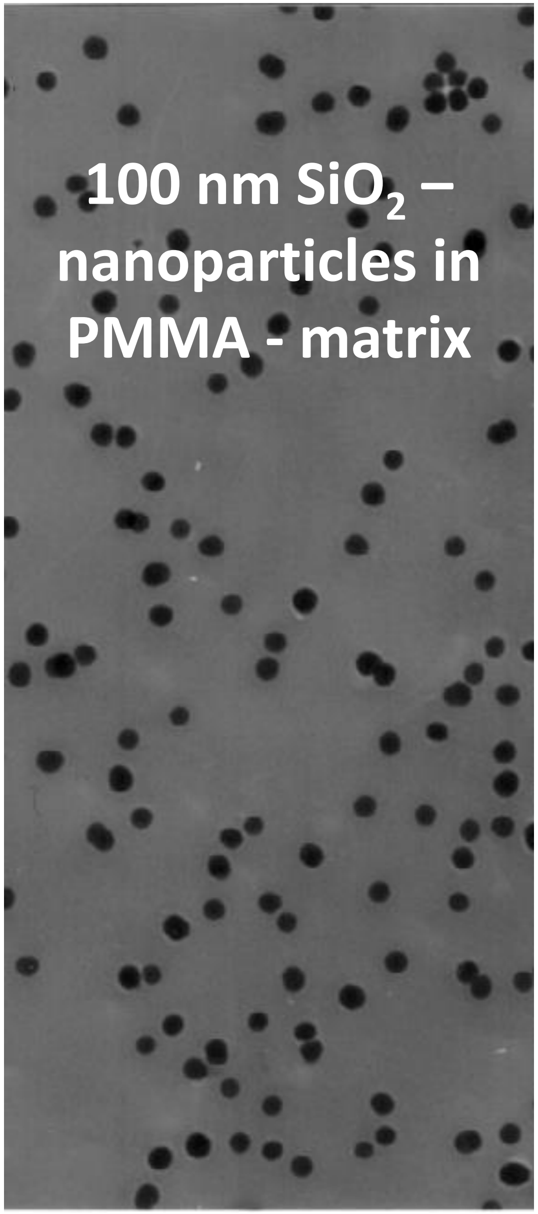
New Ideas. New Materials.

INM



POLYMERMATRIX (NANO)KOMPOSITE

Vorlesung Nanobiomaterialien WS 2016/2017

Dr. – Ing. Carsten Becker-Willinger

Generelle Zielsetzung Komposit-Bildung

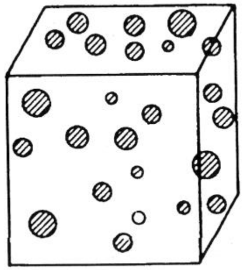
- **Verbesserung der Eigenschaften von Bauteilen / Oberflächen** durch die **Kombination von zwei oder mehreren verschiedenen Phasen**.
  - Die Materialarten der verschiedenen Phasen können gleich oder verschieden sein.

- **Beispiele**:
  - **Spannbeton**: Kombination Beton / Stahl zum Abfangen von Zugspannungen im Beton
  - **Holz**: natürliches organisches Komposit, Verbindung von Cellulose-Fasern durch Lignin
  - **Metallgeflechte in Glas**

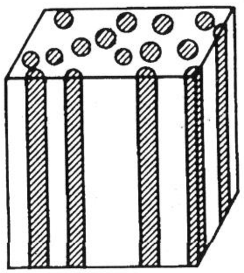
- **Zielsetzung**: hohe Festigkeit bei niedriger Dichte
  - Keramische Verbindungen aus Elementen mit niedriger Ordnungszahl (B, SiC, Al_2O_3,...)
- **Nachteil**: hohe Mikrorißempfindlichkeit, geringe Zugfestigkeit der reinen Keramiken
- **Lösung**: Einbettung in plastisch verformbare Grundmasse (z.B. Polymer)

Einteilung nach Gefügen

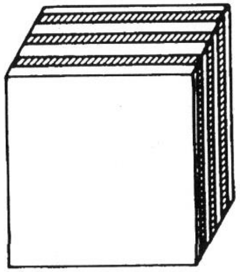
- **Isotrope Gefüge**
  - Hartmetalle, Cermets, Tränkwerkstoffe, Nanomere,…



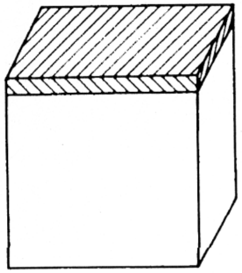
- **Faserverbunde**
  - GFK, KFK, Glaswolle, Pressspanholz, natürliches Holz,…



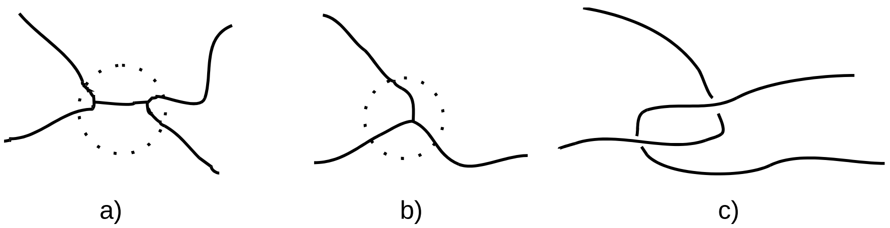
- **Laminate**
  - Sperrholz, Sicherheitsglas,…



- **Oberflächenbeschichtungen**
  - z.B. Korrosions-, Verschleiß-, Anhaftungs-,…minimierend



Strukturmodell der Polymere



•*a) 4-funktionaler, b) 3-funktionaler Vernetzungspunkt und c) Verschlaufung (unvernetztes Polymer)*

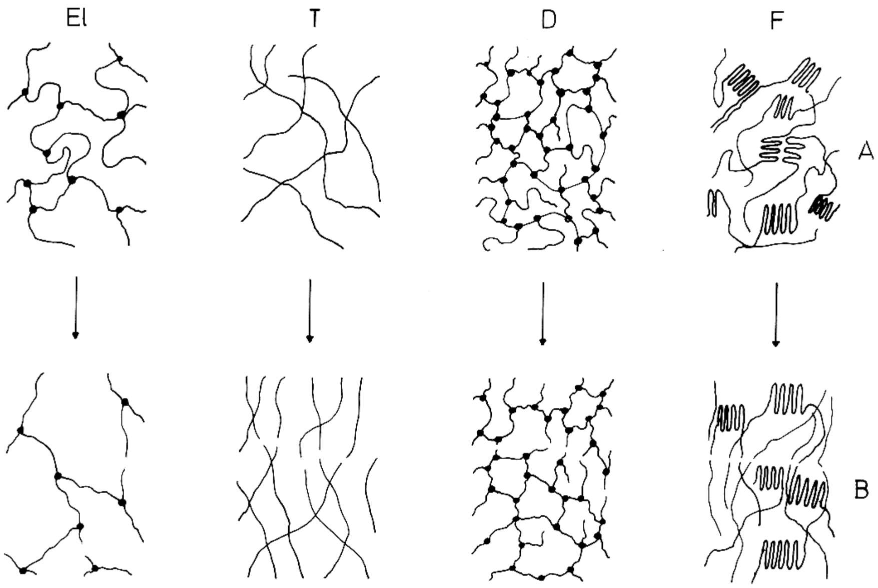


Abb. 15-1 Schematische Darstellung des Dehnungsverhaltens von Elastomeren El, Thermoplasten T, Duroplasten D und Fasern F vor der Verstreckung (A) und nach den Bruch (B). • Vernetzungen.

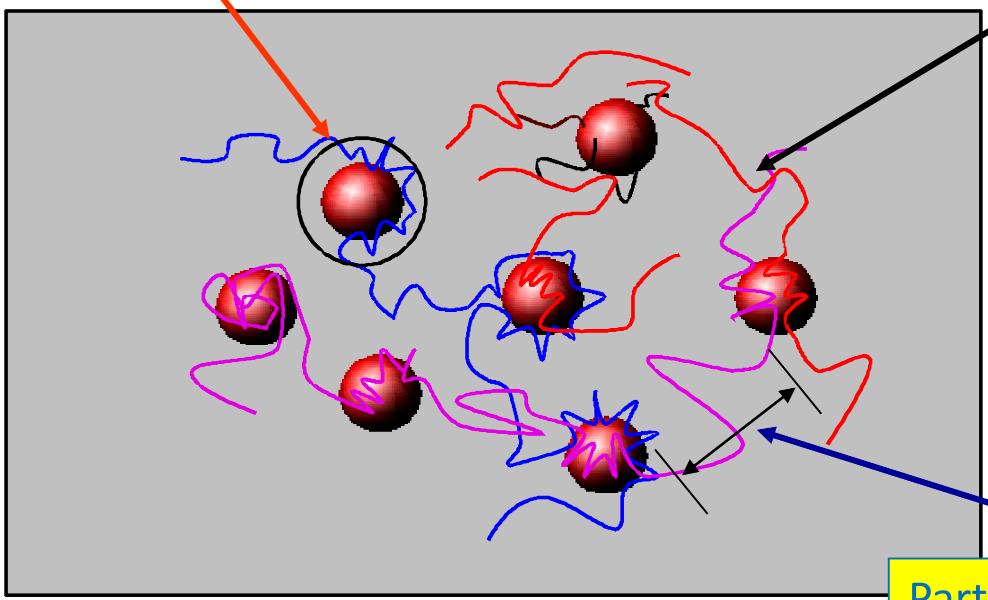
Quelle:
H.G. Elias,
Makromoleküle

Nanoparticles in polymer matrix (idealised view)

Polymer type matrix + inorganic nanoparticles = nanocomposite

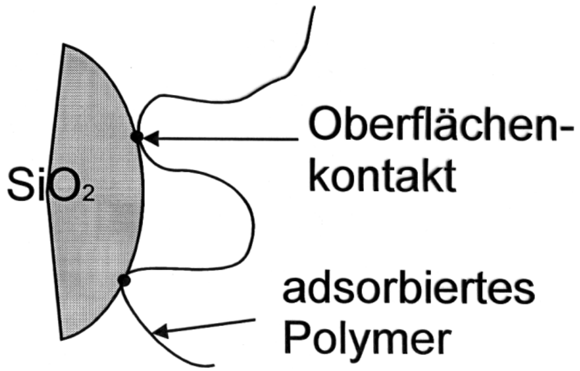
Polymer / particle contacts:
Interfacial layers of adsorbed
Polymer molecules

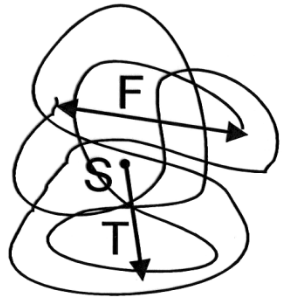
Free linear chain molecules
Entanglements
Covalent network points



Particle / particle contacts:
Interparticulate distance
(matrix ligament thickness)

Größenverhältnisse



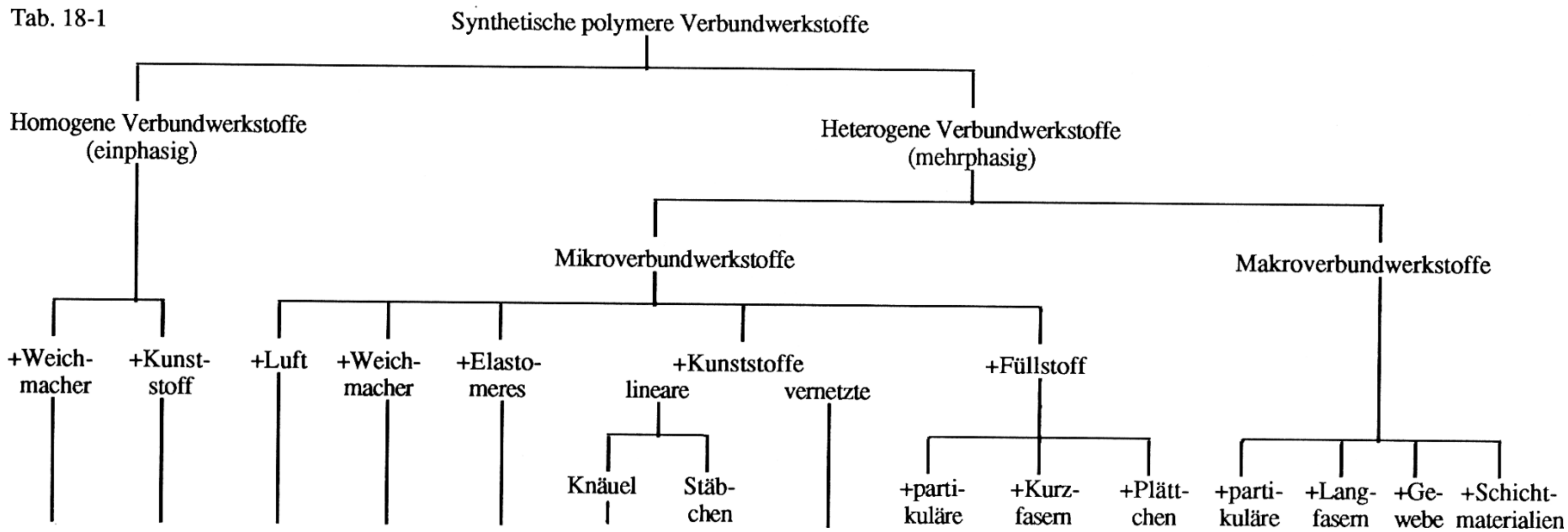


ϕ Nanopartikel: ca. 5 - 15 nm

- **Dimensionen der Polymermoleküle**
- unvernetztes PMMA: $M_n = 1*10^6$ g/mol
- ca. 10.000 Monomereinheiten
- gestreckte Kette: 2,5 µm
- Fadenendenabstand (F): 30 nm
- Trägheitsradius (T): 12 nm

