New Ideas. New Materials.

UNIVERSITÄT DES SAARLANDES

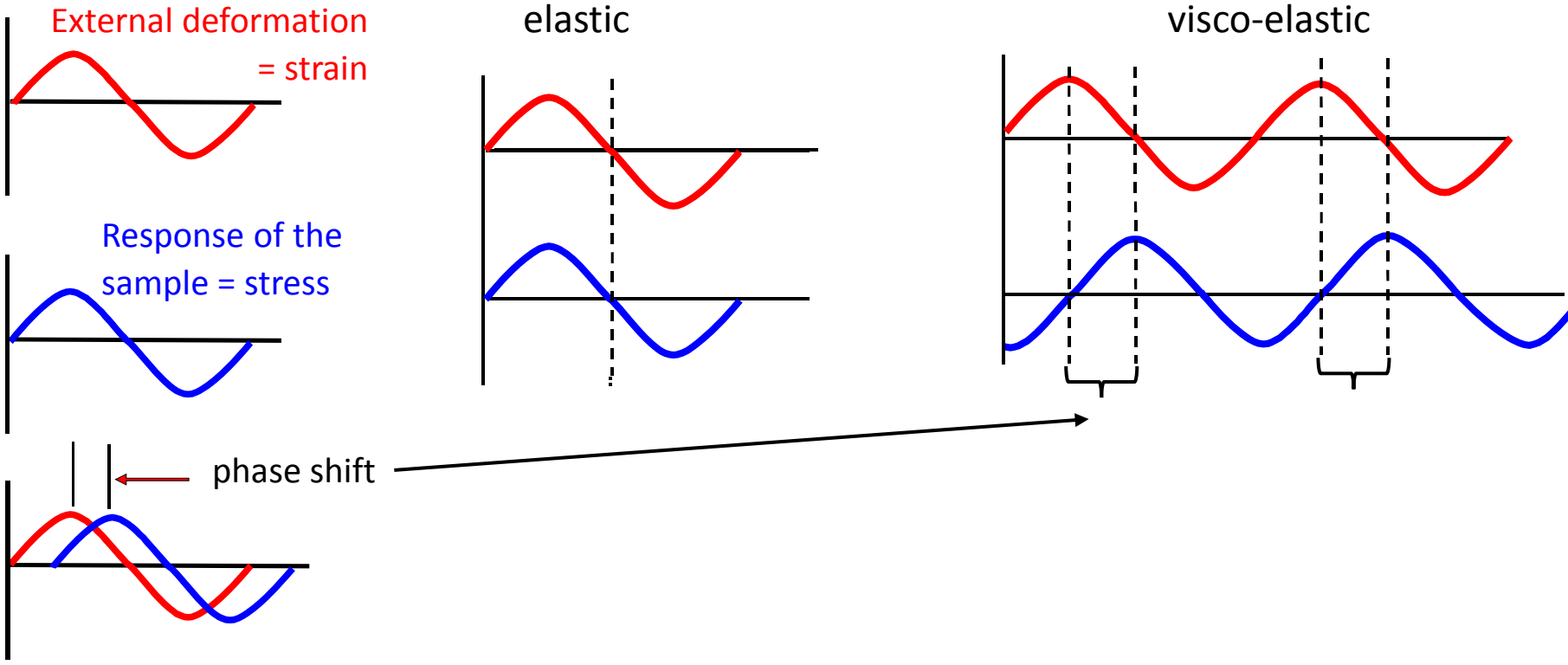
INM

TECHNOLOGIE POLYMERE & KOMPOSITE

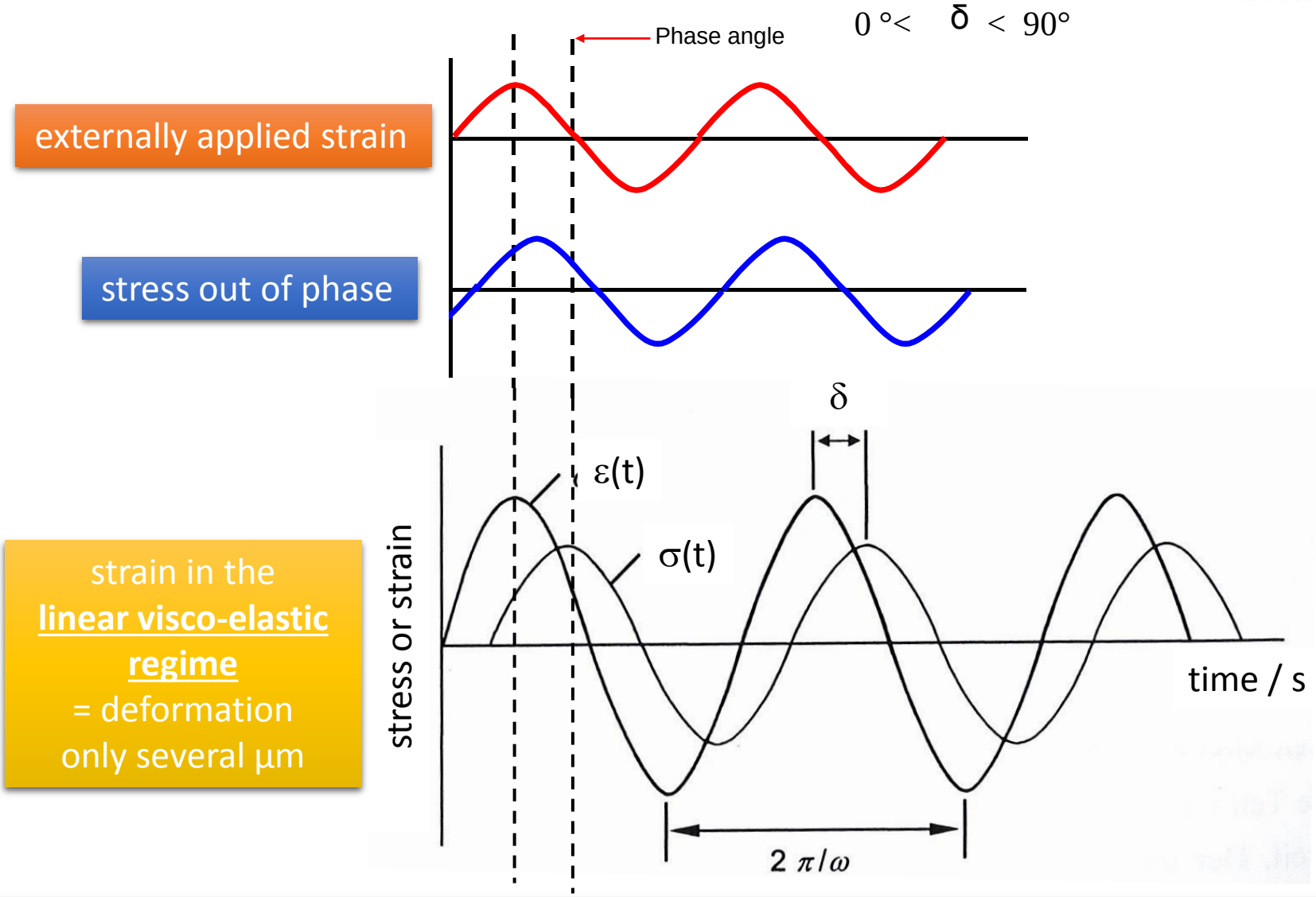
MC07, UdS WS 2019/2020

Chapter 6: Dynamic mechanical behaviour

Dynamic-mechanical-thermal (DMTA) experiment: Enforced damped vibration

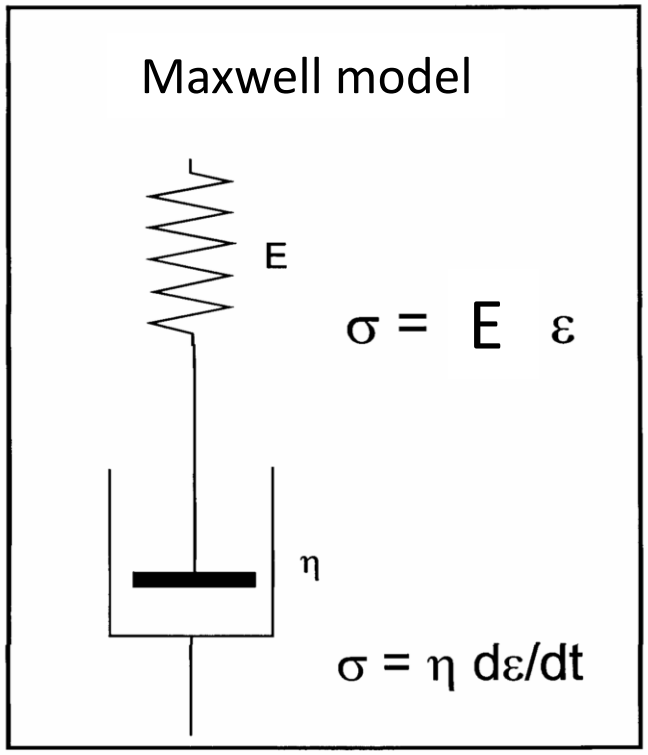


Principle of dynamic-mechanical measurements



strain in the **linear visco-elastic regime** = deformation only several µm

Dynamic mechanical thermal analysis (DMTA): principle



„elastic“

„viscous“

Polymers = visco – elastic materials

$E'' = \tan \delta * E'$

storage modulus E‘:	elastic components
tan δ:	damping behaviour
loss modulus E‘‘:	viscous components

Maxwell element to describe relaxation

- For time dependent changes in strain

$$\frac{d\varepsilon}{dt} = \left(\frac{1}{E}\right)\left(\frac{d\sigma}{dt}\right) + \frac{\sigma}{\eta}$$ at constant shear rates $$\left(\frac{d\varepsilon}{dt} = 0\right)$$ the result is $$\frac{d\sigma}{dt} + \frac{E\sigma}{\eta} = 0$$

If a Maxwell element is subjected to a fixe strain then the stress decreases over the time exponentially.

$$\sigma = \sigma_0 \exp\left(-\frac{tE}{\eta}\right)$$

At the time

$$t_R = \left(\frac{\eta}{E}\right)$$ t_R : relaxation time

the stress is reduced to 1/e of the initial value.

σ: stress
ε: strain
t: time
E: stiffness of the spring or elastic modulus
η: damping constant or viscosity.

