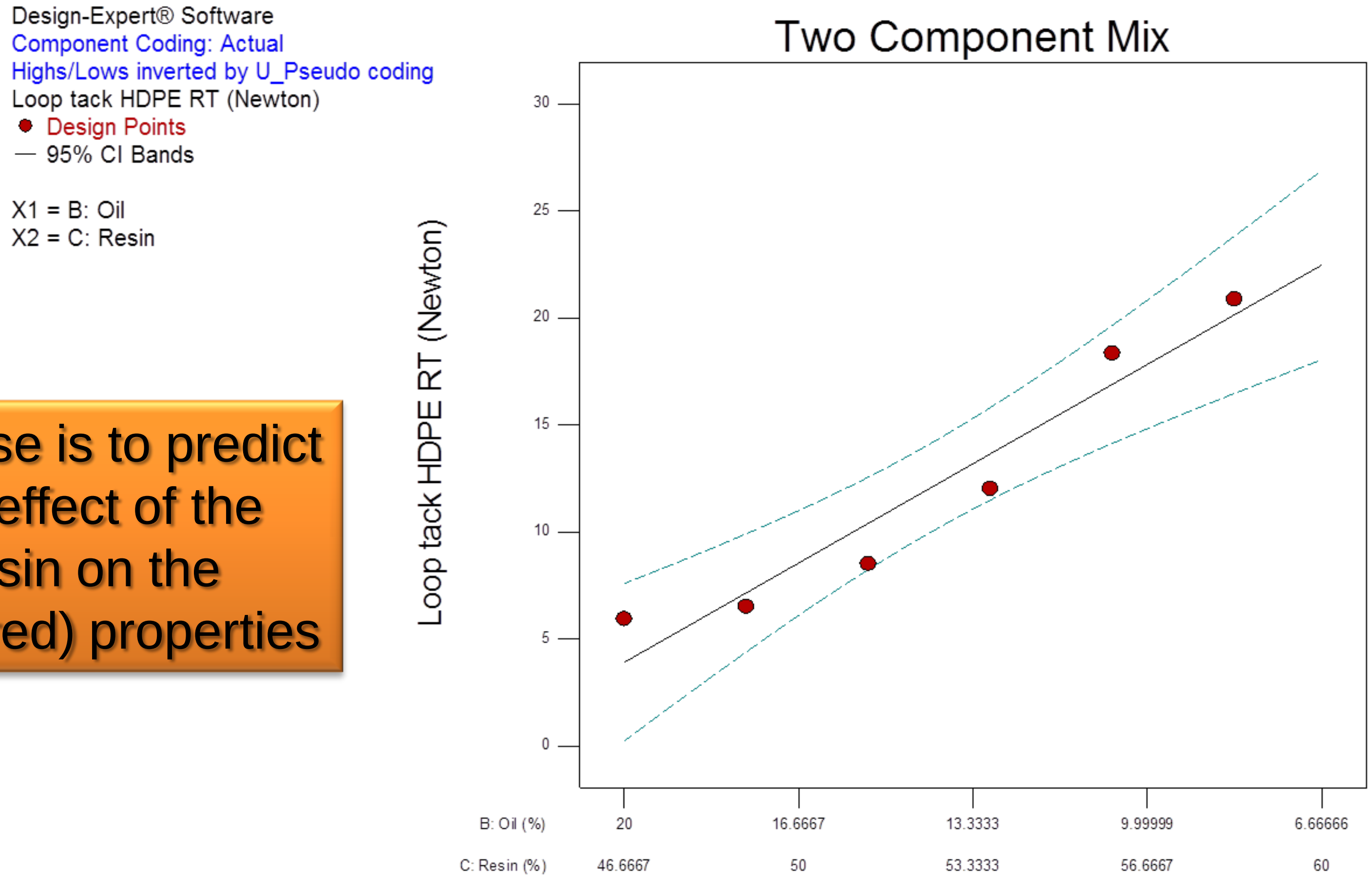


Formulation influence on Peel



Expanding to a DoE Model: prediction vs actual

Purpose is to predict the effect of the resin on the (required) properties



Conclusions

Modeling of Pressure Sensitive Adhesives

- **(SBC-HM) PSA systems and the *Burgers* model have matching viscoelastic profiles**
  - **Model defines the PSA key parameters.**
- **The *Luth-Burgers* DMA parameters:**
  - **Also describe real PSA systems**
  - **Allow a straightforward connection between viscoelastic and adhesive properties**
- **LB-Model is sound basis for step 2**
  - **(non-linear) interactions study using *DoE***
  - **Predicting performance**
- **Hypothesis: “adhesion is a bulk phenomenon” is *not* disproven**

Contact details

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  Roelof Luth (roelof.luth@azchem.com)

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