Übersicht polymere Verbundwerkstoffe

Tab. 18-1

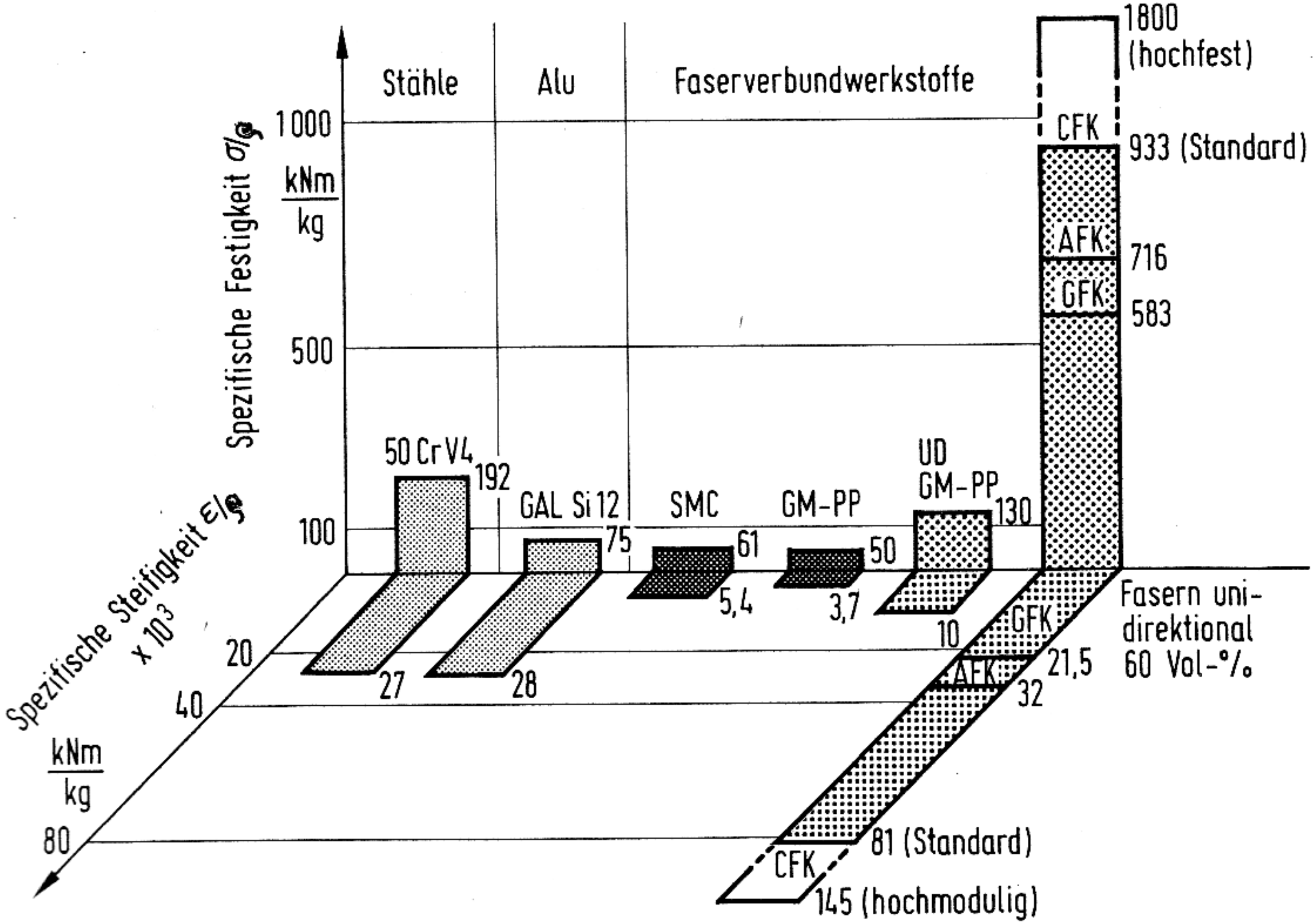


+Weichmacher	+Kunststoff	+Luft	+Weichmacher	+Elastomeres	Knäuel	Stäbchen	vernetzte	+partikuläre	+Kurzfasern	+Plättchen	+partikuläre	+Langfasern	+Gewebe	+Schichtmaterialien
Spezielle Namen falls $T_G > T_{Gebrauch}$ bei der kontinuierlichen Phase aus Kunststoffen														
Weichgemachtes Polymer	Polymer-Blend; Polymer-Legierung	Hartschaumstoff*)	Weichgemachter Kunststoff	schlagzäher Kunststoff	Polymer-Blend	Molekularer Verbundstoff	Interpenetrierendes Netzwerk	Gefüllter (verstärkter) K.	Faserverstärkter Kunststoff	Verstärkter Kunststoff	Polymerzement	Faserverstärkter K.	Harzmatte	Laminat
Spezielle Namen falls $T_G < T_{Gebrauch}$ bei der kontinuierlichen Phase aus Elastomeren														
Öl-plastifizierter Gummi	Gummimischung	Weichschaumstoff**)	-	Gummi-Mschg.	Thermoplastisches Elastomeres	-	-	verstärkter Gummi	-	-	-	-	-	-

*) auch: zellulärer Kunststoff, Hart-Schaumkunststoff; **) auch: Schaumgummi

Quelle: Saechtling

Spezifische Steifigkeit, spezifische Festigkeit



Quelle: Saechtling

Steifigkeits-Festigkeitsrelation

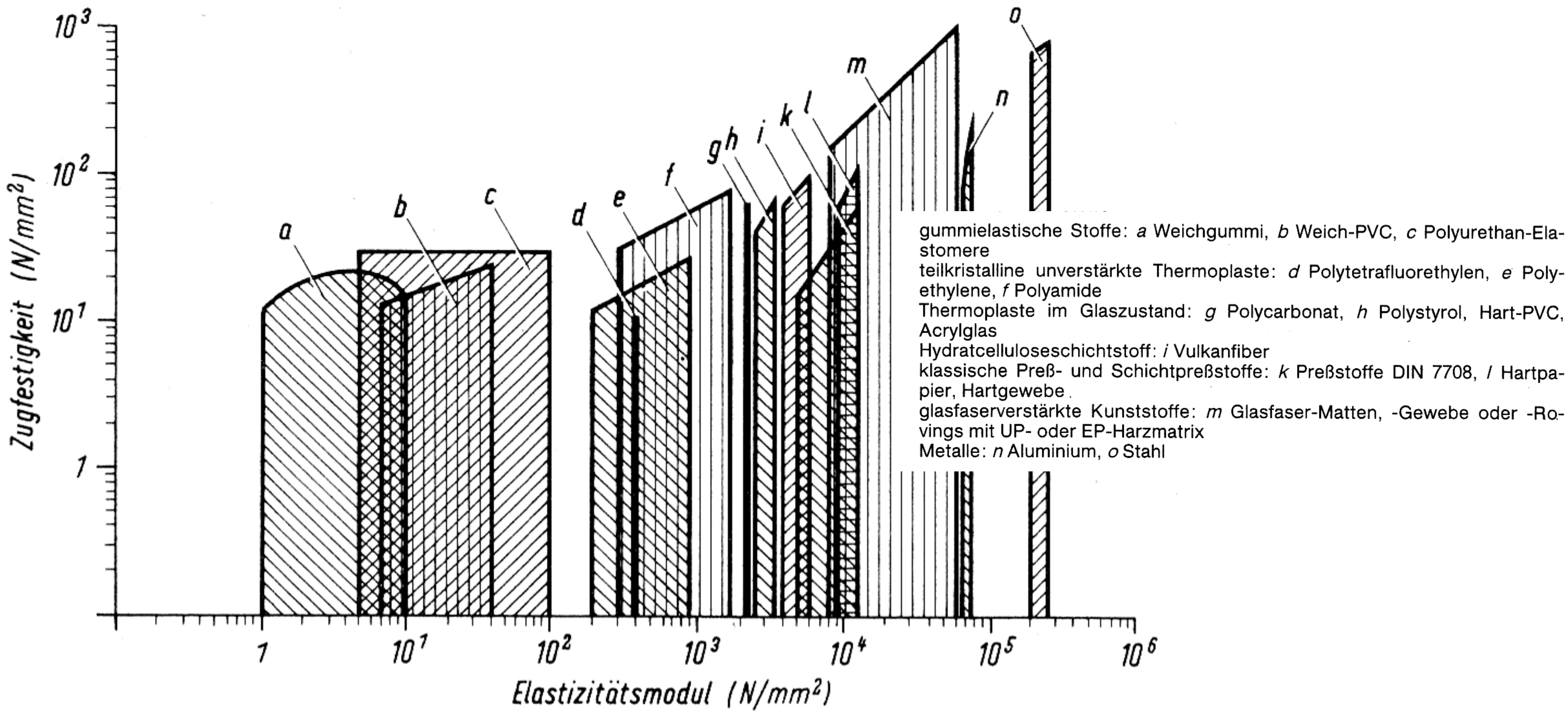
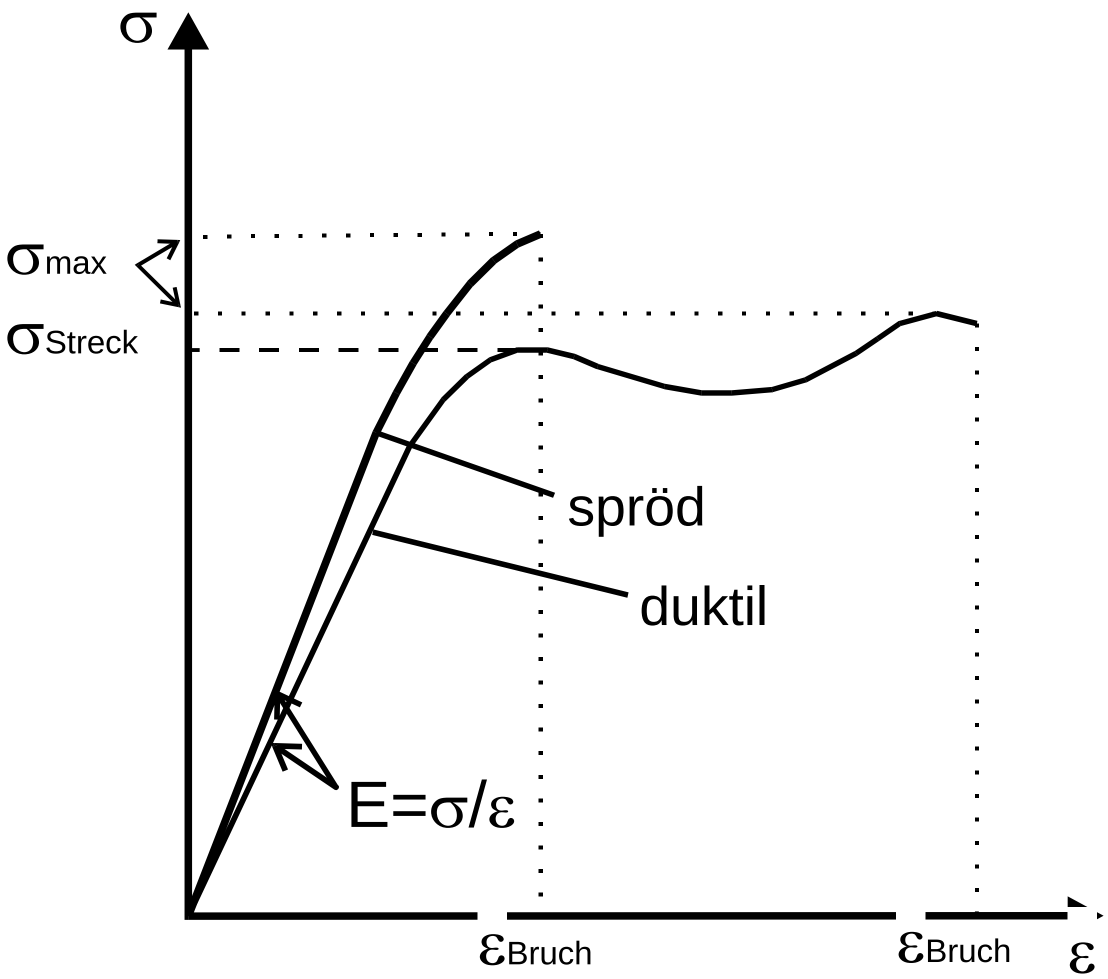


Bild 1.7. Zugfestigkeits- und Elastizitätsmodul-Bereiche gummielastischer bis stahlelastischer Werkstoffe

Quelle: Saechtling

Mechanische Eigenschaften spröder und duktiler Polymere (z.B. Zugversuch)



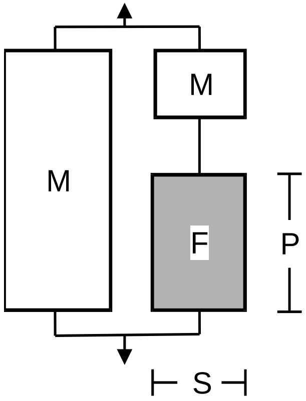
Modellbetrachtung zum E-Modul von Kompositen

Guth - Gold - Smallwood

$$E_K = E_M \left(1 + (1 + A)\frac{\phi}{\phi_{max}} + 14{,}1\,\phi^2 \right)$$

ϕ_{max}: maximaler Füllstoffgehalt,

$$A = \frac{7 - 5\mu}{8 - 10\mu}$$: Konstante, μ: Poisson-Verhältnis



Kerner - Lewis - Nielsen

$$\frac{G_K}{G_M} = \frac{1 + AB\phi_F}{1 - B\psi\phi_F}$$

$$B = \frac{(G_F / G_M) - 1}{(G_F / G_M) + A}$$

$$\psi\phi_F = \left[1 + \left(\frac{1 - \phi_{max}}{\phi_{max}^2} \right) \phi_F \right] \phi_F$$

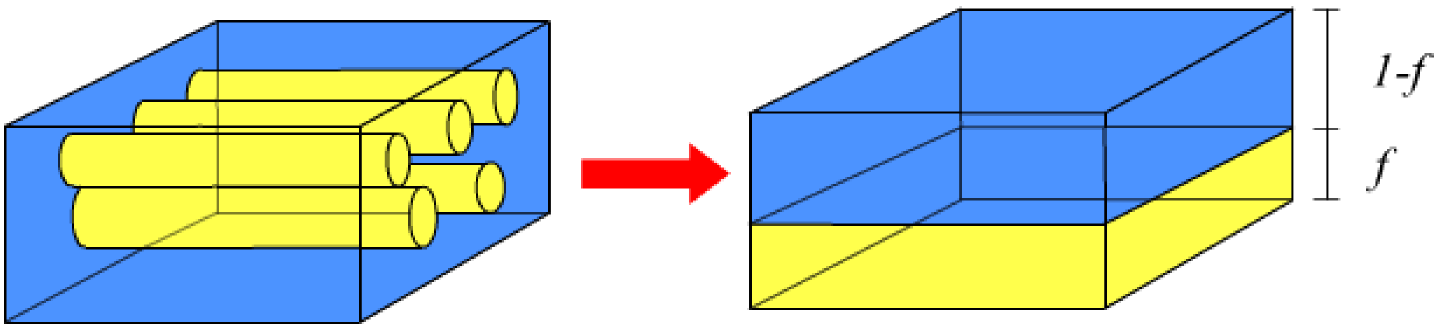
Obergrenze:

$$E_{seriell} = (1 - \phi) E_M + \phi E_F$$

Untergrenze:

$$E_{parallel} = \left(\frac{1 - \phi}{E_M} + \frac{\phi}{E_F} \right)^{-1}$$

The rule of mixtures and the inverse rule of mixtures



Composite material showing aligned fibres within the matrix

The approximation used in the Rule of Mixtures

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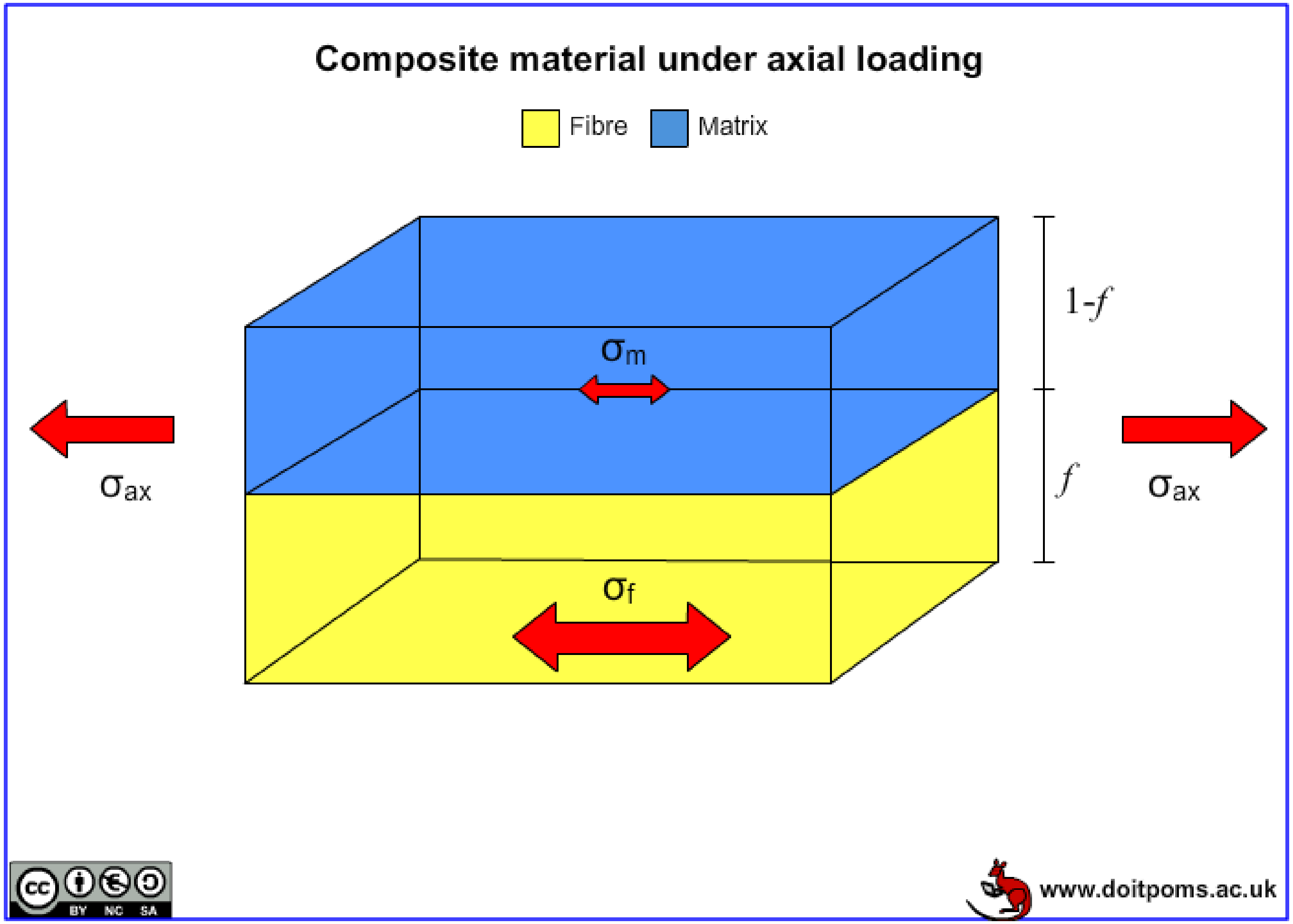
http://www.doitpoms.ac.uk/tlplib/bones/derivation_mixture_rules.php

Force applied in a direction parallel to the long axes of the fibres

equal strain



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http://www.doitpoms.ac.uk/tlplib/bones/derivation_mixture_rules.php

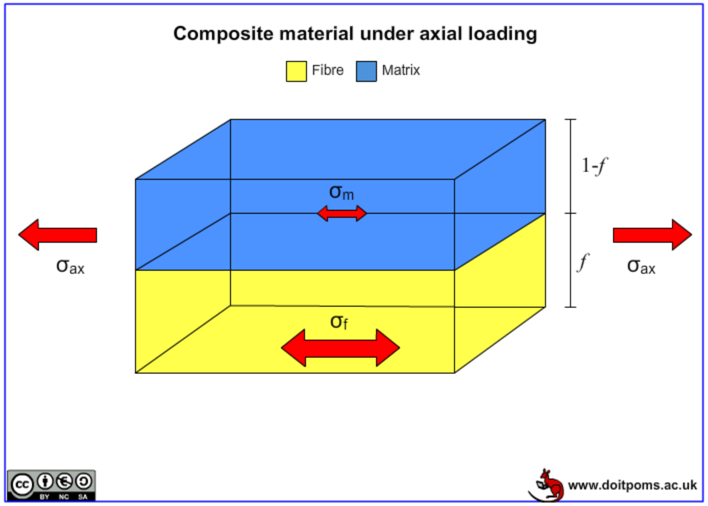
Force applied in a direction parallel to the long axes of the fibres (II)

$$\varepsilon_{ax.} = \varepsilon_f = \varepsilon_m \qquad \text{(i)}$$

equal strain

As $$\varepsilon = \frac{\sigma}{E} \qquad \text{(ii)}$$

$$\varepsilon_{ax} = \varepsilon_f = \frac{\sigma_f}{E_f} = \varepsilon_m = \frac{\sigma_m}{E_m} \qquad \text{(iii)}$$



As stress is force per unit area, it can also be seen that the overall stress,

$$\sigma_{ax} = f\sigma_f + (1-f)\sigma_m \qquad \text{(iv)}$$

Combining equations (iii) and (iv) gives an expression for the axial Young's Modulus

$$E_{ax.}\varepsilon_{ax.} = fE_f\varepsilon_f + (1-f)E_m\varepsilon_m \qquad \text{(v)}$$

Rule of mixtures

and since $\varepsilon_{ax.} = \varepsilon_f = \varepsilon_m$

$$E_{ax.} = fE_f + (1-f)E_m \qquad \text{(vi)}$$

see analogy

$$E_{seriell} = (1-\phi)E_M + \phi E_F$$

(= serial coupling S from Kerner's equation)

This is known as the **Rule of Mixtures**.

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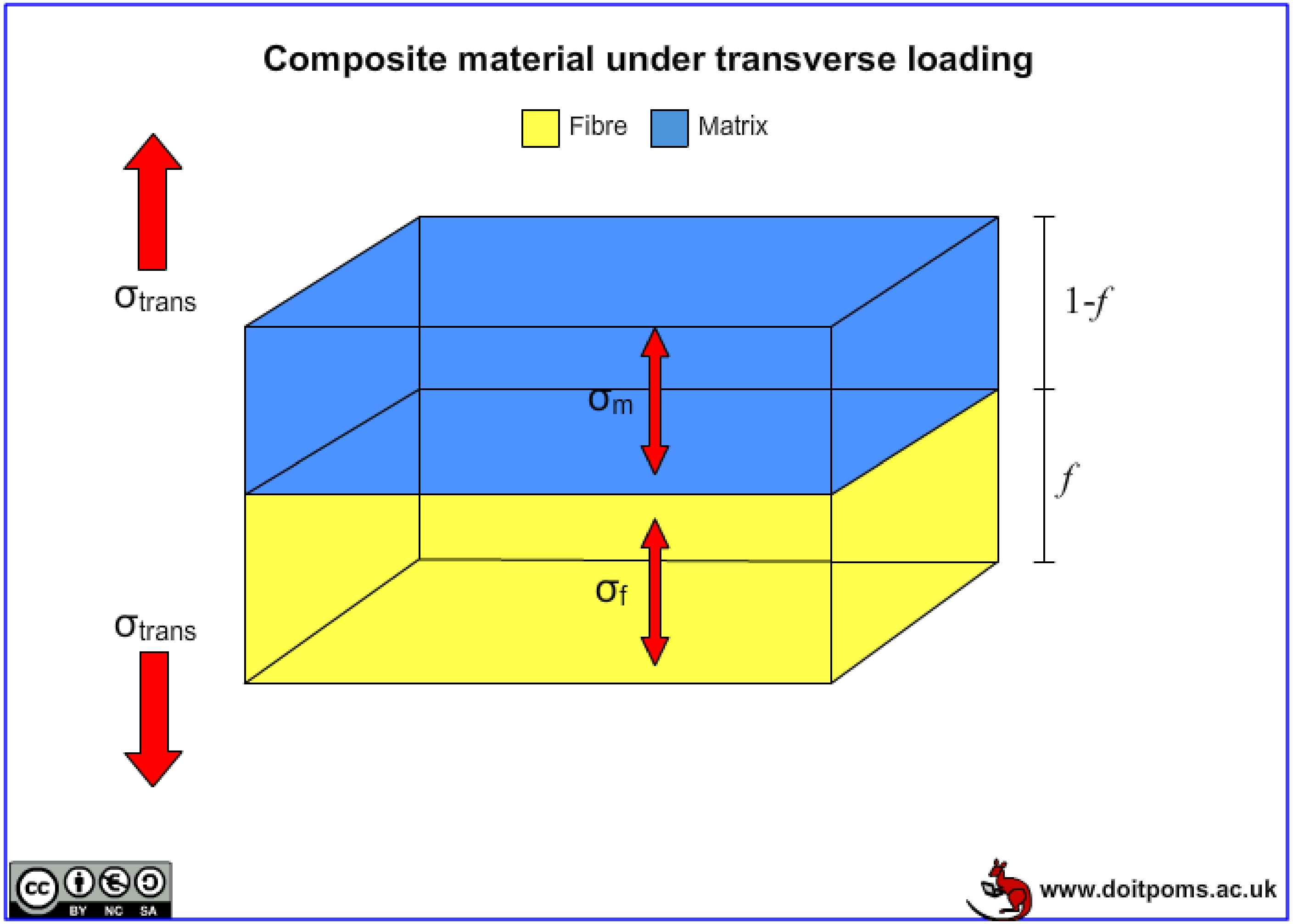
http://www.doitpoms.ac.uk/tlplib/bones/derivation_mixture_rules.php

Transverse stiffness:
Load is applied perpendicular to the fibres

equal stress



http://www.doitpoms.ac.uk/tlplib/bones/derivation_mixture_rules.php

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Transverse stiffness if the load is applied perpendicular to the fibres (⊥)

In this case an equal stress assumption is mad'

$$\sigma_{trans} = \sigma_f = E_f \varepsilon_f = \sigma_m = E_m \varepsilon_m \qquad \text{(vii)}$$

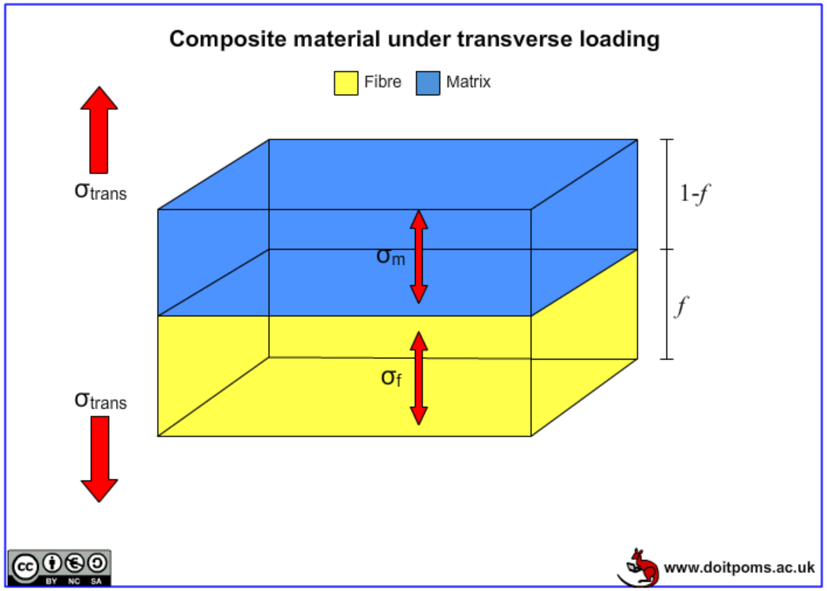
equal stress

The overall strain in the composite is:

$$\varepsilon_{trans.} = f\varepsilon_f + (1-f)\varepsilon_m \qquad \text{(viii)}$$

The transverse modulus of the composite is then given by:

$$E_{trans.} = \frac{\sigma_{trans}}{\varepsilon_{trans}} = \frac{\sigma_f}{f\varepsilon_f + (1-f)\varepsilon_m} = \left[\frac{f}{E_f} + \frac{(1-f)}{E_m}\right]^{-1}$$



This is known as the **Inverse Rule of Mixtures**. It is not as accurate as the Rule of Mixtures because the equal stress assumption is not entirely valid – parts of the matrix will be shielded from stress by the fibres.

Inverse rule of mixtures

see analogy

$$E_{parallel} = \left(\frac{1-\phi}{E_M} + \frac{\phi}{E_F}\right)^{-1}$$

(= parallel coupling P from Kerner's equation)

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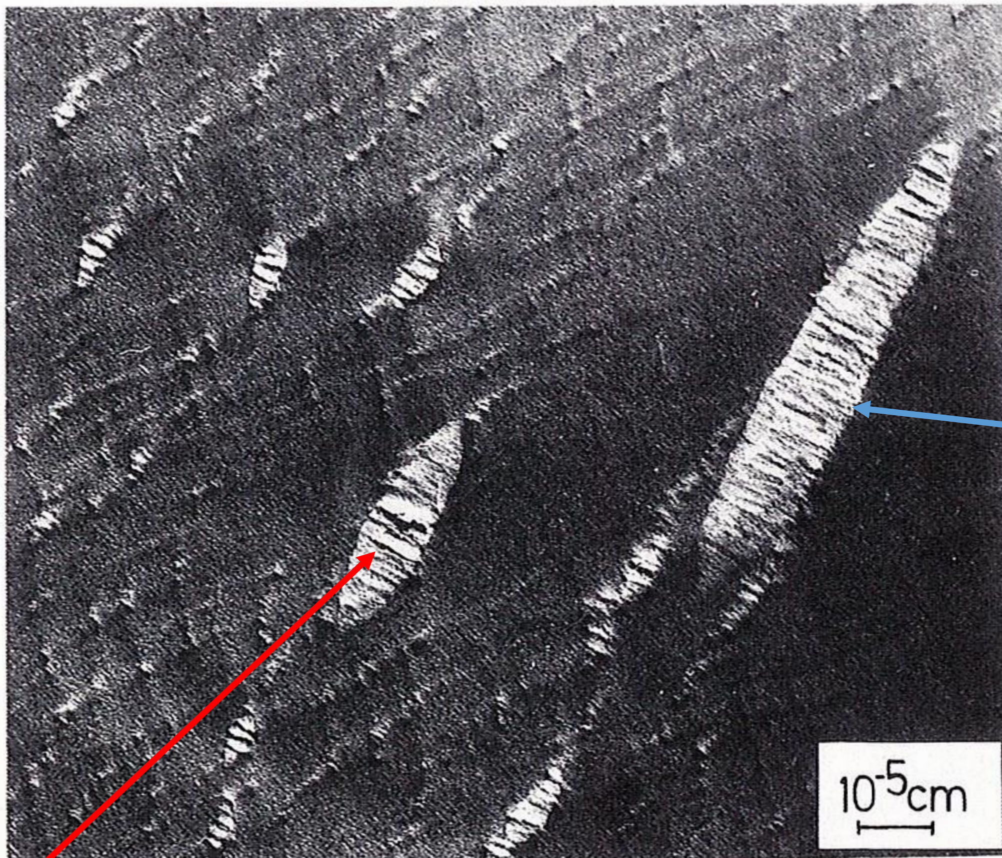
http://www.doitpoms.ac.uk/tlplib/bones/derivation_mixture_rules.php