- **time scales long compared to t_R**:
  E approaches 0 + Maxwell element shows pure viscous reaction.
- **short loading times:** pure elastic reaction of the system

The complex modulus

The harmonic deformation can be described as a function of frequency ω and amplitude ε_0 in complex manner:

$$\varepsilon^* = \varepsilon_0 \exp(i\omega t)$$

$\omega = 2\pi\nu$
ν: frequency
$i^2 = -1$

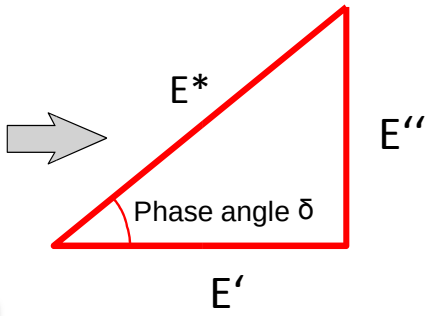
The relation between changing deformation (strain) and stress is

$$\sigma^* = \varepsilon^* E^*(\omega)$$

$E^*(\omega)$ as the frequency dependent dynamic modulus:

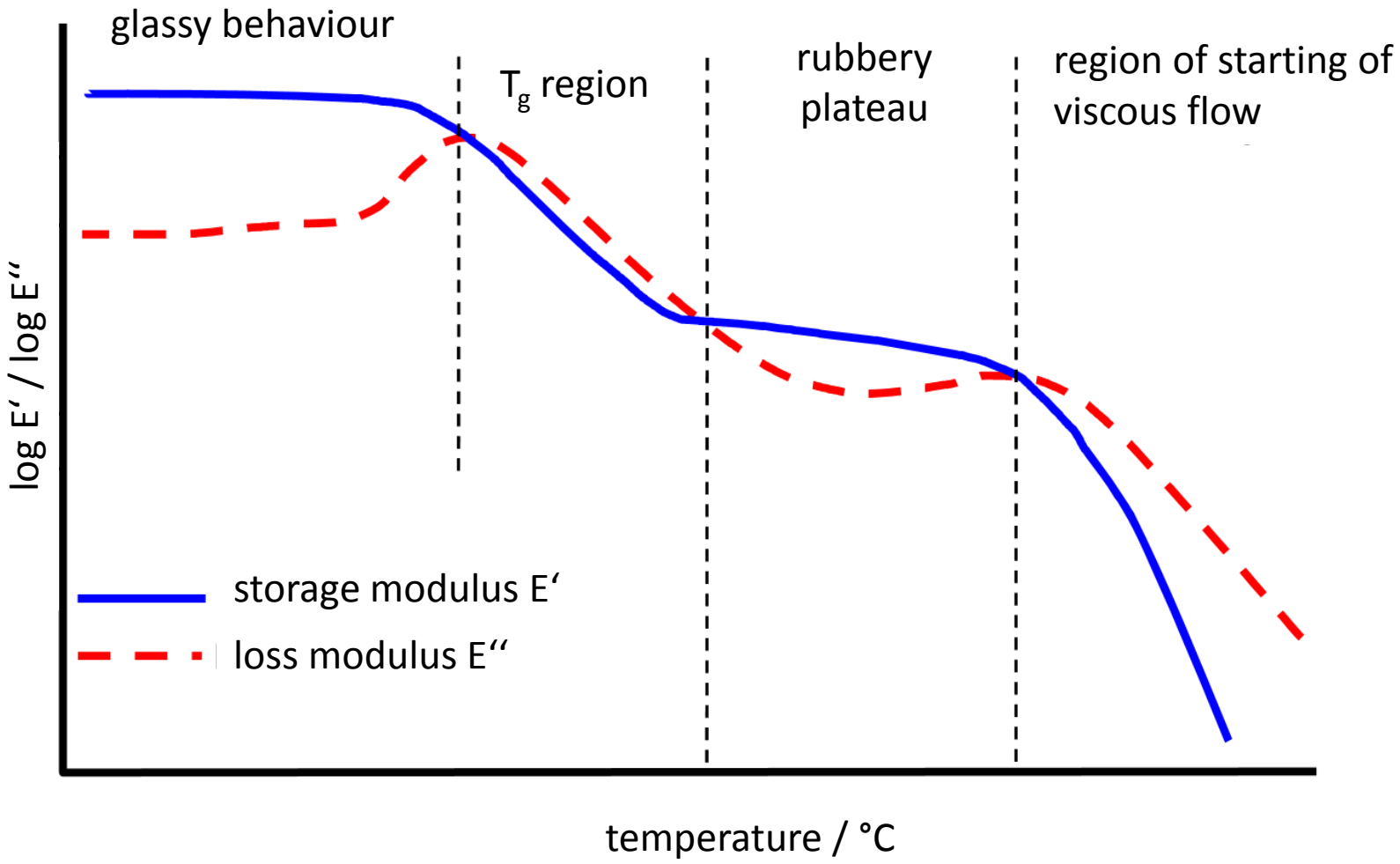
$$E^*(\omega) = E'(\omega) + iE''(\omega)$$

$$\tan\delta = \frac{E''(\omega)}{E'(\omega)}$$

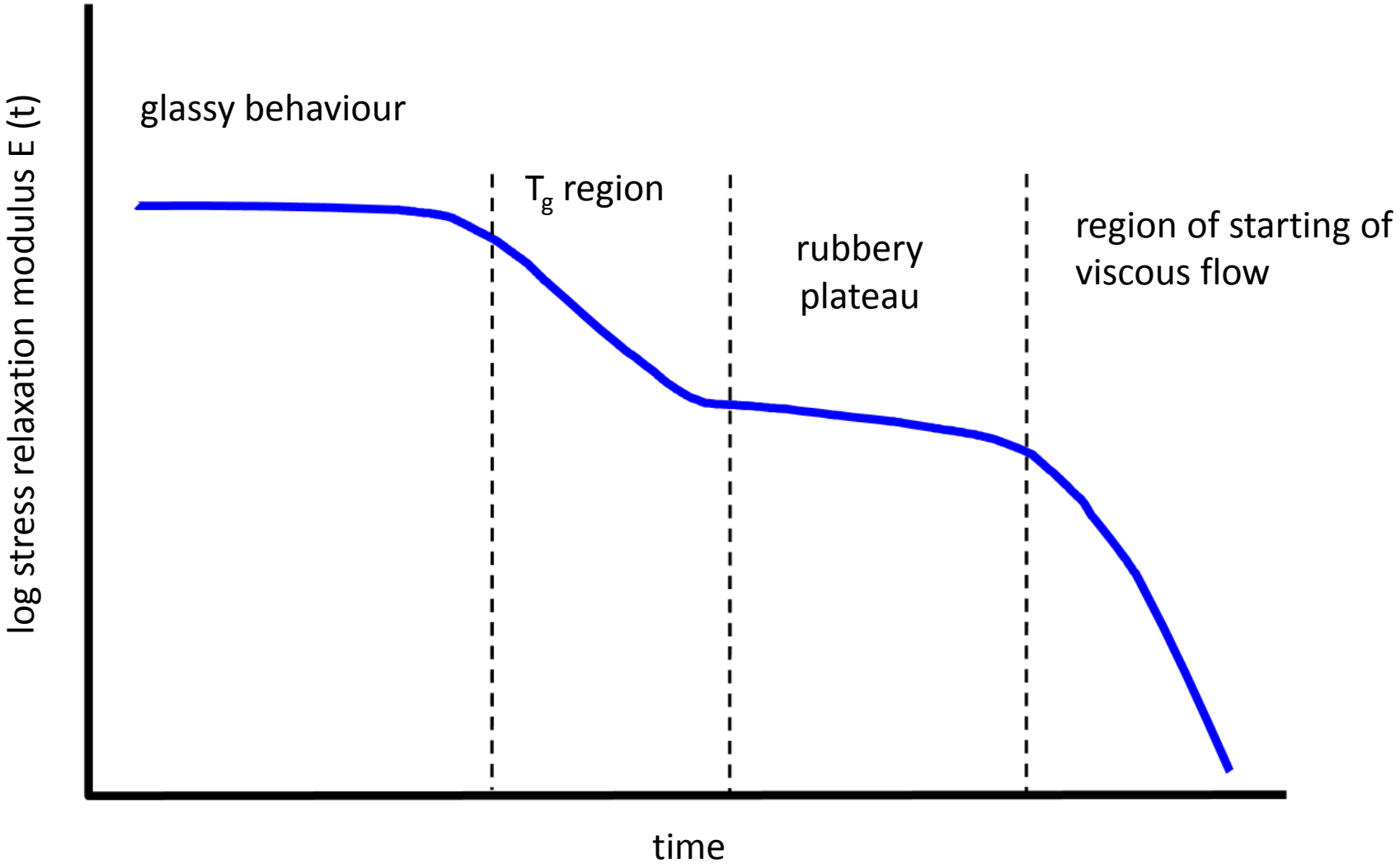


storage modulus E‘:	elastic components
tan d:	damping behaviour
loss modulus E‘‘:	viscous components

The typical transition regions detectable in DMTA measurements



Time temperature analogy also visible in DMTA when performed as a stress relaxation experiment



Different types of rheometer

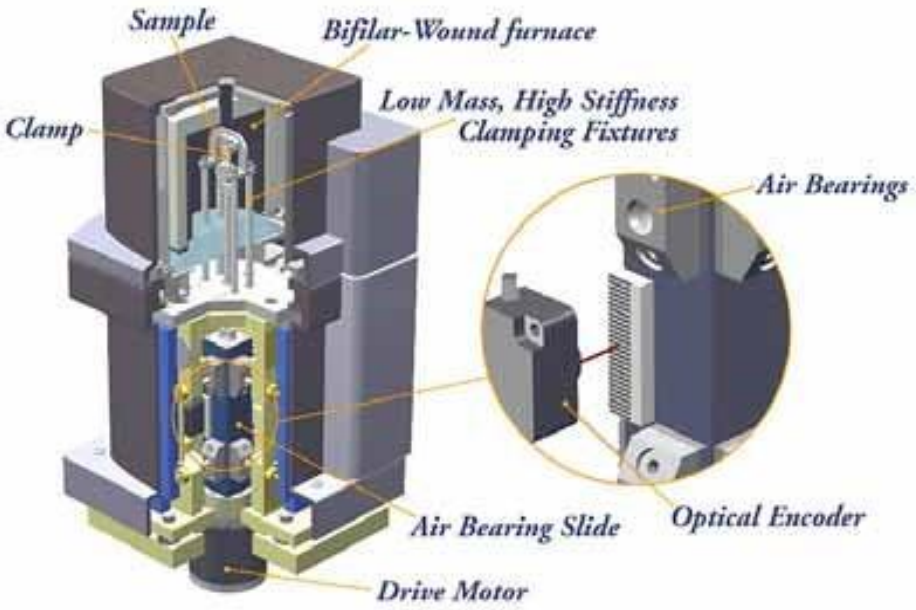
oscillating rheometer
e.g. RSA G2 TA Instruments

static and dynamic viscosity of
- dispersions, emulsions
- molten polymers

dynamic-mechanical-thermal analysis
e.g. Q800 TA Instruments

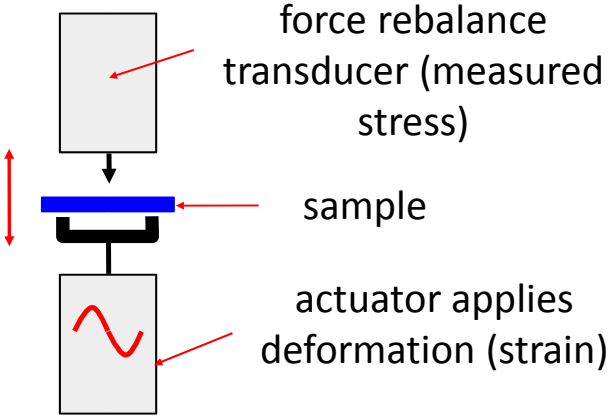
- dynamic-mechanical analysis of polymers
- stress relaxation experiments
- creep experiments

Features of dynamic-mechanical thermal analysis (DMTA)

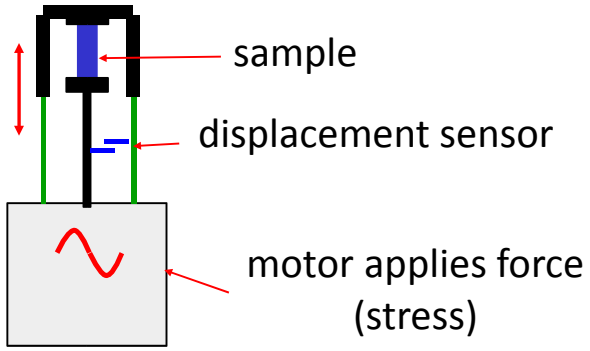


insight view measurement head Q800

RSA G2
controlled strain



Q800
controlled stress

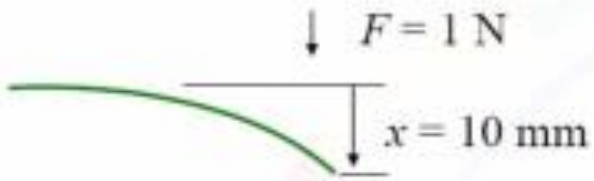


Broad measurement range

	TA Instrument DMA Specifications	
	Q800	RSA G2
Max Force	18 N	35 N
Min Force	0.0001 N	0.0005 N
Force Resolution	0.00001 N	0.00001 N
Frequency Range	0.01 to 200 Hz	2E-5 to 100 Hz
Dynamic Sample Deformation Range	+/- 0.5 to 10,000 µm	+/- 0.05 to 1,500 µm
Strain Resolution	1 nm	1 nm
Modulus Range	10^3 to $3*10^{12}$ Pa	10^3 to $3*10^{12}$ Pa
Modulus Precision	+/- 1%	+/- 1%
Tan delta Sensitivity	0.0001	0.0001
Tan delta Resolution	0.00001	0.00001
Temp range	-150 to 600°C	-150 to 600°C
Heating Rate	0.1 to 20°C/min	0.1 to 60°C/min
Cooling Rate	0.1 to 10°C/min	0.1 to 60°C/min
Isothermal Stability	+/- 0.1°C	+/- 0.1°C