Morphology of the crazes



ε = 25 %

polystyrene
M_w: 97.000 g/mole

craze

tensile load

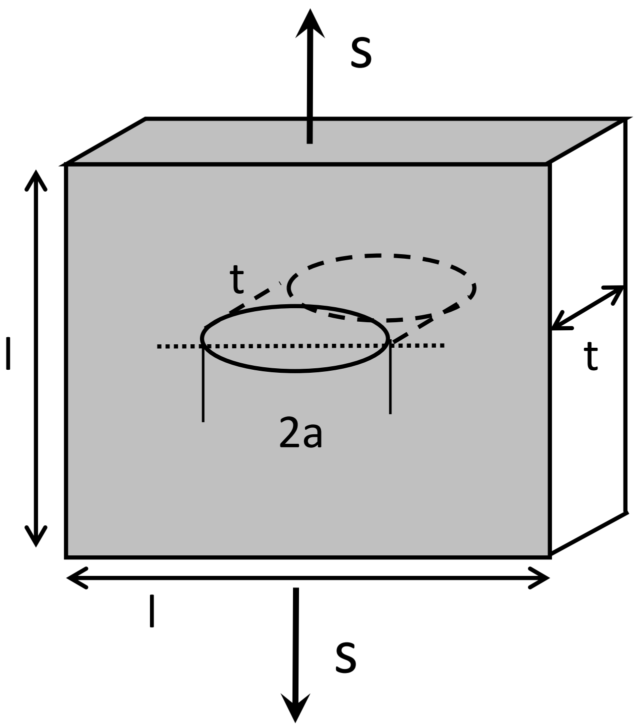
polymer fibrils

crack propagation

S. Wellinghof, E. Baer

Griffith theory

elastic plate (l→∞) with elliptic crack



released elastic deformation energy (driving force):

$$U_E = -\frac{1}{2}\sigma\varepsilon(V_{el}) = -\frac{1}{2}\sigma\varepsilon\left(2\pi a^2 t\right) = -\frac{\sigma^2\pi a^2 t}{E}$$

required surface energy (acts again crack propagation)

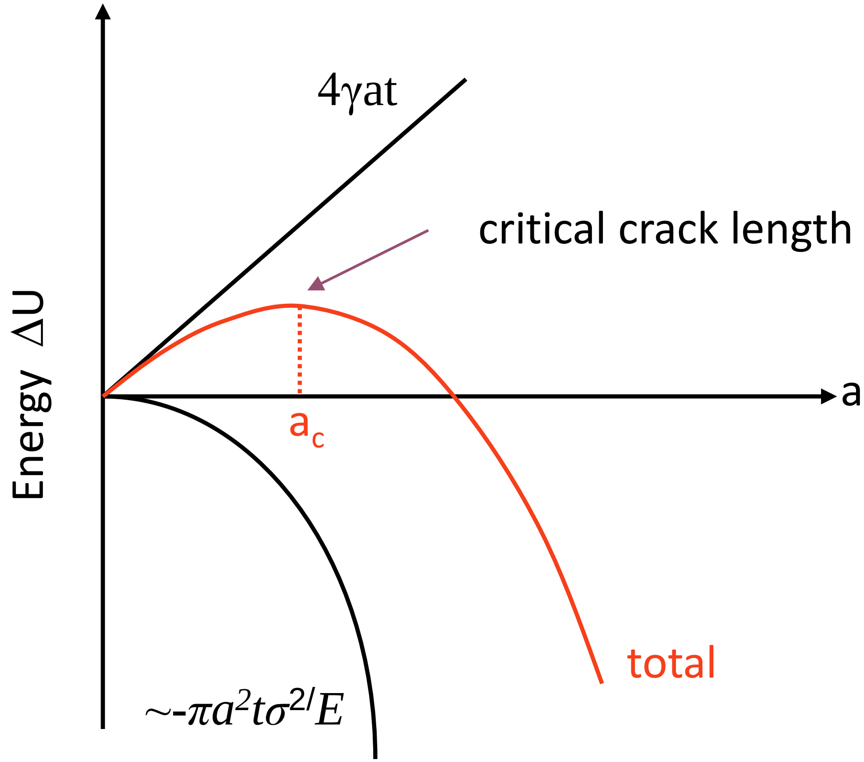
$$U_{OF} = 2\left(\gamma A_{crack}\right) = 2\left(\gamma 2at\right) = 4\gamma at$$

change of the potential energy by crack formation

$$\Delta U = U_{OF} + U_E = 4\gamma at - \frac{\sigma^2\pi a^2 t}{E}$$

Griffith theory

graphic presentation



Griffith theory

- crack propagates under applied constant stress if $U_E > U_{OF}$

- requirement for (instable) equilibrium:

$$\frac{d\Delta U}{da} = 0 = \frac{d(U_E + U_{OF})}{da} = -\frac{2\pi a \sigma^2 t}{E} + 4\gamma t = 0$$

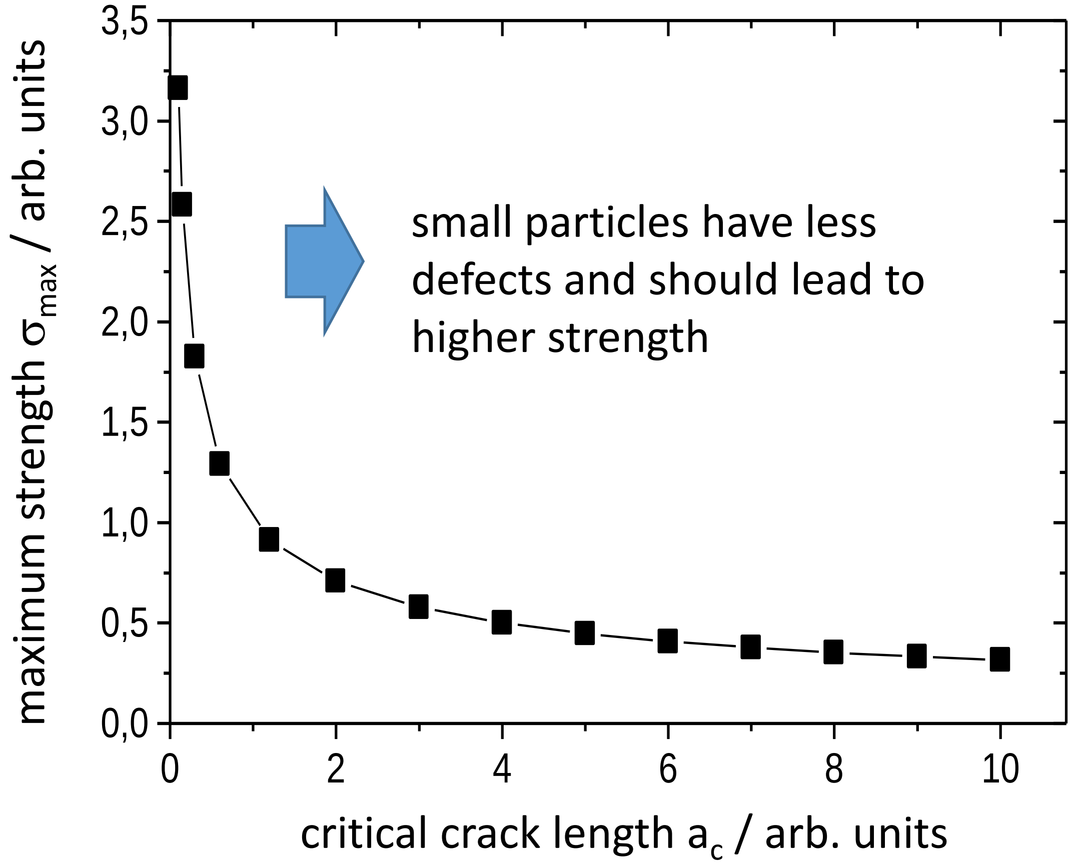
- required stress of break for instable crack propagation:

$$\boxed{\sigma \geq \sigma_C = \sqrt{\frac{2\gamma E}{\pi a}}}$$

Model calculation to critical crack length (Griffith theory)

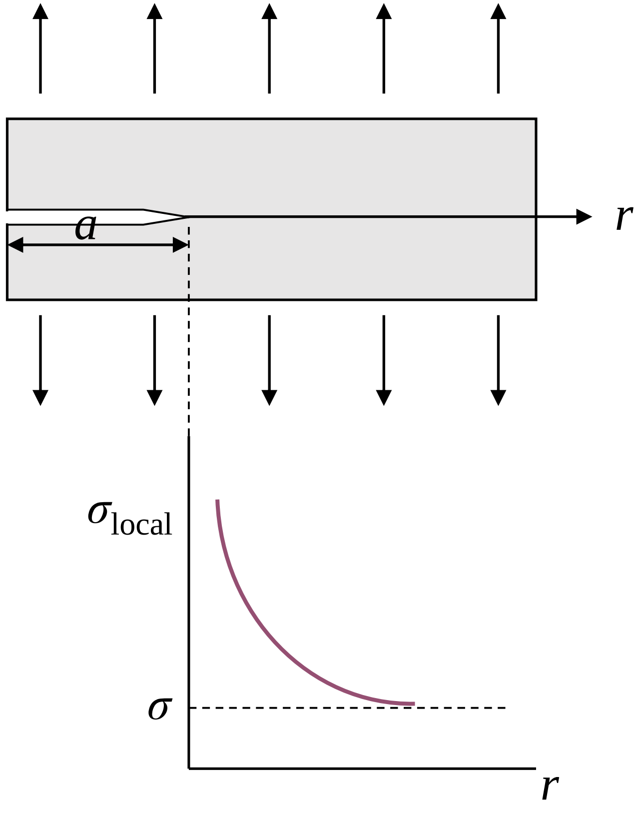
$$\sigma \geq \sigma_C = \sqrt{\frac{2\gamma E}{\pi a}}$$

$$\sigma_{max} \propto \frac{1}{\sqrt{a_c}}$$



Failure mechanics

- brittle materials:
- high stress concentrations at the crack tip
- elastic deformations that reduce the strength below σ_{th}



$$\sigma_{local} = \sigma\left(1 + Y\sqrt{\frac{\pi a}{2\pi r}}\right)$$

near the crack ($a >> r$) :

$$\sigma_{local} = Y\frac{\sigma\sqrt{\pi a}}{\sqrt{2\pi r}}$$

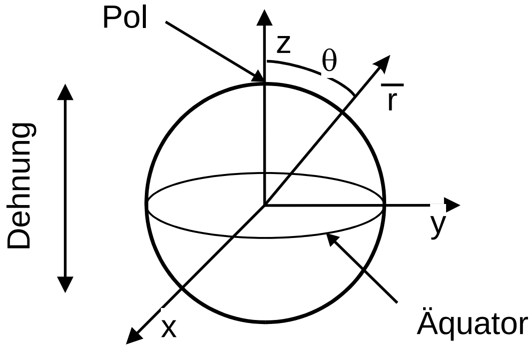
stress intensity factor

$$K_I = Y\sigma\sqrt{\pi a}$$

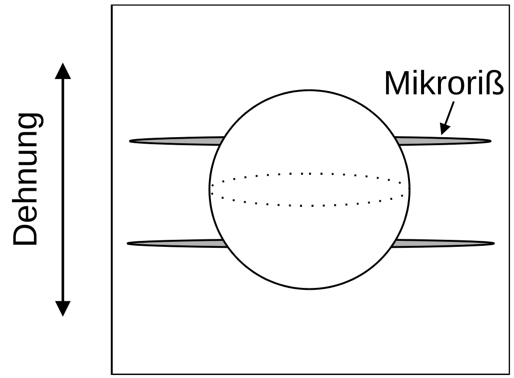
fracture occurs if:

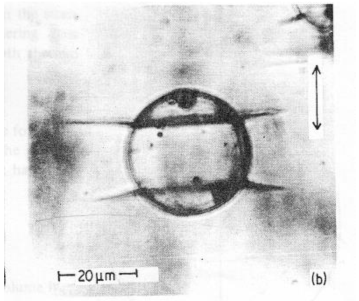
$$K_I > K_{IC}$$

Mikrodeformationsverhalten in Kompositen

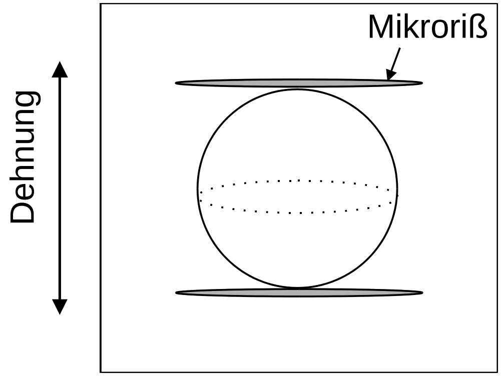


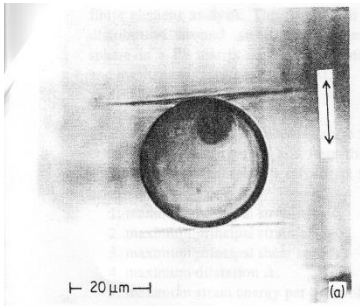
Schlechte Phasenanbindung





Gute Phasenanbindung





M.E.J. Dekkers, D. Heikens,
J. Mater.Sci. 18 (1983), 3281-3287

Mikrodeformationsverhalten in Kompositen

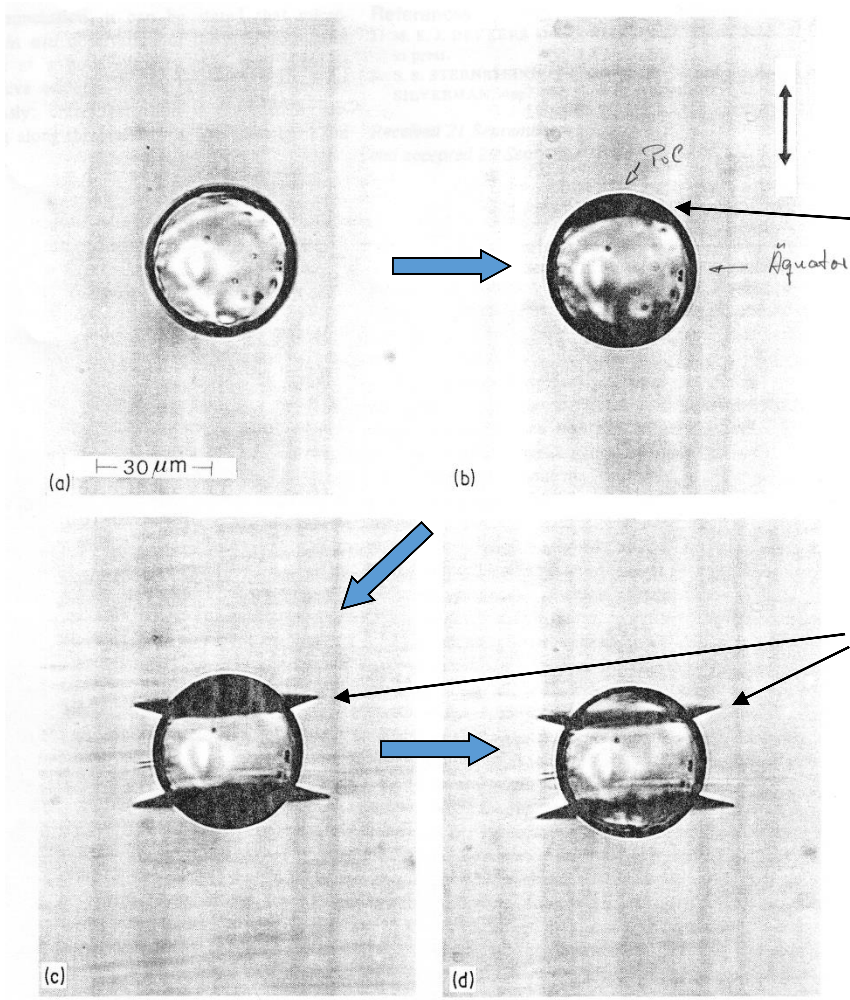


Figure 1 Successive stages of the craze formation process at a poorly adhering glass bead. (a) Specimen before straining; (b) dewetting; (c) craze formation; (d) craze pattern after removal of the applied strain. The arrow indicates the applied strain direction. Note that, besides at the glass bead, crazes are also formed at surface flaws. Two small surface crazes are clearly visible in Figs. 1c and d at the left side of the bead near the equator. These crazes were observed to grow from the surface of the specimen into the material where they reached the bead.