Adjusting to samples with different elastic modulus and stiffness

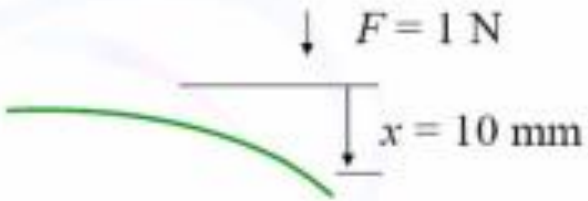
thick and thin samples of different materials can show the same stiffness



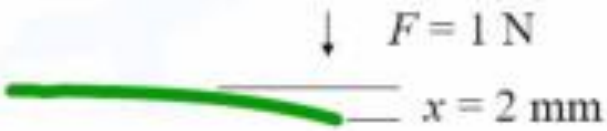
material with high modulus

material with low modulus

thick and thin samples of the same material show the same elastic modulus



sample with low stiffness



sample with high stiffness

Possible measurement modes DMTA

single/dual cantilever

3-point bending

tension film

tension fibre

shear sandwich

compression

submersible compression

submersible tension

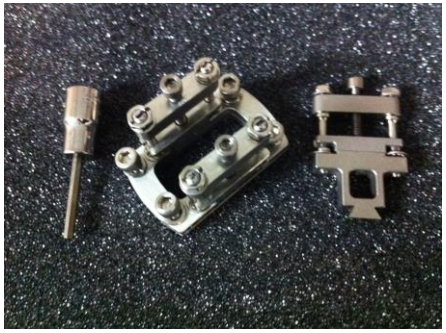
Different clamps available

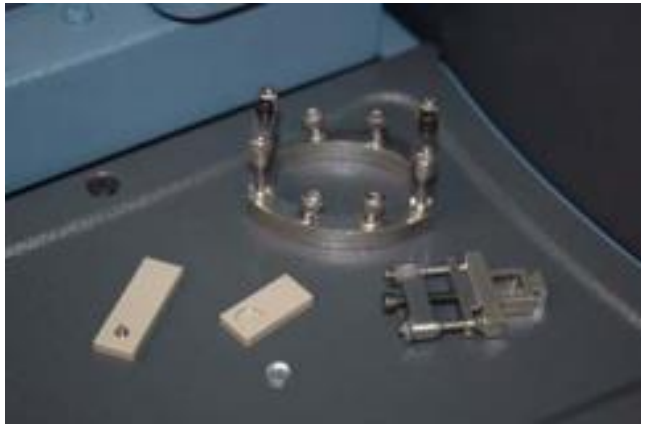
- All the necessary types of clamps for testing
  - Solid bars
  - Elastomers
  - Soft foams
  - Thin films
  - Fibres
- Designed using FEA, optimizing
  - Low mass
  - High stiffness/Low compliance
- Automatic compliance calibration (and correction) **for each clamp**

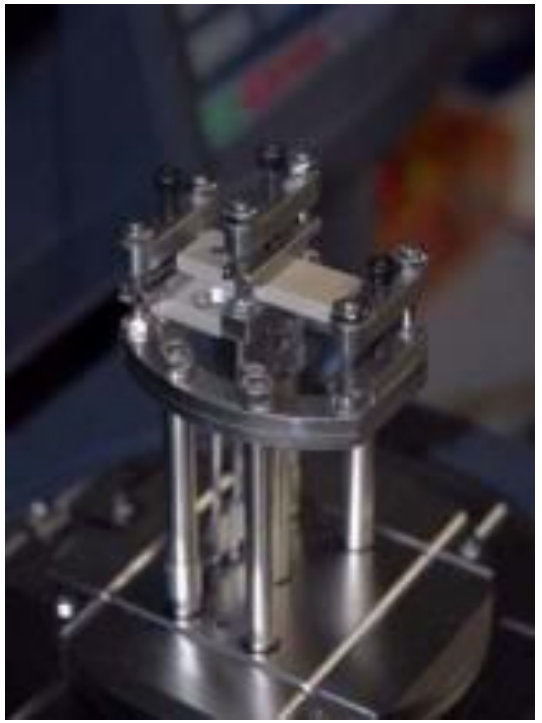
Choose the correct clamps for testing

- Sample Dimension
  - Films and fibers: tension clamps
  - Bars and cylinders: bending clamps
  - O-rings and tablets: compression and/or shear
- Deformation Mode
  - E [tension, compression and bending]
  - G [shear]
- Sample Stiffness
  - Machine range fixed: 100 - 10, 000,000 N/m. Stiffness of sample related to its dimensions [l, w, t]. Stiffness may limit sample size to below clamp maximum.

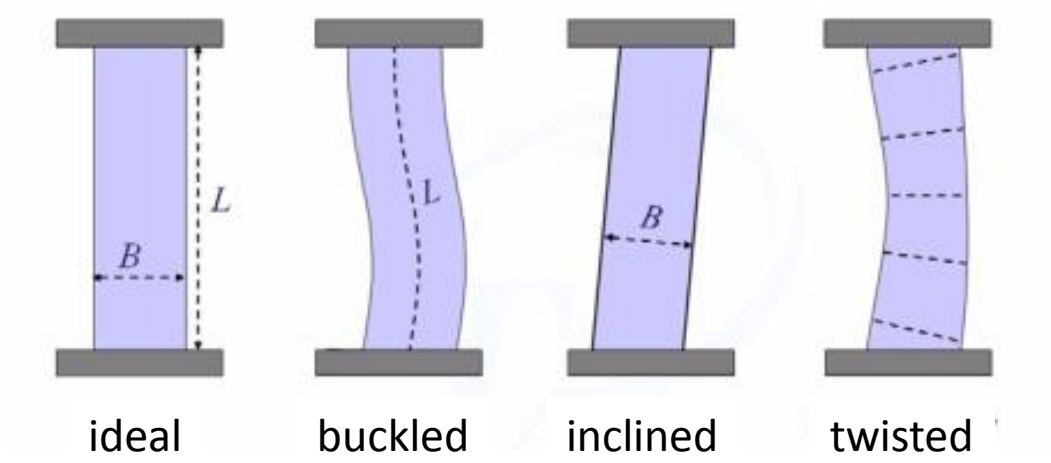
Mounting of different measurement heads

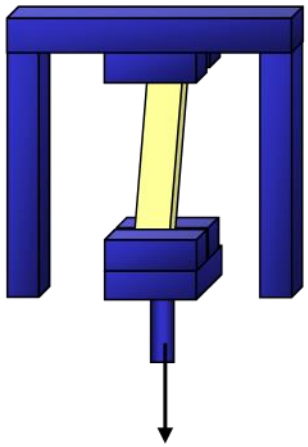


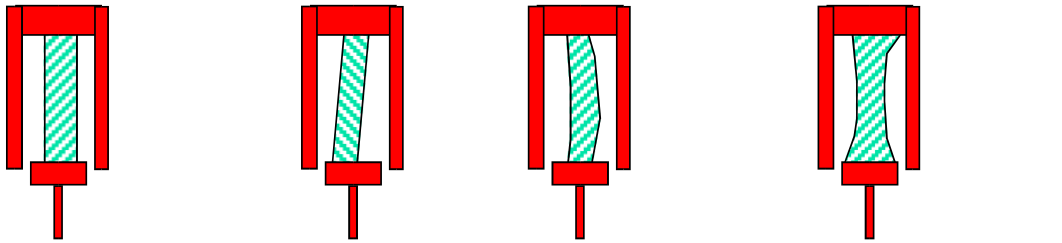




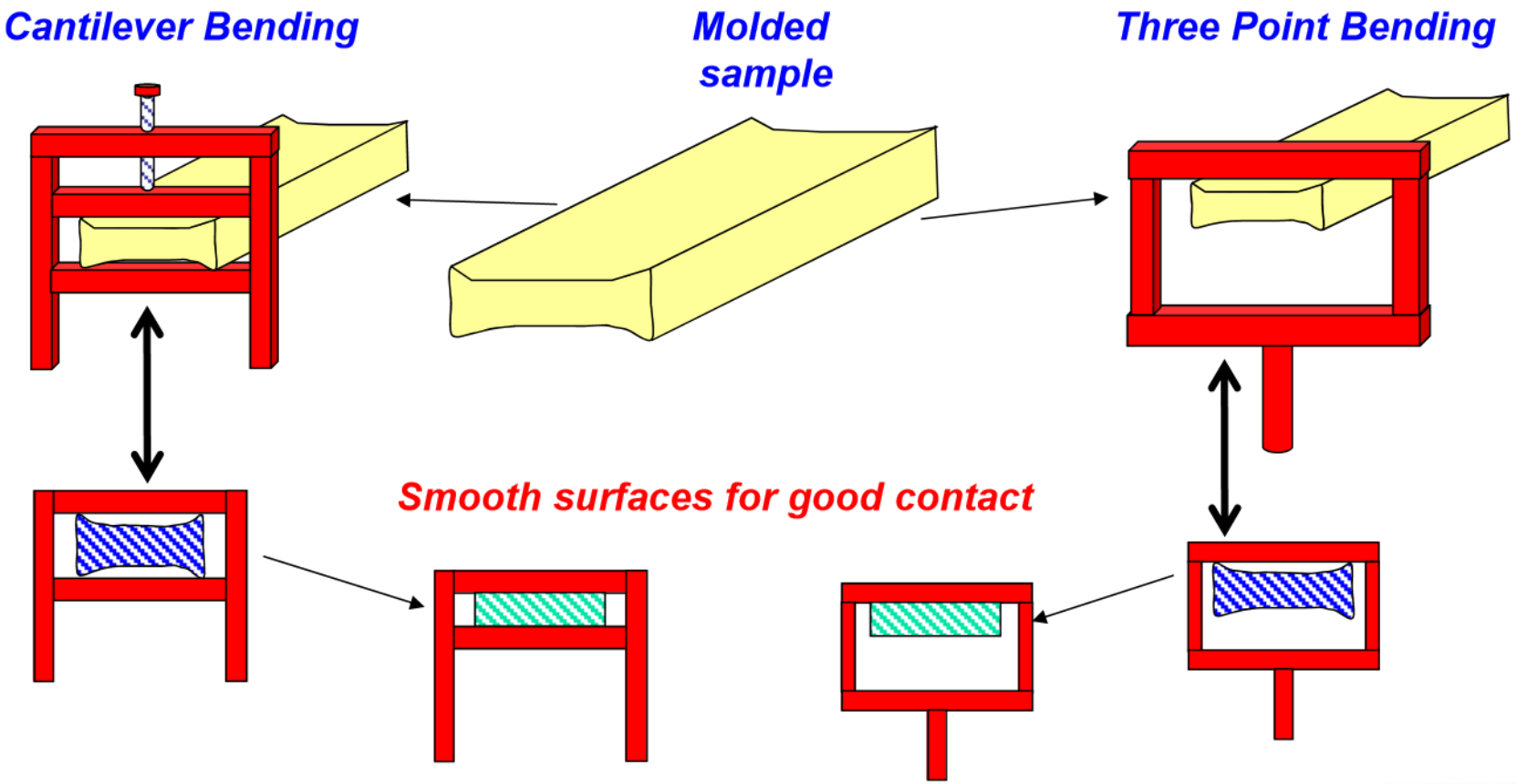
Alignment of the sample in e.g. tensile mode





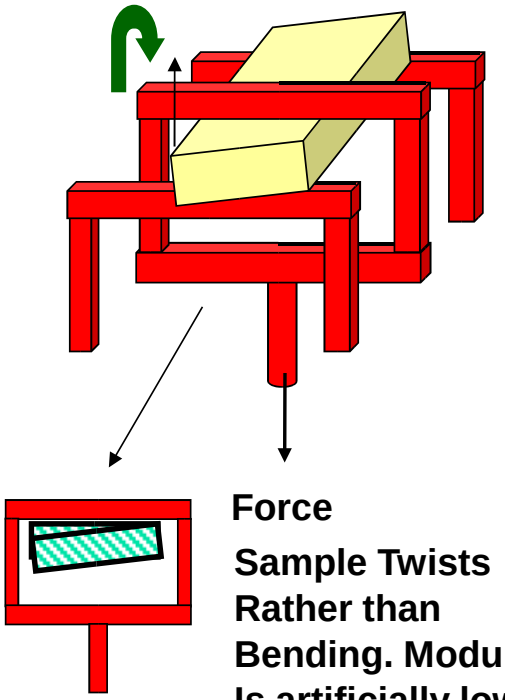


Sample preparation: Shape is important



Sample preparation: Shape is important

Three Point Bending

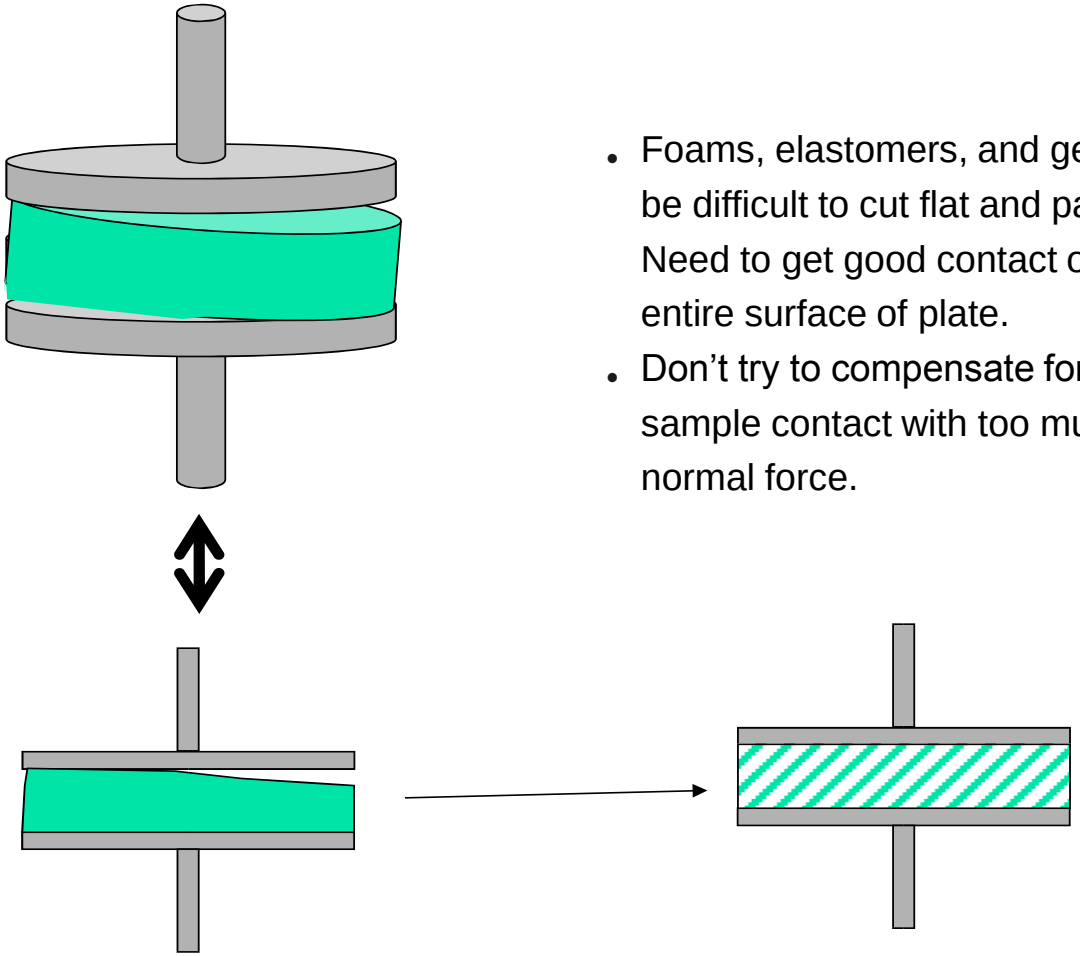


Force

Sample Twists Rather than Bending. Modulus Is artificially low.

- Alternate 3 point bending clamp
- Rocking action eliminates artifacts due to twist in the sample
- Rolling action eliminates friction
- "Rock-n-Roll" Clamp!

Sample preparation: Shape is important



- Foams, elastomers, and gels can be difficult to cut flat and parallel. Need to get good contact over entire surface of plate.
- Don’t try to compensate for poor sample contact with too much normal force.

Special sample preparation tubes

Parallel Razor
Blade Cutter

Good for Films and
Sheets of rubber.

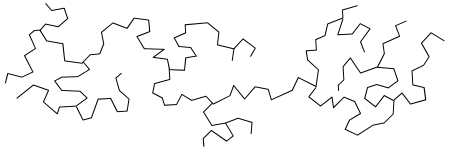
Cork Borer

Good for stiff foams and
Sheets of rubber.

Measurement frequency

- Single Frequency
  - Temperature ramp most popular for rapid evaluations 1 Hz or 10 Hz (6.28 or 63 rad/sec) for most experiments
- Multiple Frequencies
  - Frequency sweeps at ambient for viscoelastic properties
  - Frequency sweeps at multiple temperatures for Time-Temperature Superpositioning (TTS)
  - Run from high to low frequencies for faster initial data acqusition
- Data Collection Rate
  - Lower frequencies take longer time - control experiment
  - More frequencies = longer experiment

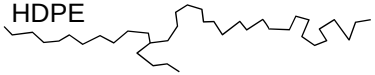
The effect of M_W and branching of polymers



HDPE and LDPE.

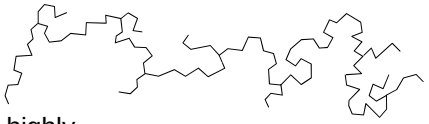
Highly branched with much lower crystalline content

HDPE

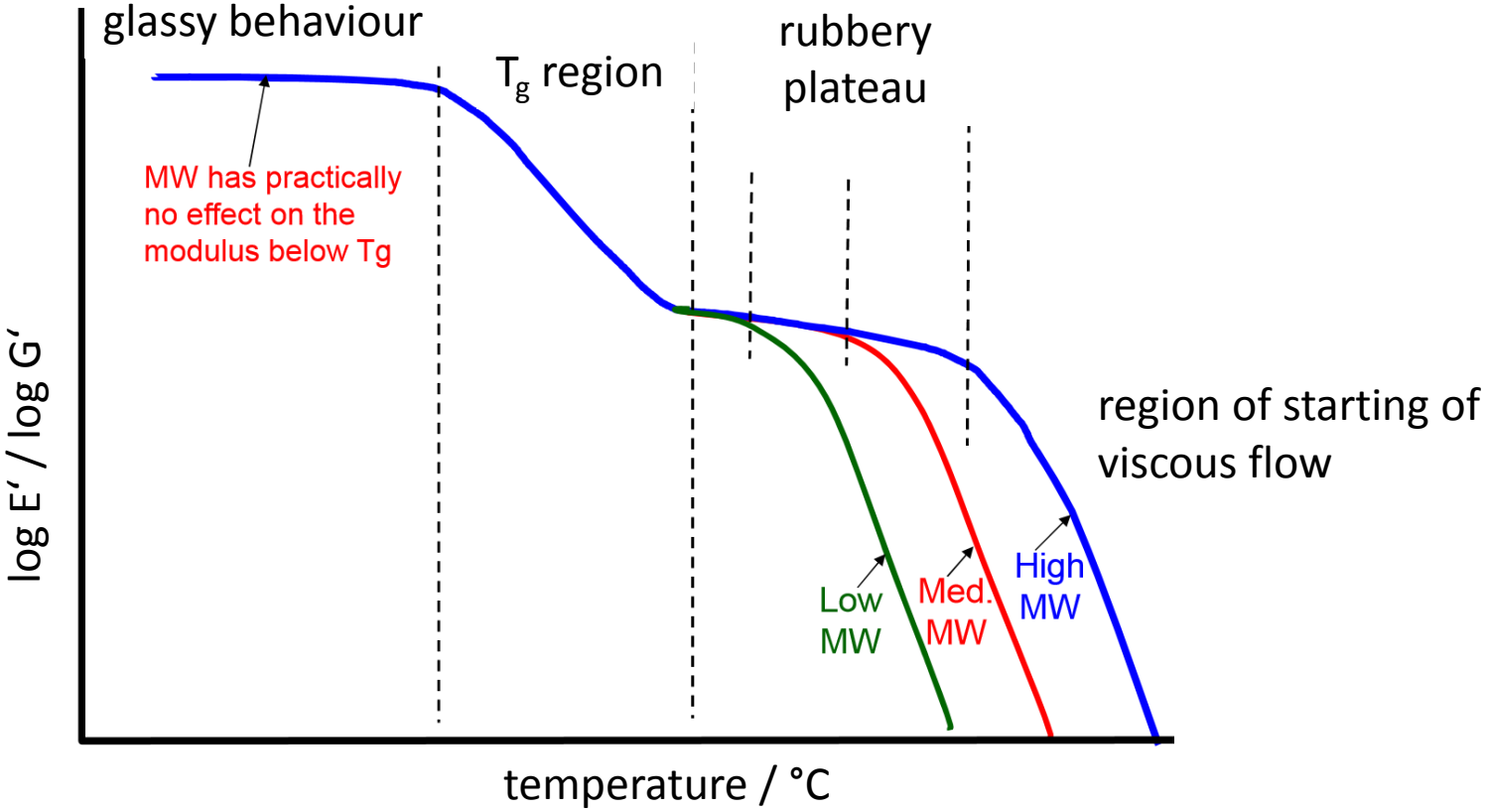


Structurally regular chain with few branch points.