dewetting, voiding

bei schlechter Phasenanbindung

crazing

M.E.J. Dekkers, D. Heikens,
J. Mater.Sci. Lett. 3 (1984), 307-309

Composites with (short) fibres

- mechanical load **perpendicular to fibre orientation ($\perp$)**:
  - yield stress, max. stress and elongation at break:
    - determined by the weaker phase (if not interfacial adhesion getting lost)
- mechanical load **in fibre orientation (II):**
  - external stress σ_β is acting via **shear stress** $\tau_{\alpha\beta}$ on the fibre surface
- $\tau_{\alpha\beta} > \sigma_\beta$ $\Rightarrow$ rupture of the fibres
- $\tau_{\alpha\beta} < \sigma_\beta$ $\Rightarrow$ deformation of the matrix, de-lamination, pull-out

- critical fibre length is defined as

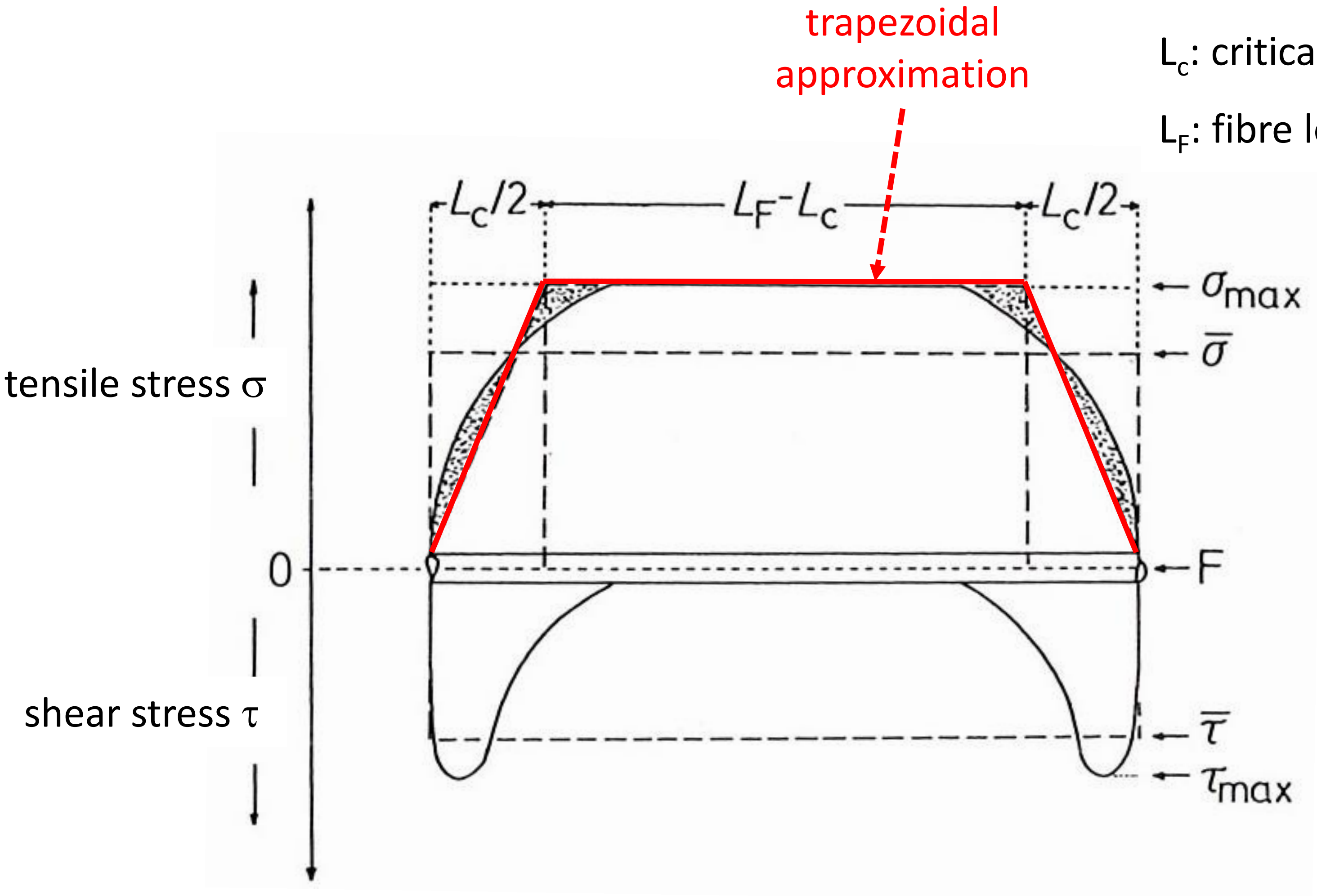
- $L_c = \dfrac{\sigma_\beta \; r_F}{\tau_{\alpha\beta}}$

= length of those fibres that can be pulled out of the matrix <u>without break</u>

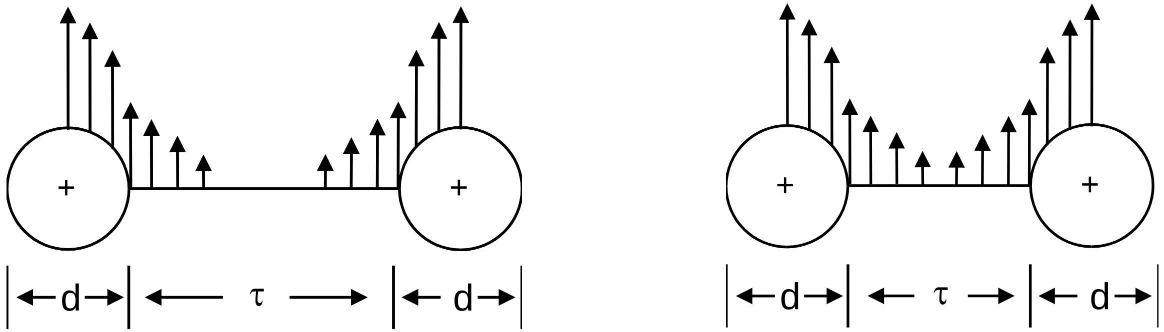
Stress distribution along fibres

L_c: critical length fibre

L_F: fibre length



Partikel als Spannungskonzentratoren und Überlappung von Spannungsfeldern



Ziel: kontrollierte Rißausbreitung zum Erhalt von Zähigkeit

Interpartikulärer Abstand als wichtige Größe

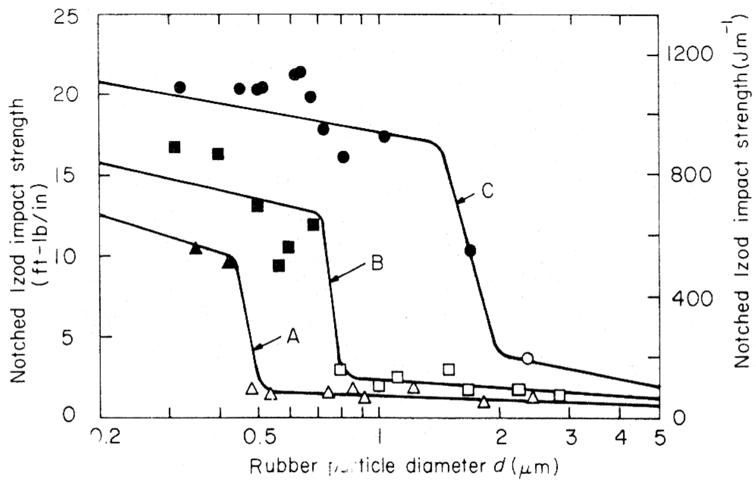


Figure 3 Notched Izod impact strength *versus* PR-rubber number-average particle diameter d_n at constant adhesion $G_a = 8100\ \mathrm{J\ m^{-2}}$ and constant rubber contents curve A: 10%; curve B: 15%; and curve C: 25% by weight. Solid symbols are for tough fracture; open symbols are for brittle fracture

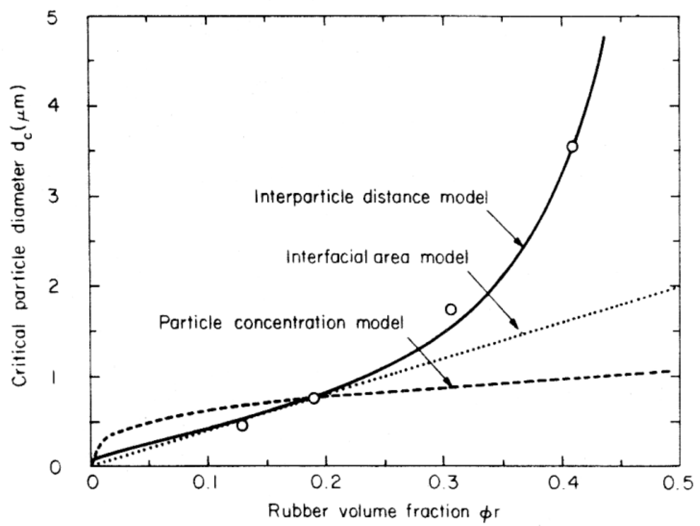


Figure 7 Critical particle diameter for toughening in notched impact *versus* rubber volume fraction. The lines ((———); (·····); (- - - - -)) are theoretical results; (○) experimental results. $T_c = 0.304\ \mu\mathrm{m}$; $N_c = 0.831\ \mu\mathrm{m}^{-3}$; $A_c = 1.508\ \mu\mathrm{m}$

$$d_c = 6\phi_r / A_c \qquad (5)$$

$$d_c = \{(6\phi_r)/(\pi N_c)\}^{1/3} \qquad (6)$$

$$d_c = T_c\{(\pi/(6\phi_r))^{1/3} - 1)\}^{-1} \qquad (7)$$

S. Wu,
Polymer 26 (1985), 1855-1863

Interpartikulärer Abstand als wichtige Größe

CRITERION FOR RUBBER TOUGHENING

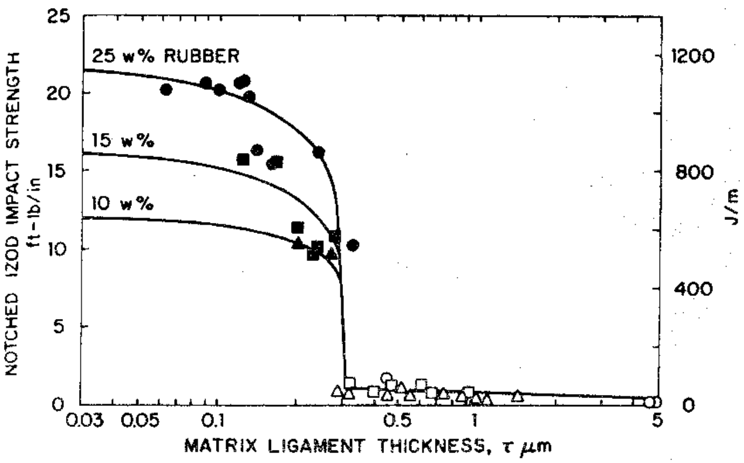


Fig. 3. Notched Izod impact strength vs. matrix ligament thickness for nylon-66/rubber blends. Replotted from Figure 1. Tough: (●) 25 w%; (■) 15 w%; (▲) 10 w% rubber; Brittle: (○) 25 w%; (□) 15 w%; (△) 10 w% rubber. After 1.

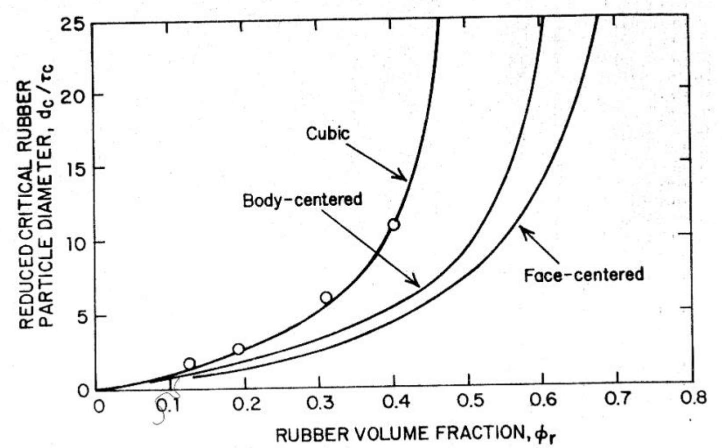


Fig. 4. Reduced critical rubber particle diameter vs. rubber volume fraction for cubic, body-centered, and face-centered lattices. Symbols are experimental for nylon/rubber blends. Lines are theoretical.

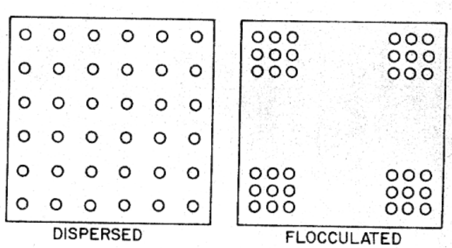


Fig. 7. Schematics of particle dispersion and flocculation.