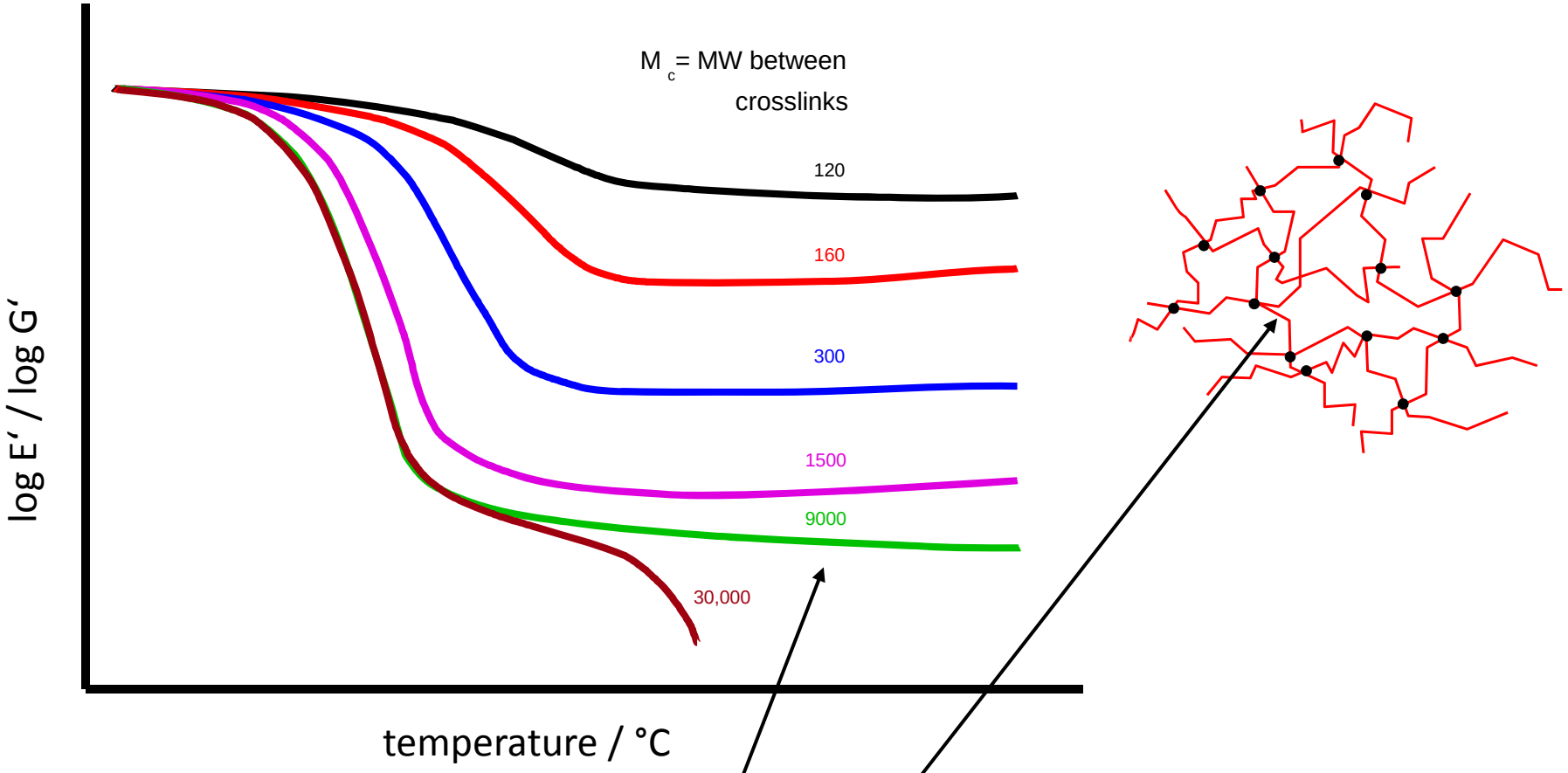
LLDPE



Polymer chains can pack efficiently resulting in a highly crystalline material with high density

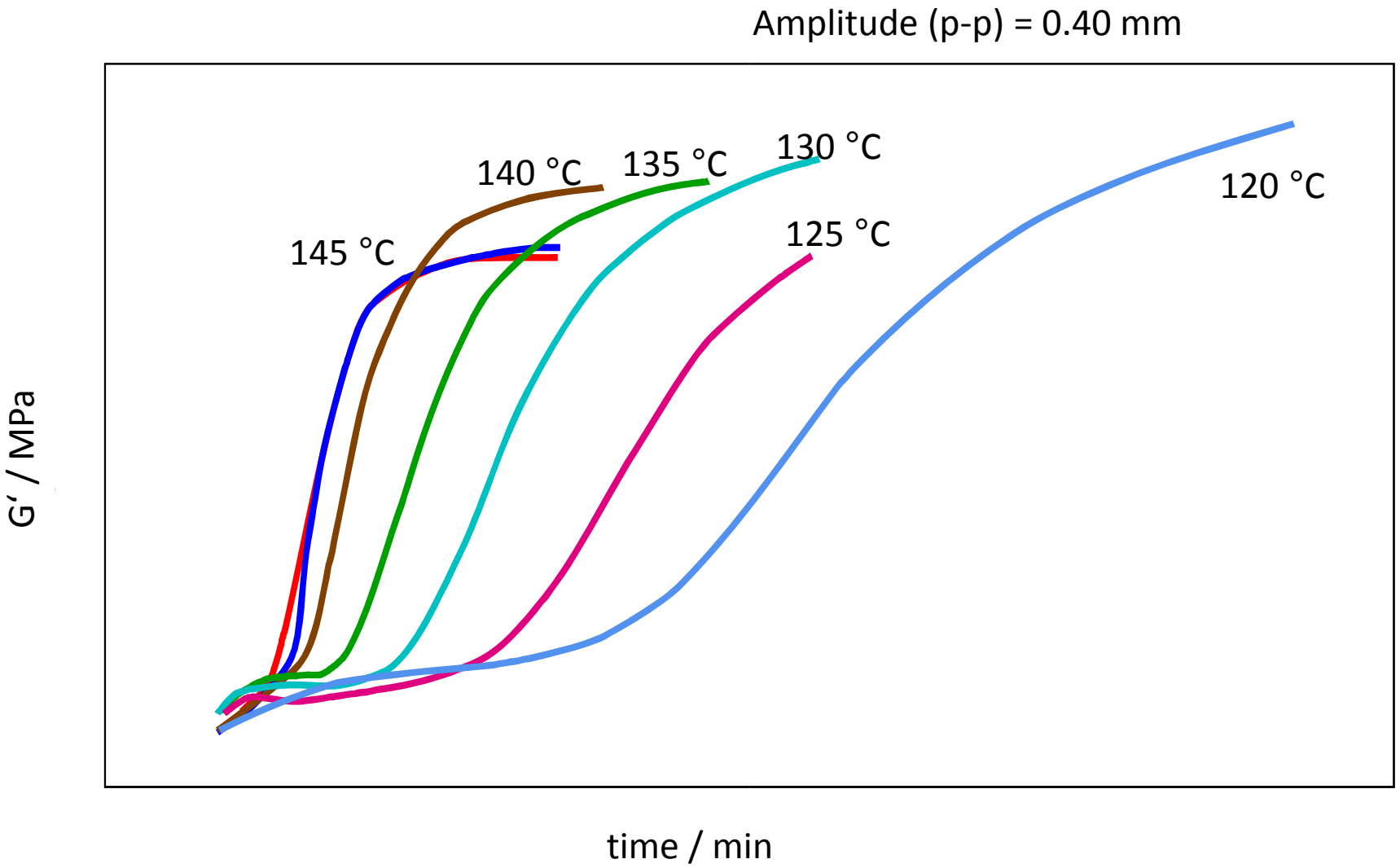


The influence on cross-linking density

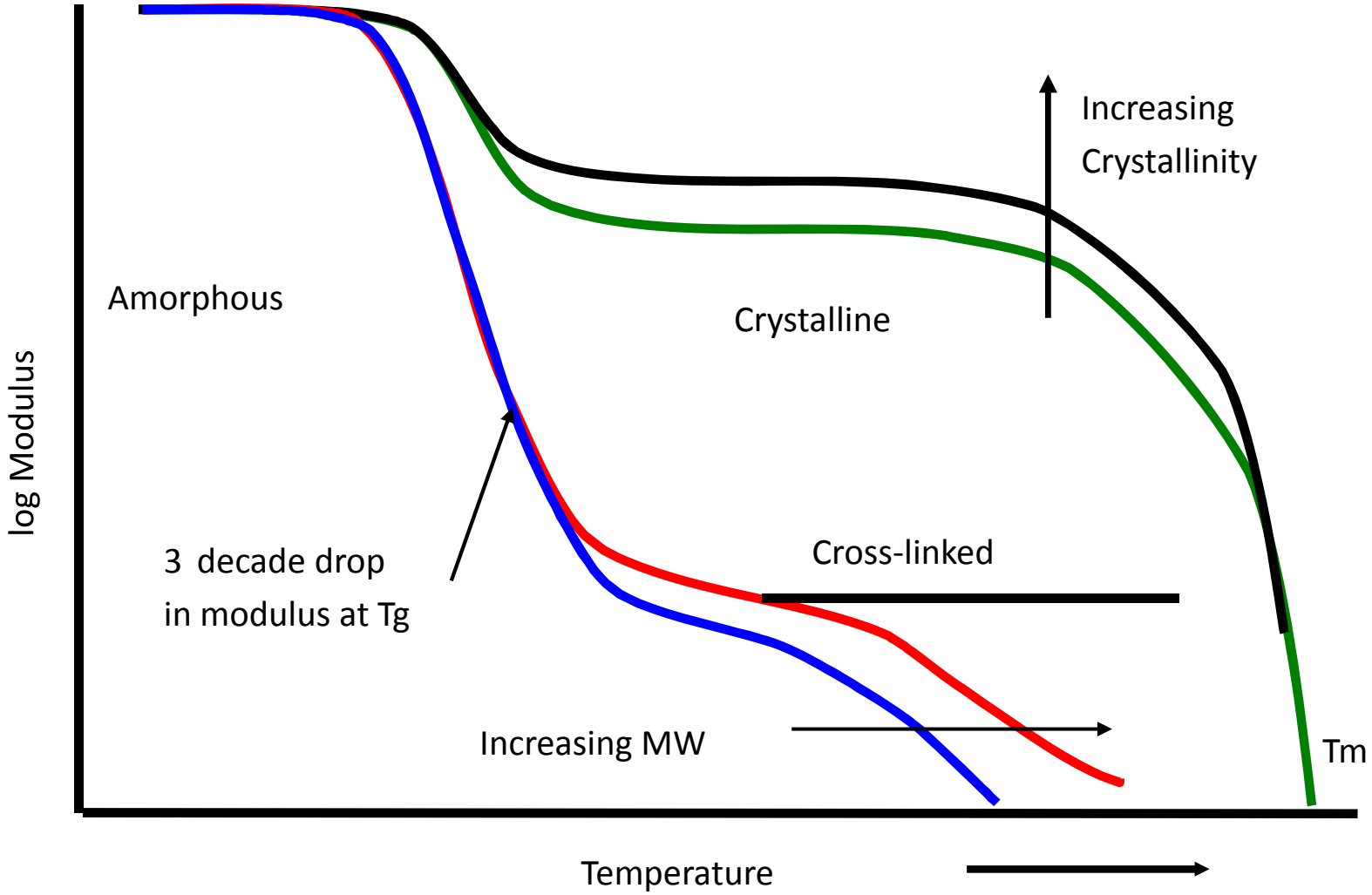


- increasing cross-linking density = lower Mw between cross-linking points
- formation of a distinct **rubbery plateau**

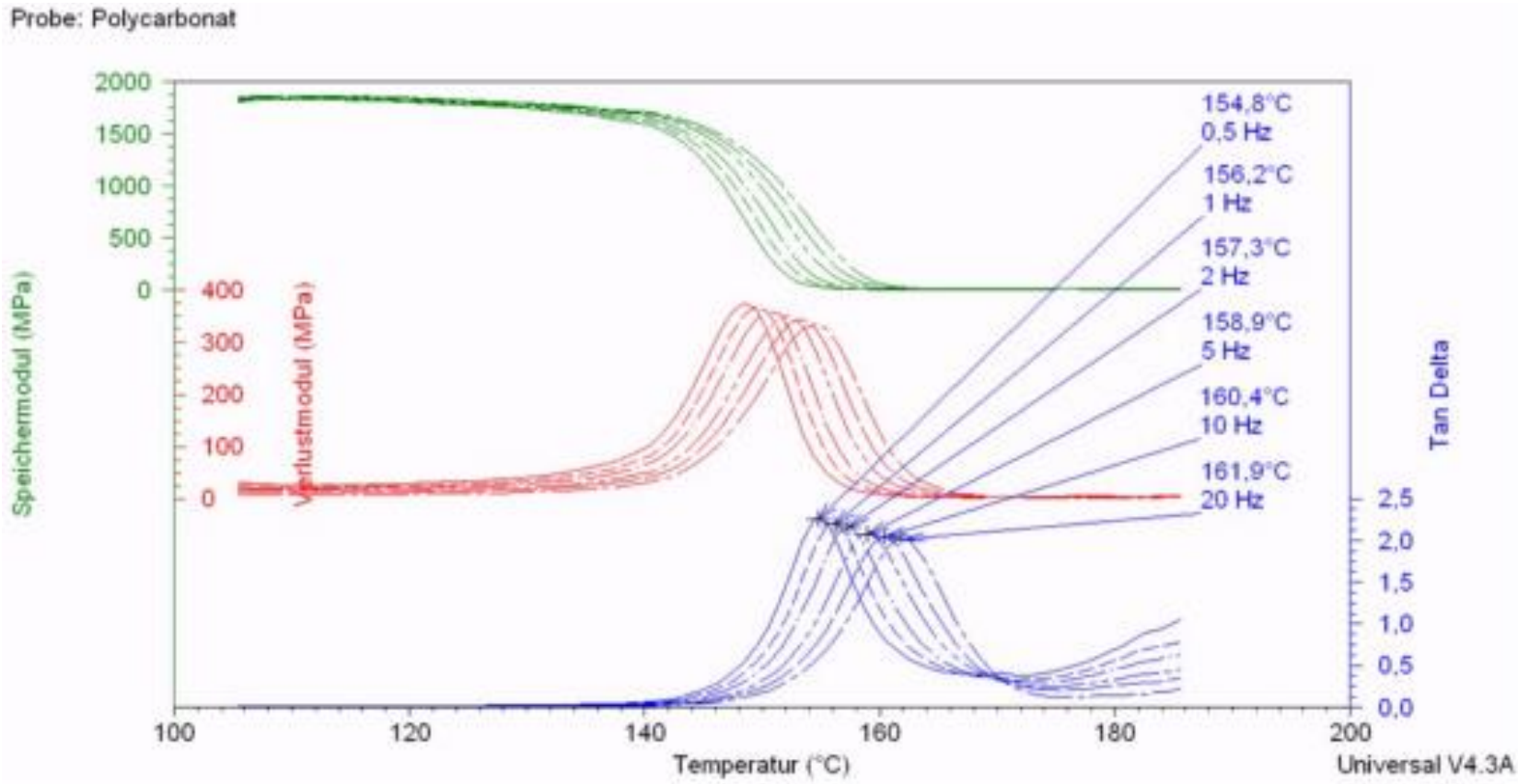
Investigation of curing behavour of resin



Summary of the different effects

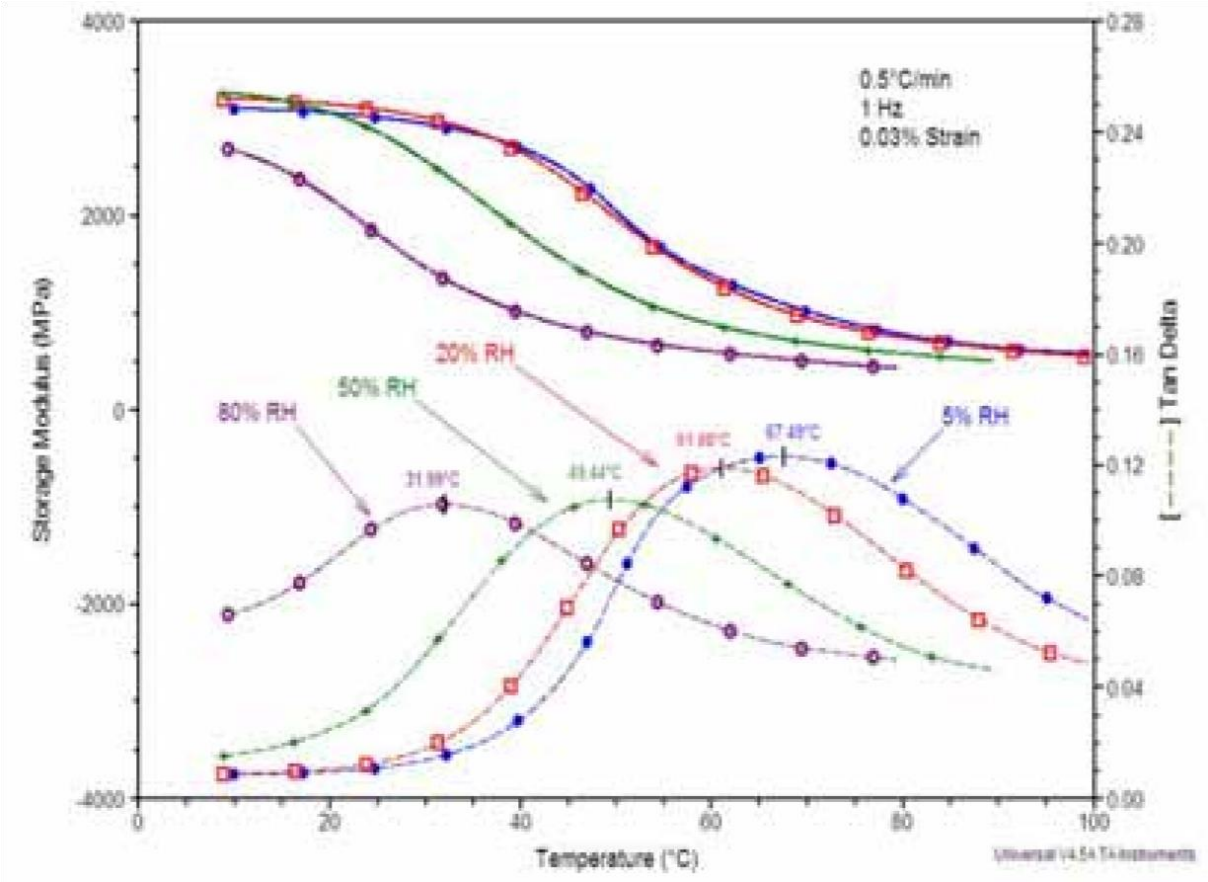


Effect of measurement frequency

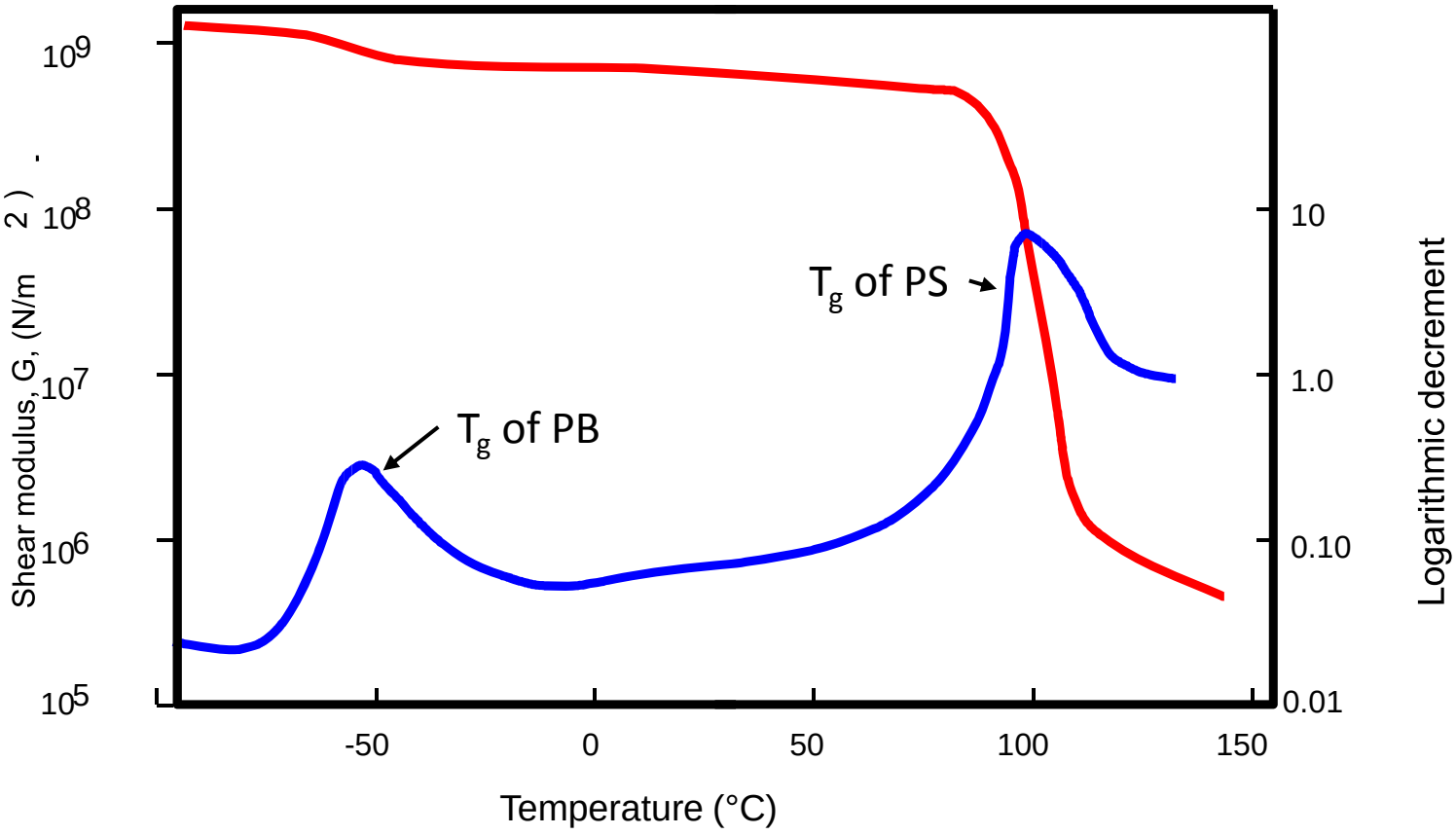


increasing Tg with increasing measurement frequency

Analysis of Nylon 6: Temperature Scans with Humidity



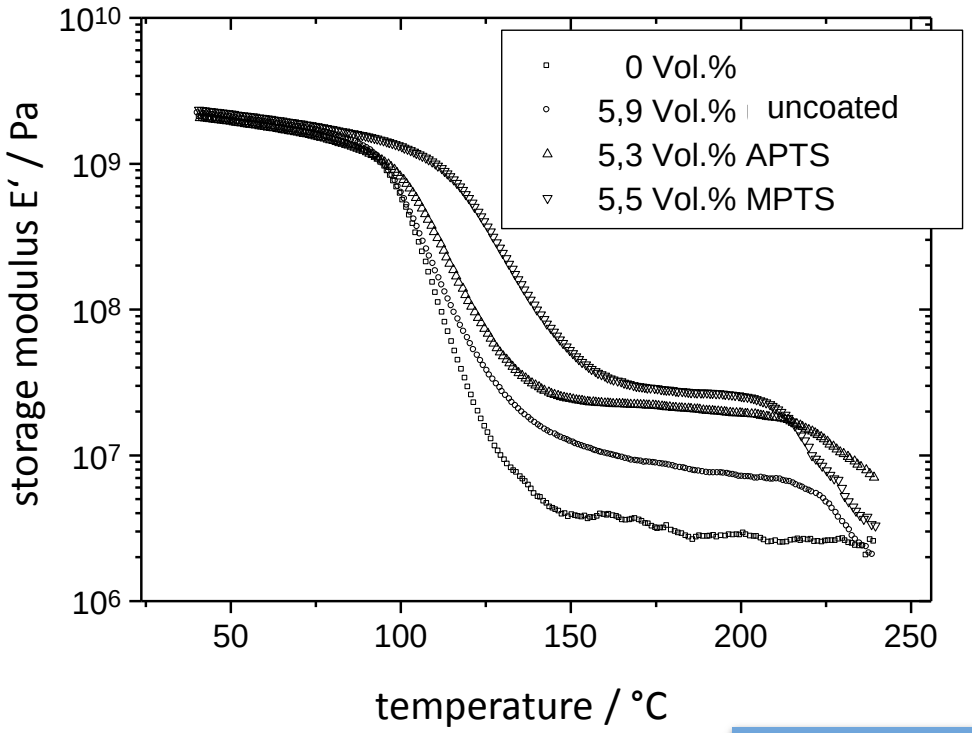
Blends from immiscible polymers: e.g. polystyrene (PS) and polybutadiene (PB)