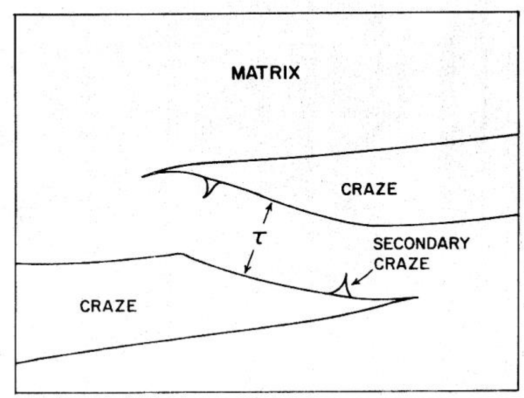


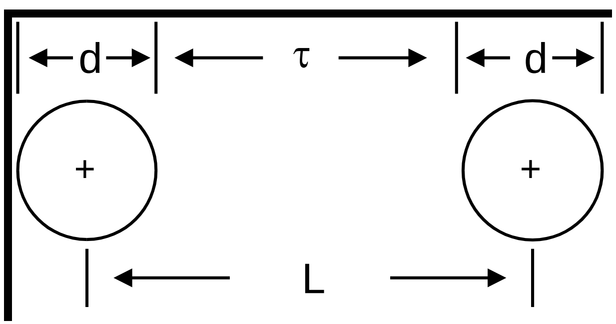
Fig. 10. Schematics of primary crazes, matrix ligament and secondary crazes in the fracture of a polystyrene/rubber blend. Drawn from Ref. 4.

S. Wu,
J. Appl.Polym.Sci 35 (1988), 549-561

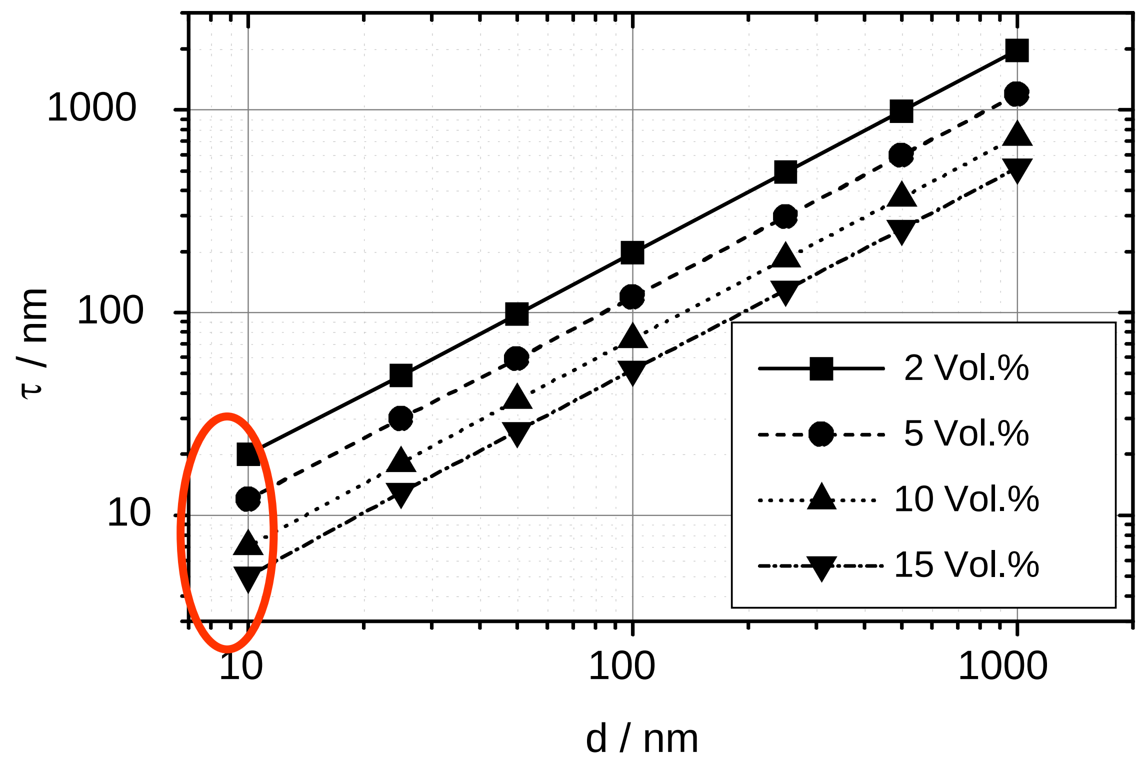
Estimation of the mean interparticulate distance τ (S. Wu et al.)

- Determining parameters: filler content ϕ

  particle size $d = 2r$

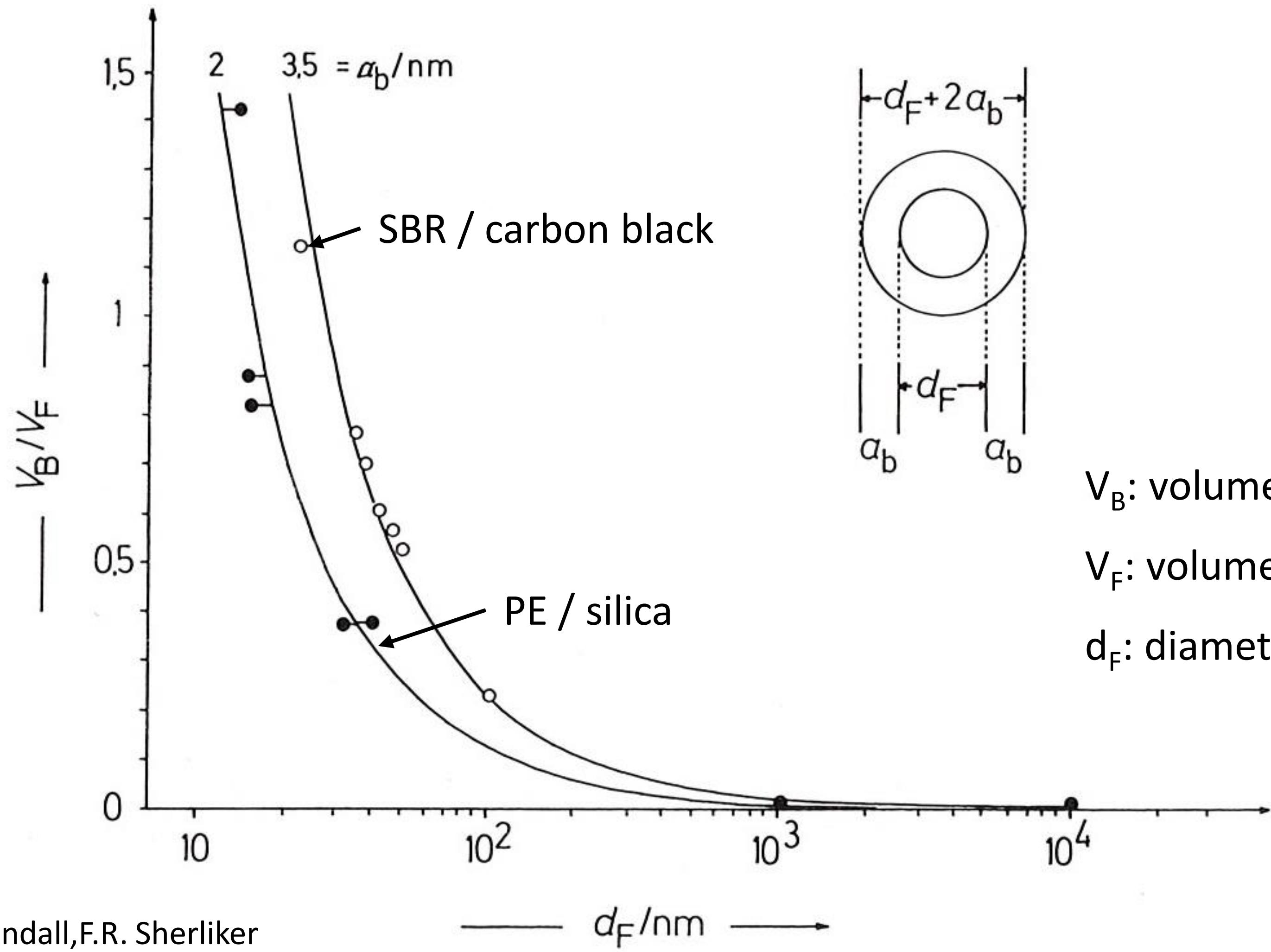


estimation for a simple cubic packing with ϕ_{max} = 0,52



- $L = 2r(\pi/6\phi)^{1/3}$
- $\tau = 2r[(\pi/6\phi)^{1/3}-1]$ = mean matrix ligament thickness

Interfacial layers in polymer matrix composites



V_B: volume bound polymer

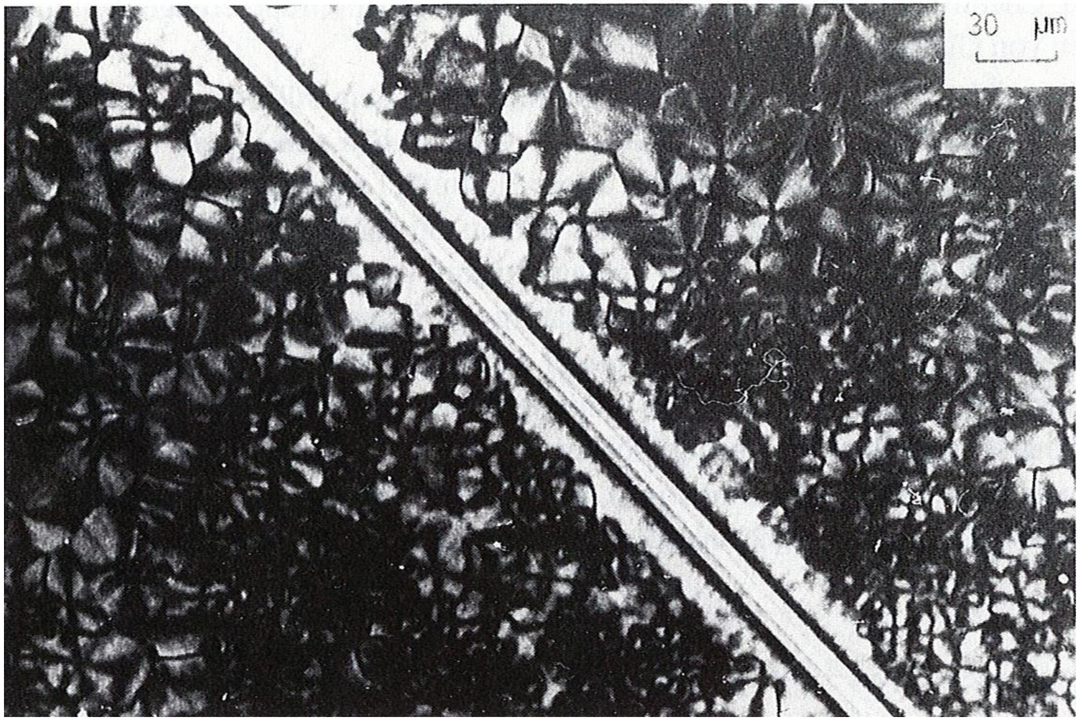
V_F: volume filler

d_F: diameter filler particle

K. Kendall, F.R. Sherliker

Example of a trans-crystalline layer on a fibre

PA-6.6 trans-crystalline layers (5-23 µm wide) on Kevlar fibres

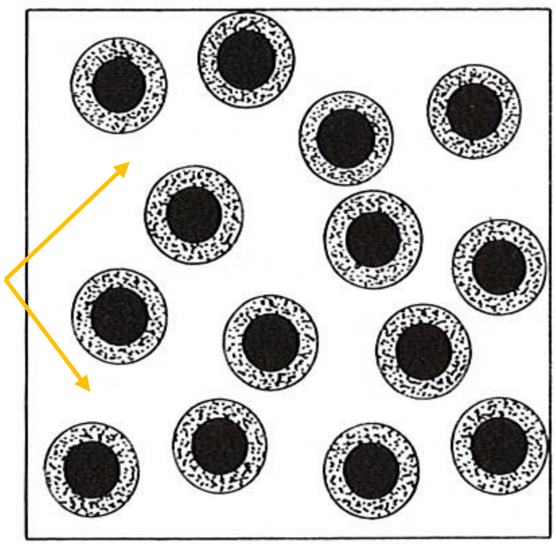


R.H. Burton, M.J.Folkes

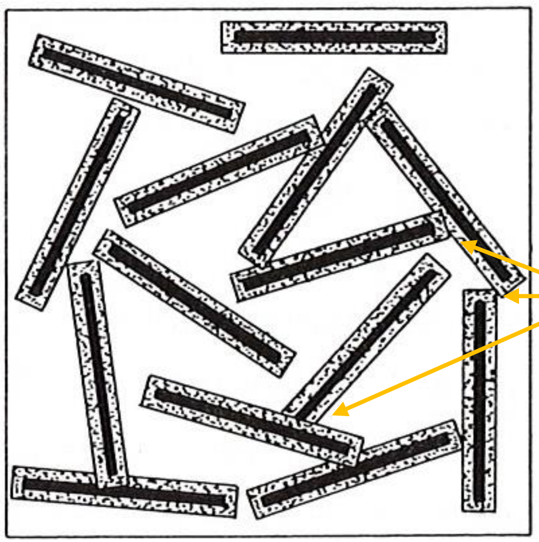
Overlap of interfacial layers in dependence on filler aspect ratio