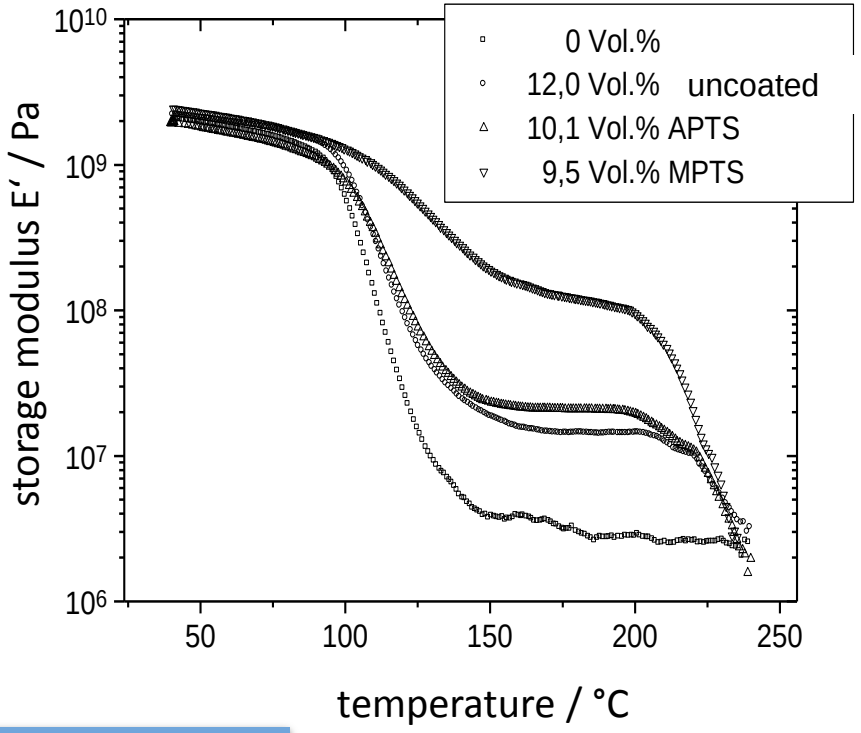
in phase separated blends out of 2 polymers also 2 T_g's are detectable

Storage modulus E‘ from DMTA for P(MMA-co-HEMA) / SiO_2 - nanocomposites

5 vol.-% 10 nm SiO_2



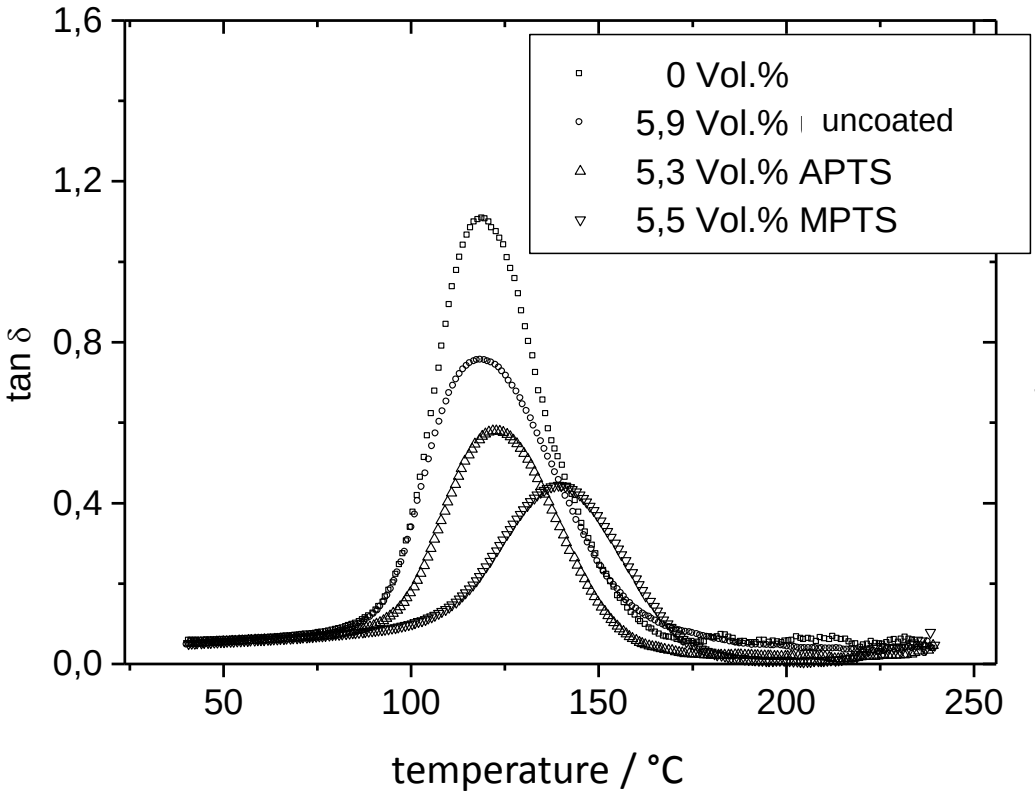
10 vol.-% 10 nm SiO_2



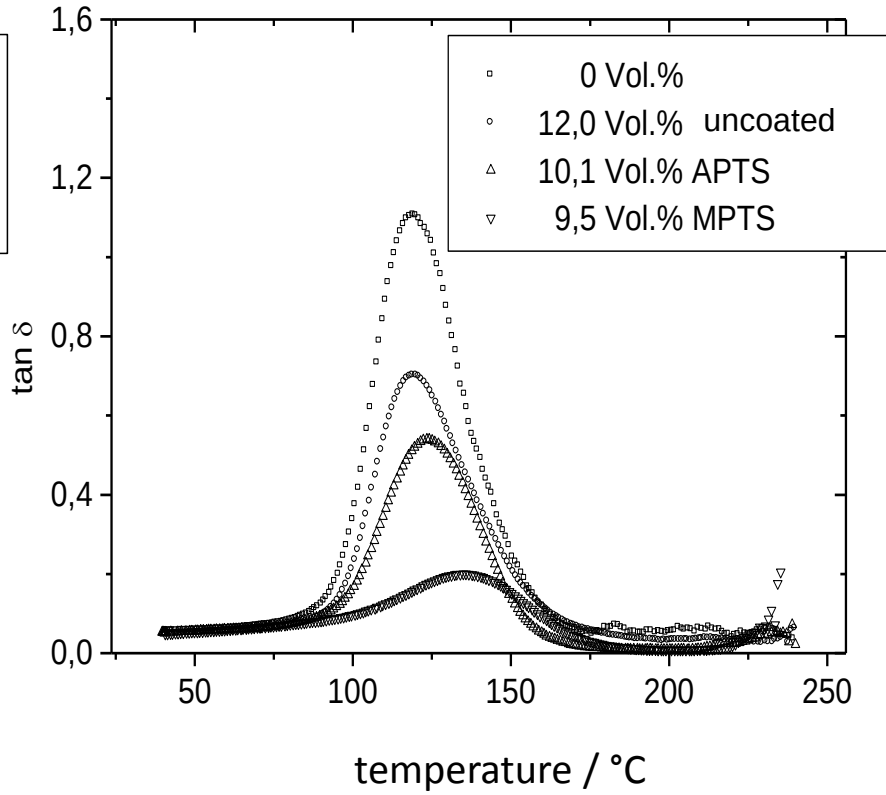
Significant rubbery plateau

Damping tan δ from DMTA for P(MMA-co-HEMA) / SiO_2 - nanocomposites

5 vol.-% 10 nm SiO_2

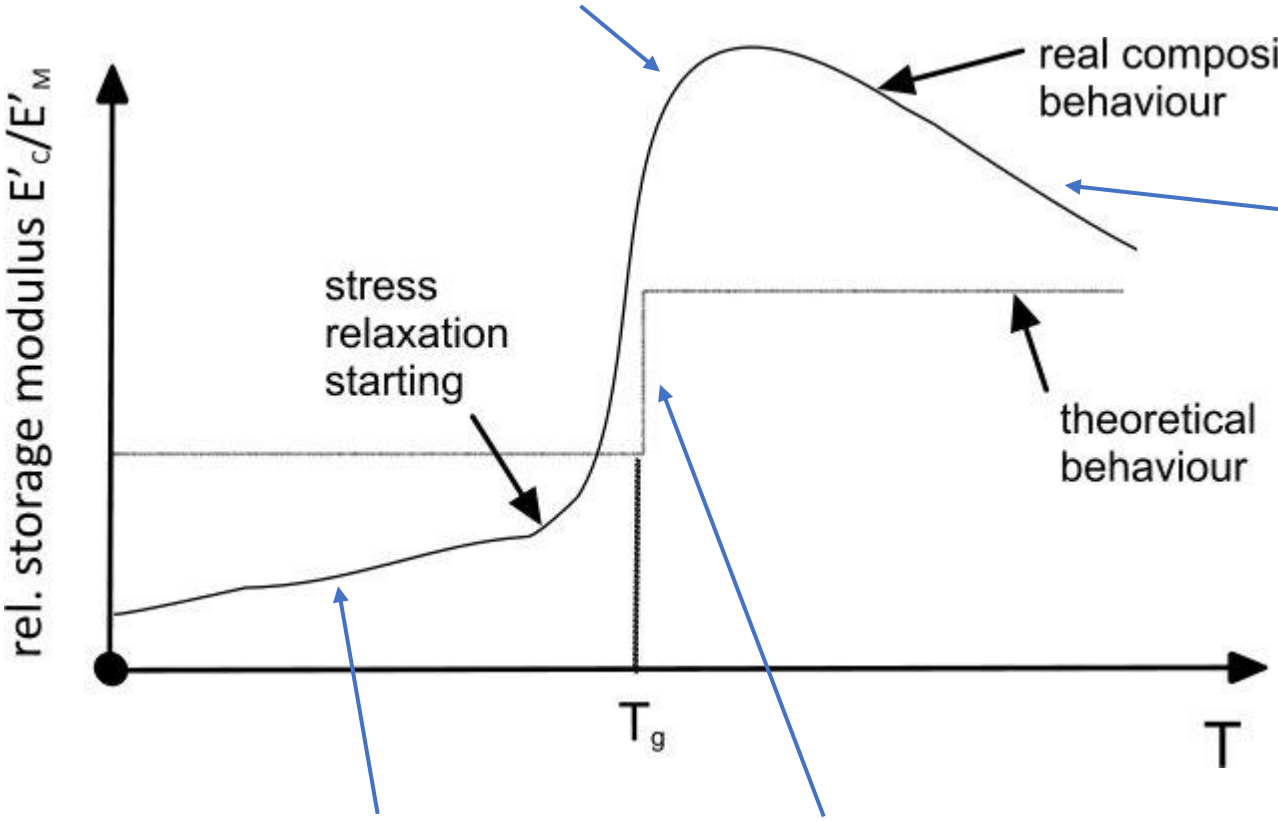


10 vol.-% 10 nm SiO_2



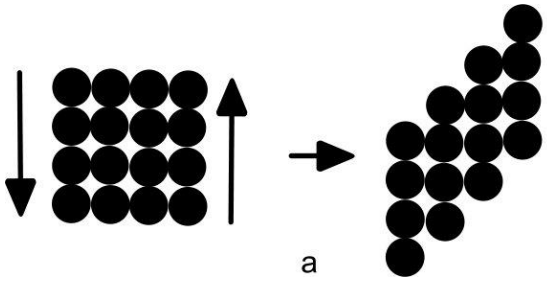
Strong cross linking tendency of the nanoparticles