epitaxial growth of crystalline matrices

no overlap



$\phi_F = 0{,}112$



overlap

$\phi_F = 0{,}112$

ϕ_F: filler volume fraction

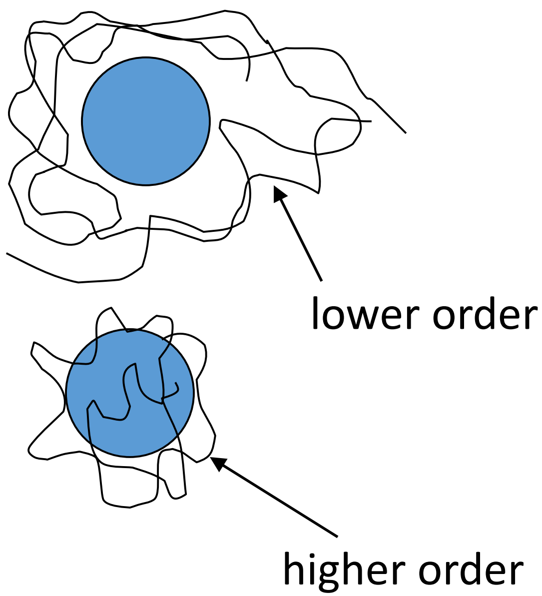
Interfacial layers in nanocomposites

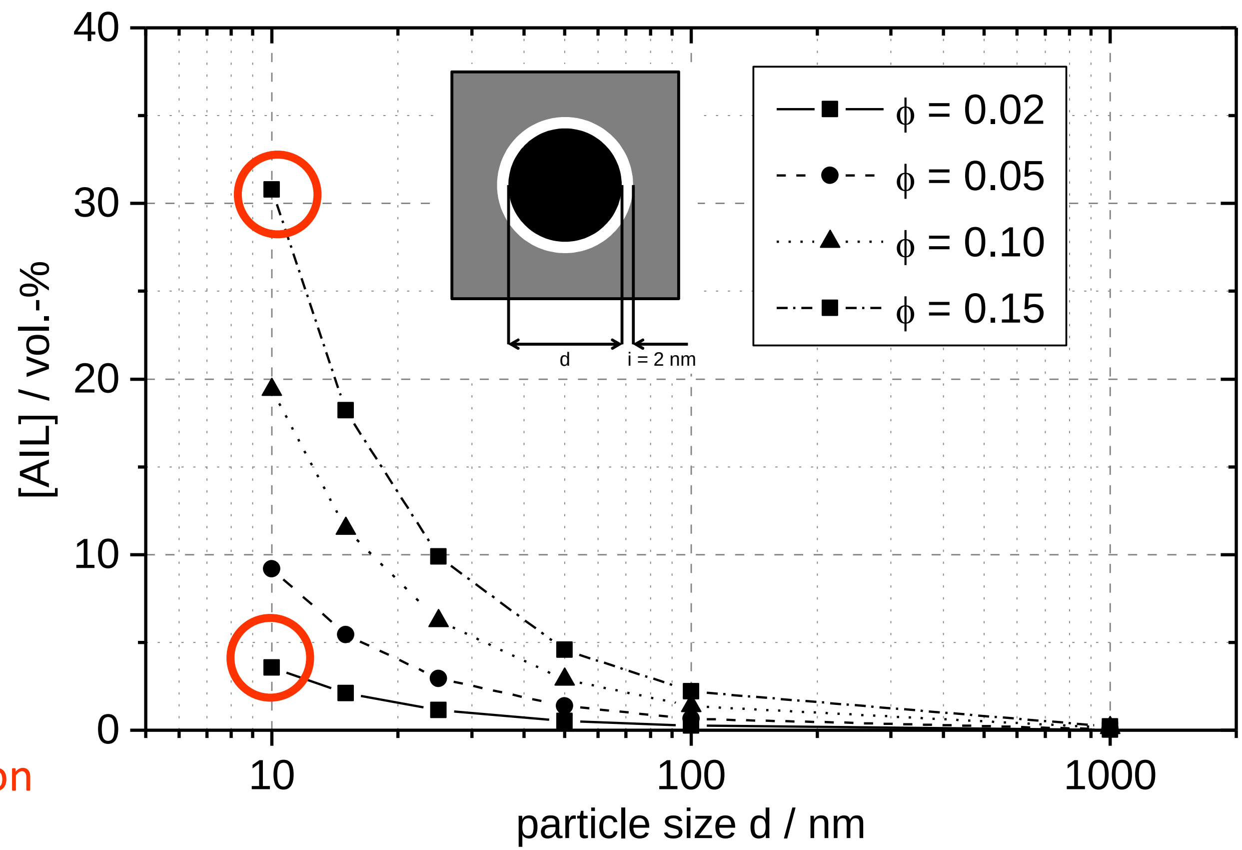
Volume fraction interfacial layer on overall matrix volume

$$[AIL] = [\phi/v(1-\phi)]*(V-v)*100$$

ϕ: filler volume fraction, $d = 2*r$: particle size, $v = 4/3\pi*r^3$: particle volume

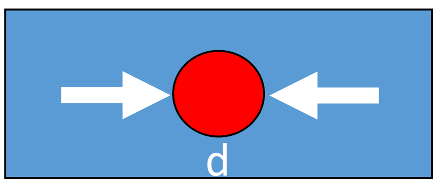
$V = 4/3\pi*(r+i)^3$: volume particle + interfacial layer, r: particle radius, i: interfacial layer thickness

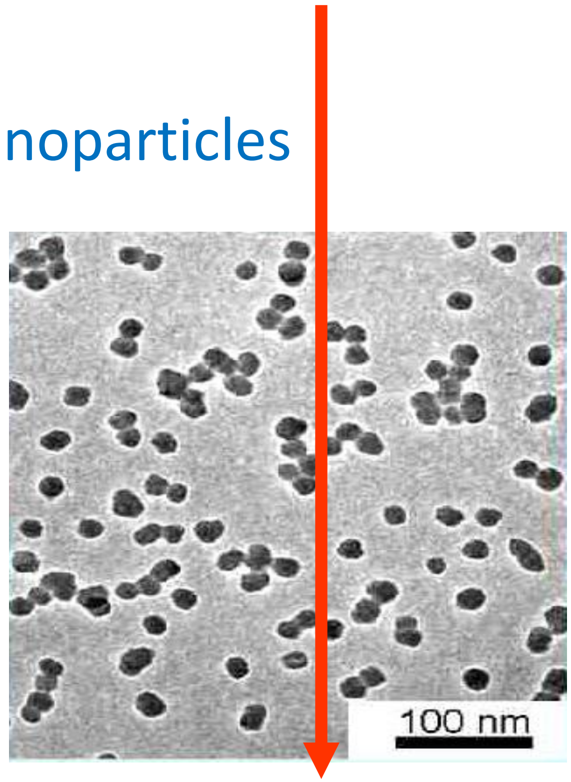


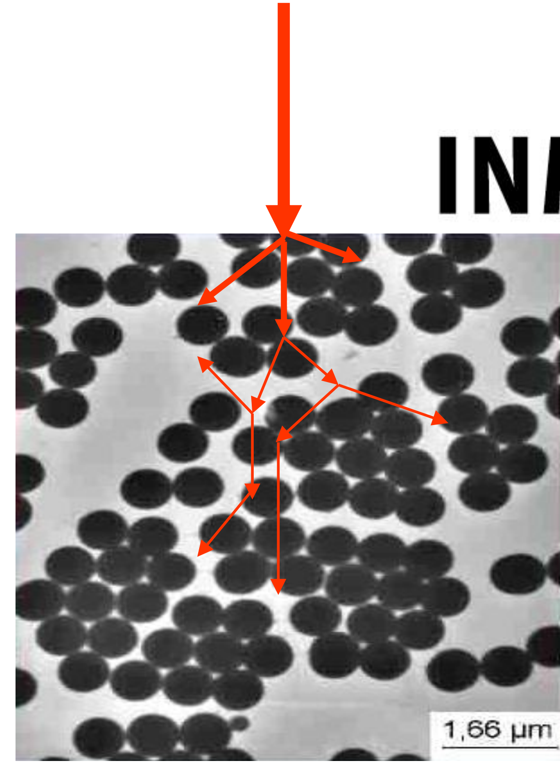


Interfacial layer with significant volume fraction

The attraction of nanoparticles





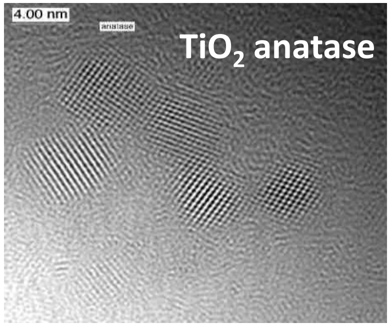


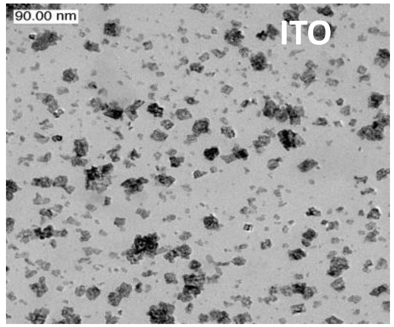
no light scattering if d < λ / 20

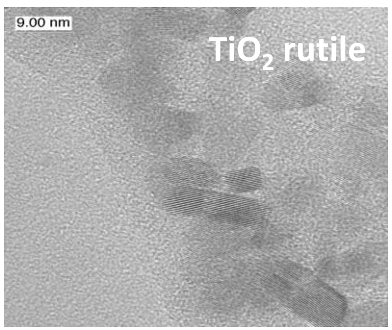
new options for optical applications
nanoparticles in transparent matrix

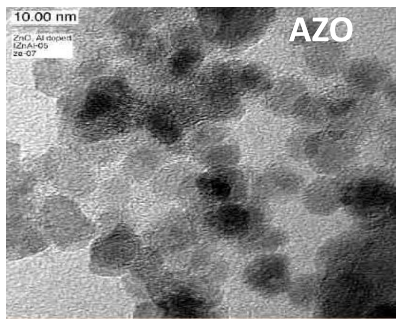
Solid state physical properties + polymer processing techniques

Examples for nanoparticles

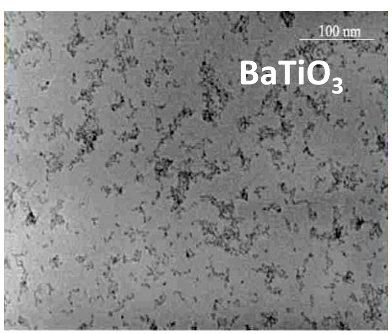


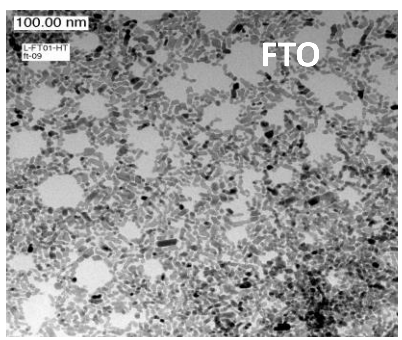


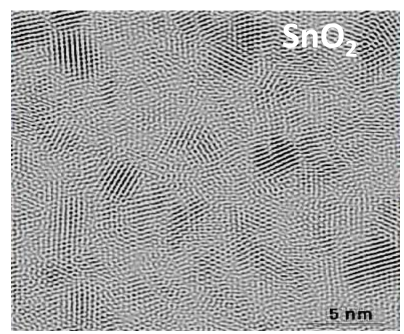


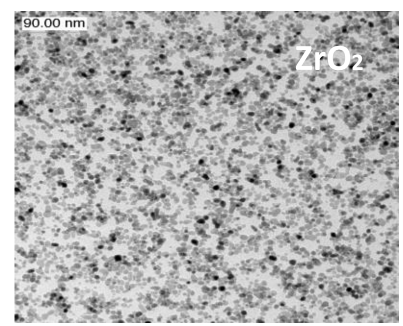


Particle dispersions in water, alcohol or organic solvent

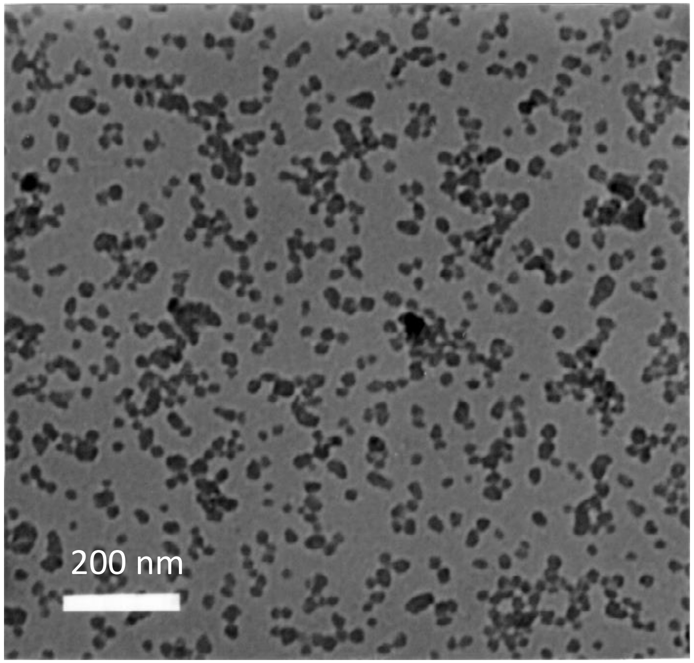








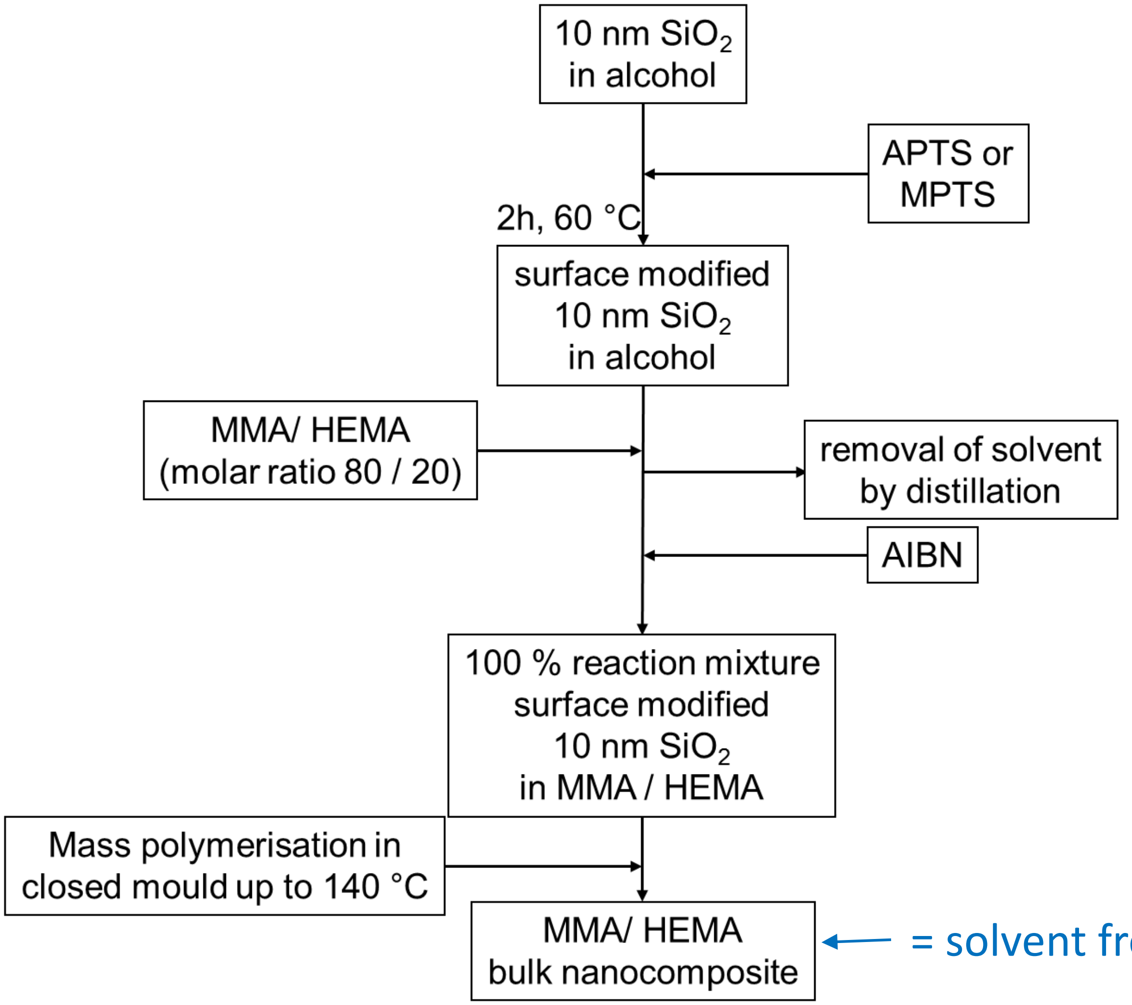
SiO_2 – nanoparticles used for following example