General dynamic-mechanical behaviour of a filled plastic



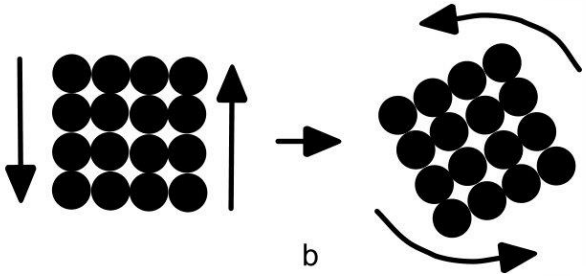
B.L. Lee, L.E. Nielsen

Dynamic mechanical thermal analysis (DMTA) for polymers filled with particles



below Tg

flexible agglomerates



above Tg

rigid agglomerates

relative storage modulus

$$E'_{rel} = E'_{Komposit}/E'_{Matrix}$$

reduced mechanical damping

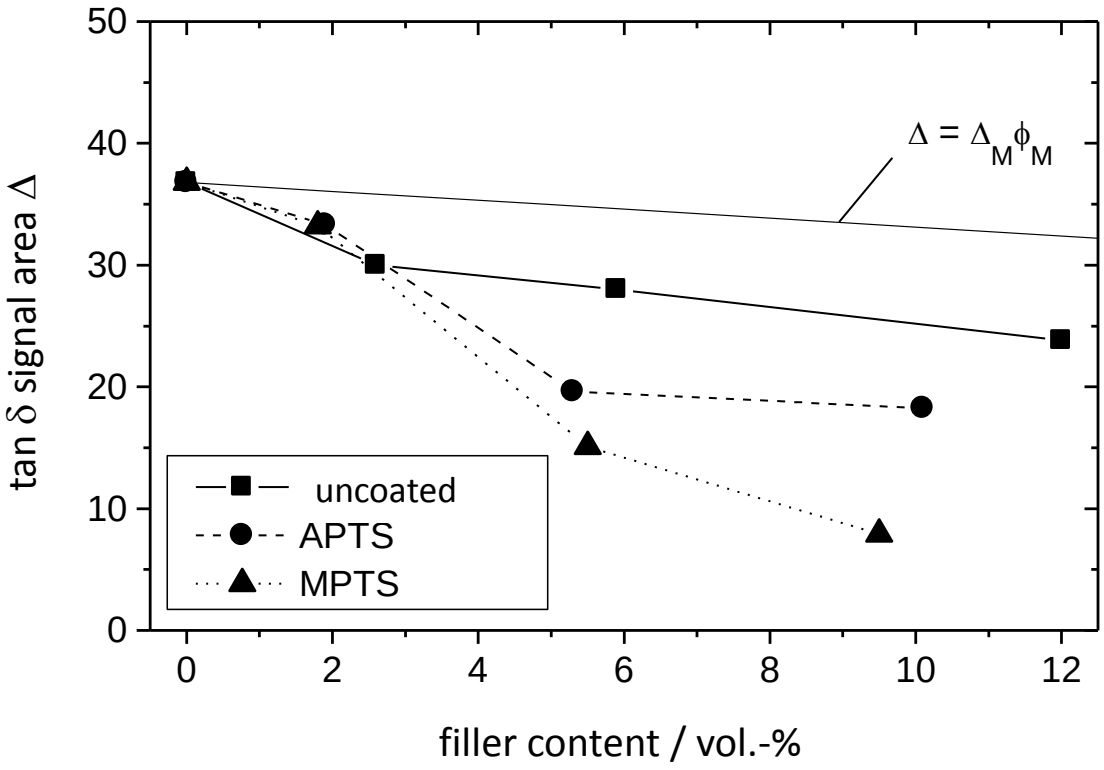
$$\Delta_{red} = \Delta/\Delta_M\phi_M$$

$\Delta_{red} < 1$	matrix = immobilised
$\Delta_{red} = 1$	matrix = unaffected
$\Delta_{red} > 1$	additional damping mechnisms

B.L. Lee, L.E. Nielsen

Mechanical damping for P(MMA-co-HEMA) / SiO_2 - nanocomposites

10 nm SiO_2 with different surface modifications



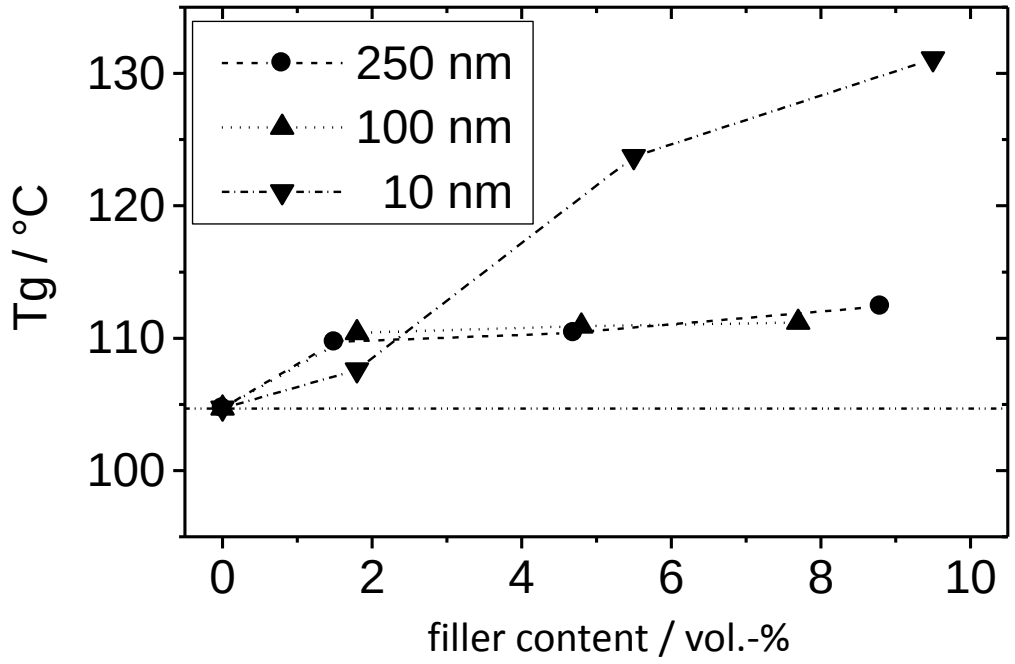
Model calculation
Δ: simple mixing rule

APTS: compatibilised
MPTS: chemical bonding

Significant decrease of damping behaviour if particles are well dispersed and carry bonding sites

Indications for immobilised polymer matrix

Tg – behaviour for P(MMA-co-HEMA) – nanocomposites containing SiO_2 – particles with different particle size

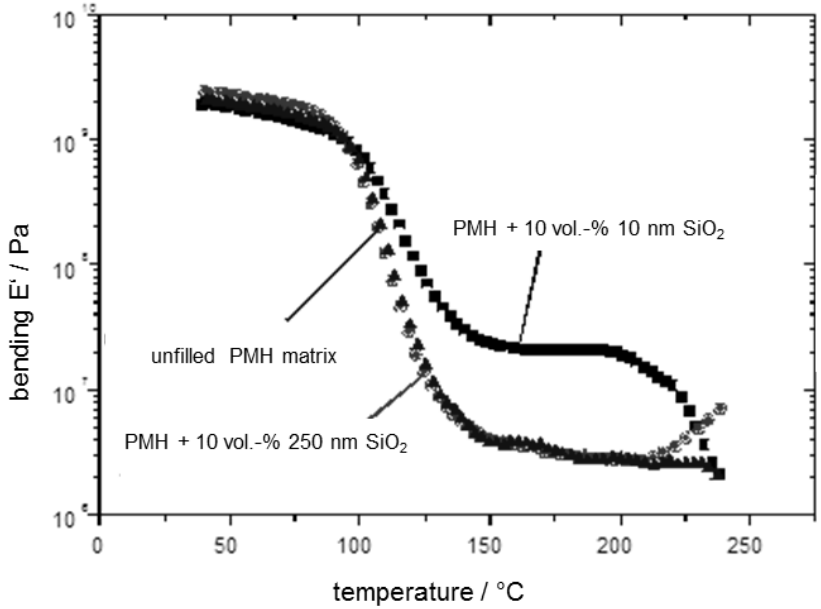


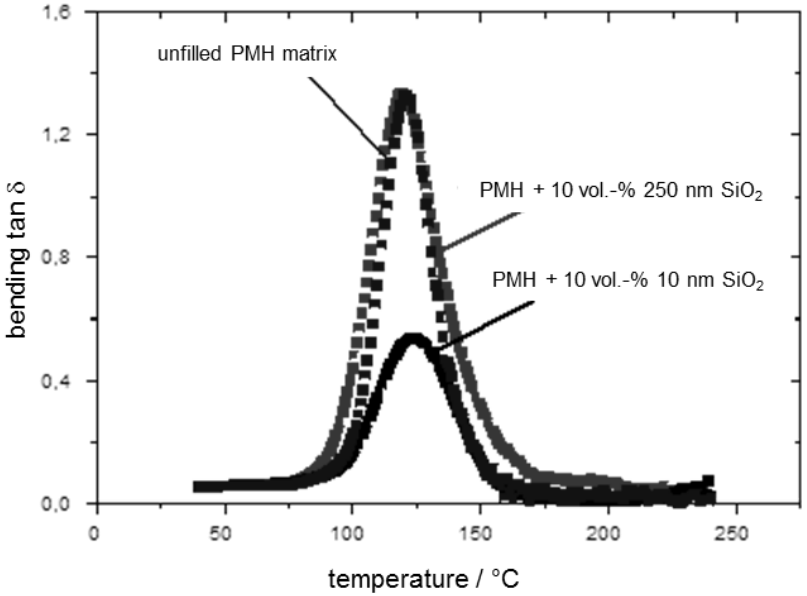
Particle size 10 nm: significant increase of Tg

Potential: Plastics with increased temperature stability

Information about the interface in polymer matrix nanocomposites ?

Dynamic mechanical thermal analysis (DMTA)





particle size 250 nm: matrix almost unaffected (small interfacial layer)

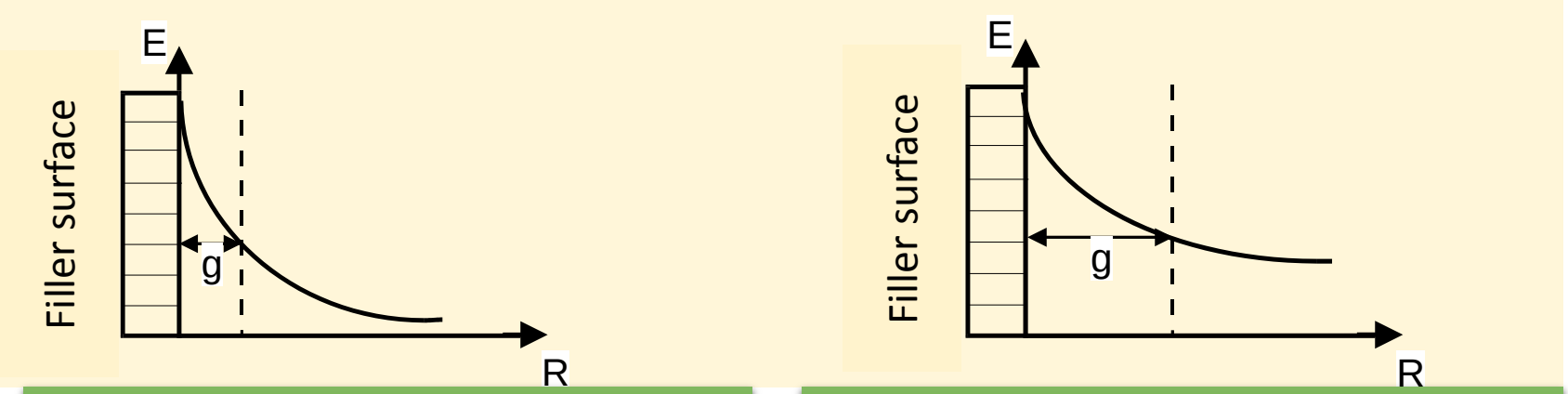
particle size 10 nm: interfacial layer with immobilised macromolecules on the large particle / matrix interface significantly affects the thermomechanical behaviour

Morphology and glass transition temperature

requirement: precise determination of the glass transition temperature

glass transition temperature
= indicator of the change in the thermodynamic properties of the polymer matrix in presence of the filler particles

energy distribution of the polymer molecules close to the particle surface



weak particle / matrix interaction

Tg almost unaffected

strong particle / matrix interaction

Tg ↑ (hindered chain mobility)