Nissan MA-ST
$d_{90} < 15$ nm
colloidal SiO_2
in methanole

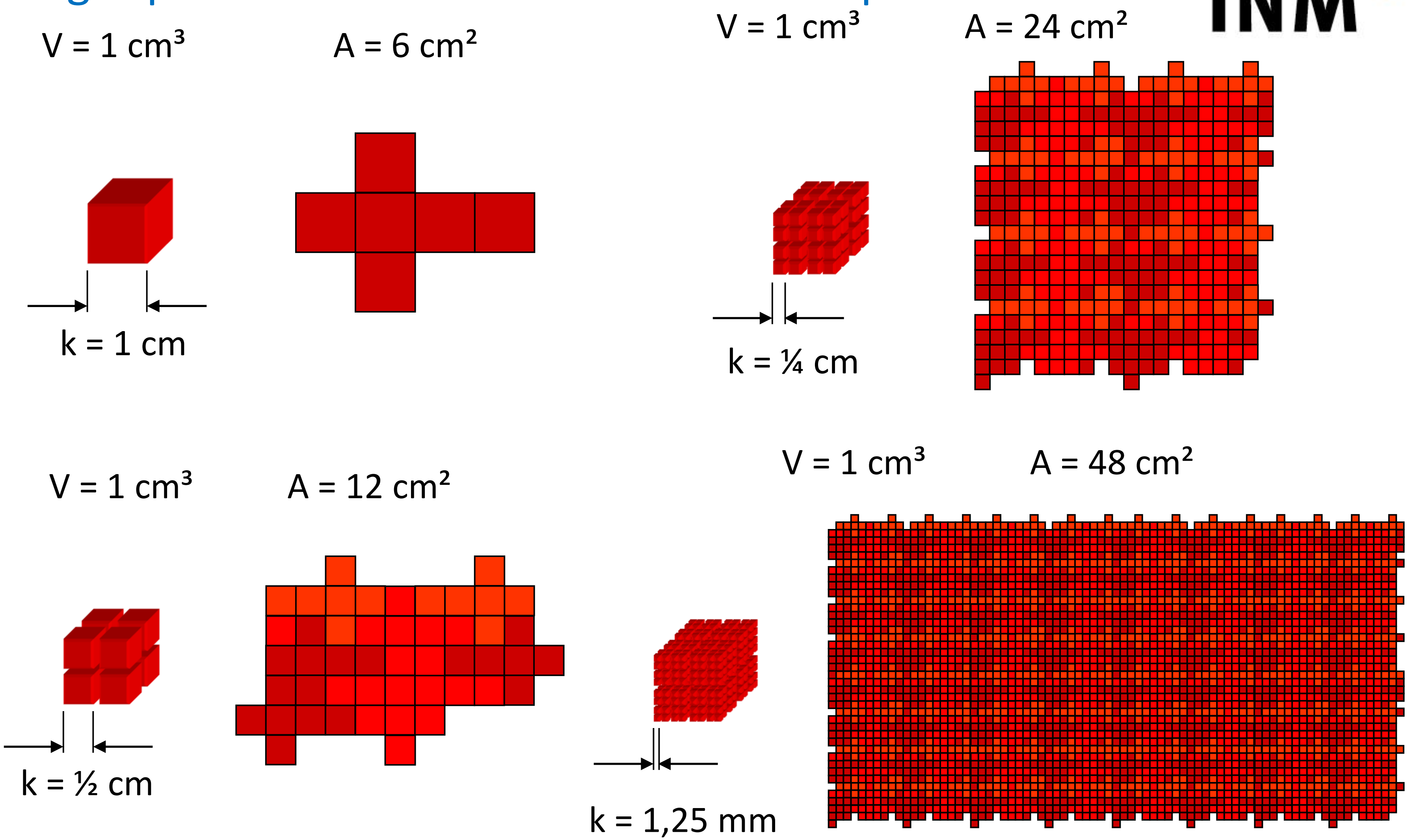
TEM – micrograph from the unmodified diluted dispersion
primary particles separable

Investigations on example P(MMA-co-HEMA) + nanoscaled SiO_2



= solvent free reaction mixture

Large specific surface area in case of nanoparticles



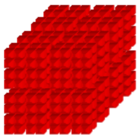
large interface between nanoparticles and matrix

Thermodynamics in nanocomposites

- incompatibility polymer / inorganic filler (nanoparticle)

agglomeration caused by high interfacial free energy

large interface particle / matrix in case of nanoparticles



- **approach: minimisation of the interfacial free energy**

by tailored surface modification of the nanoparticles

= compatibilisation

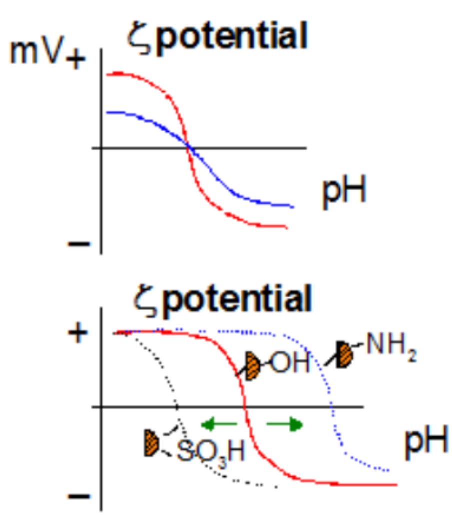
homogeneous distribution of the nanoparticles over the matrix

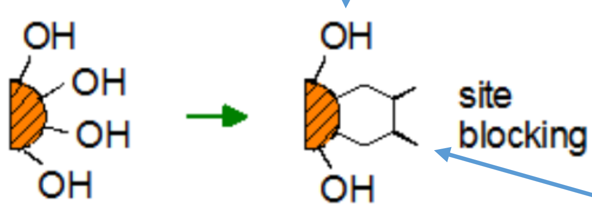
+

effective use of the intrinsic solid state physical properties of the nanoparticles

particle synthesis bottom-up from liquids

- chemically controlled precipitation process
  - control of nucleation (ΔG_n, ΔG_D, σ_N)
  - control of particle growth (ΔG_G, ΔG_D, σ_S)





point of zero charge

$$I = Ae^{\frac{-(\Delta G_n + \Delta G_D)}{kT}}$$

with

$$A = 2n_v v^{1/3}\frac{kT}{h}\sqrt{\frac{\sigma}{kT}}$$

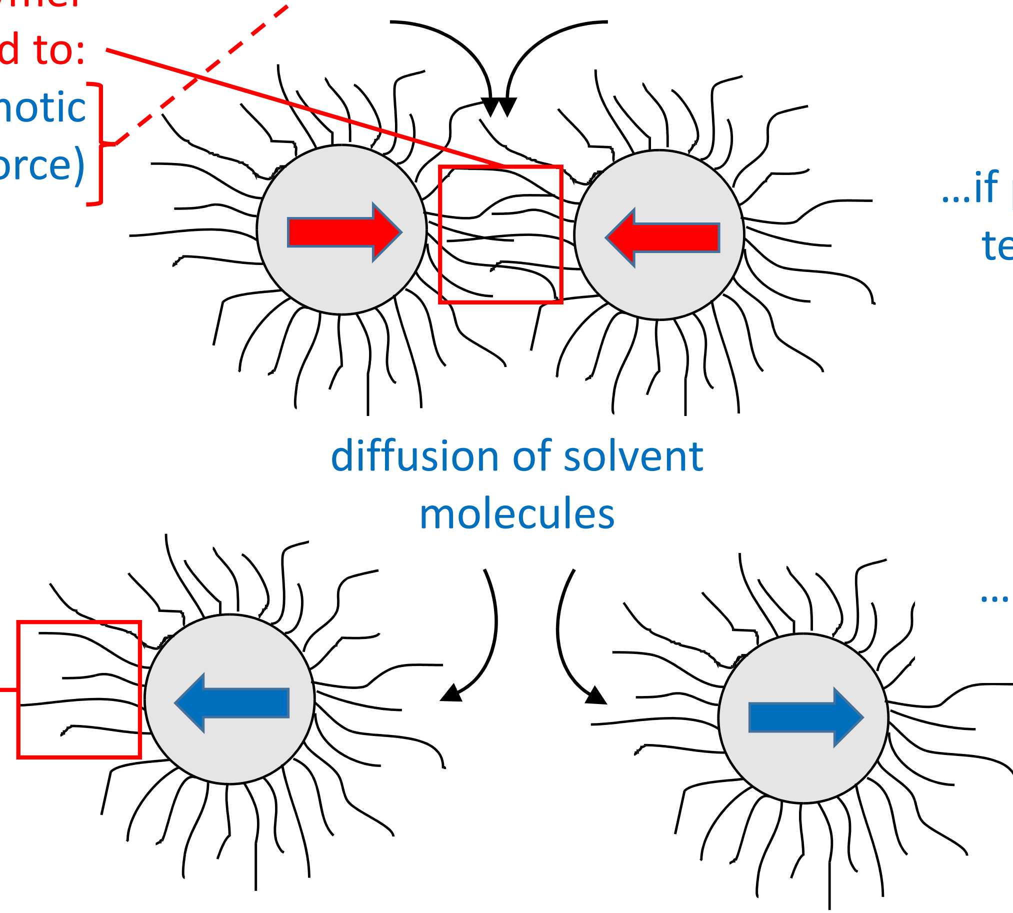
key point: control of electrostatic / steric / electro-steric stabilisation

Principle of steric stabilisation

overlap of segments of stabilising polymer chains lead to:

increase of osmotic pressure (= driving force)

diffusion of solvent molecules



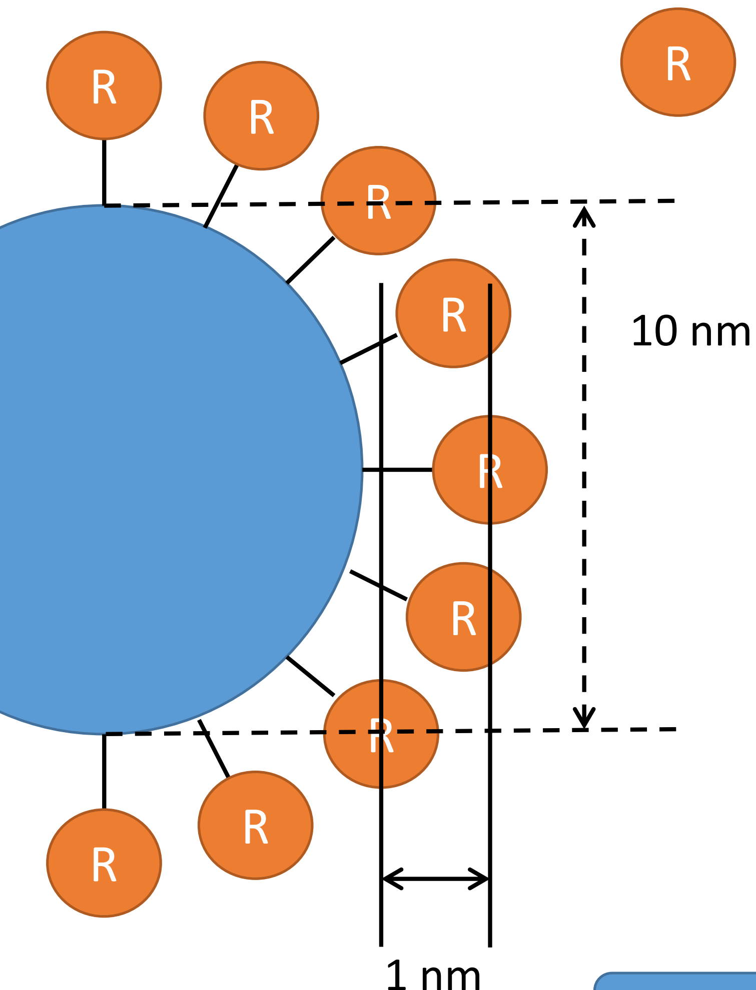
...if particles approach and tend to agglomerate...

diffusion of solvent molecules

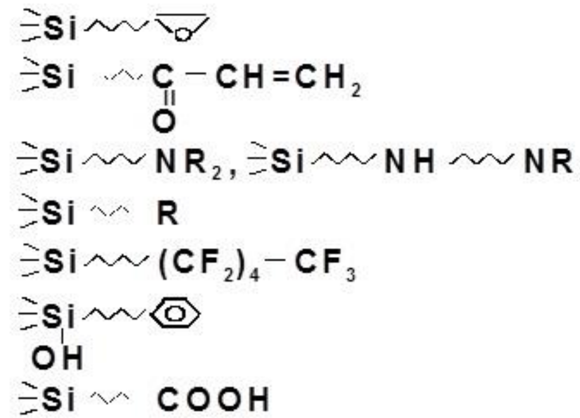
stabilising polymer chains adsorbed on the surface of the particles

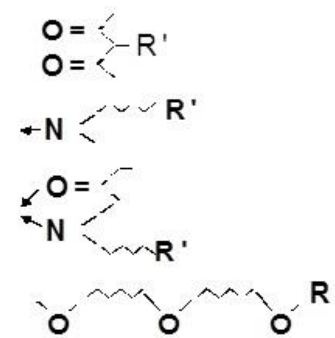
...solvent pushes them apart...

Compatibilisation by surface modification



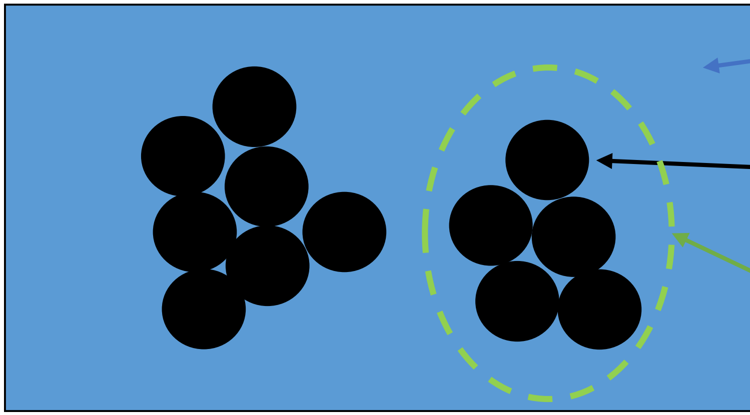
- silanes
  - acidic
  - basic
  - non reactive
  - polymerisable
  - polycondensable
  - adhesion
  - anti-adhesion
  - hydrophilic
  - hydrophobic
- β-di-ketones
- complexing agents
- chelating agents
- oligomers





SMSM-principle: Small Molecule Surface Modification

Thermodynamics in nanocomposites

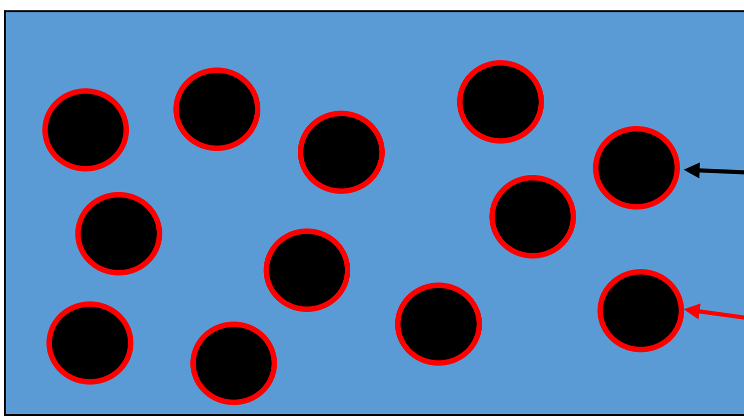


polymer matrix

primary particle

agglomerate consistent out of several primary particles

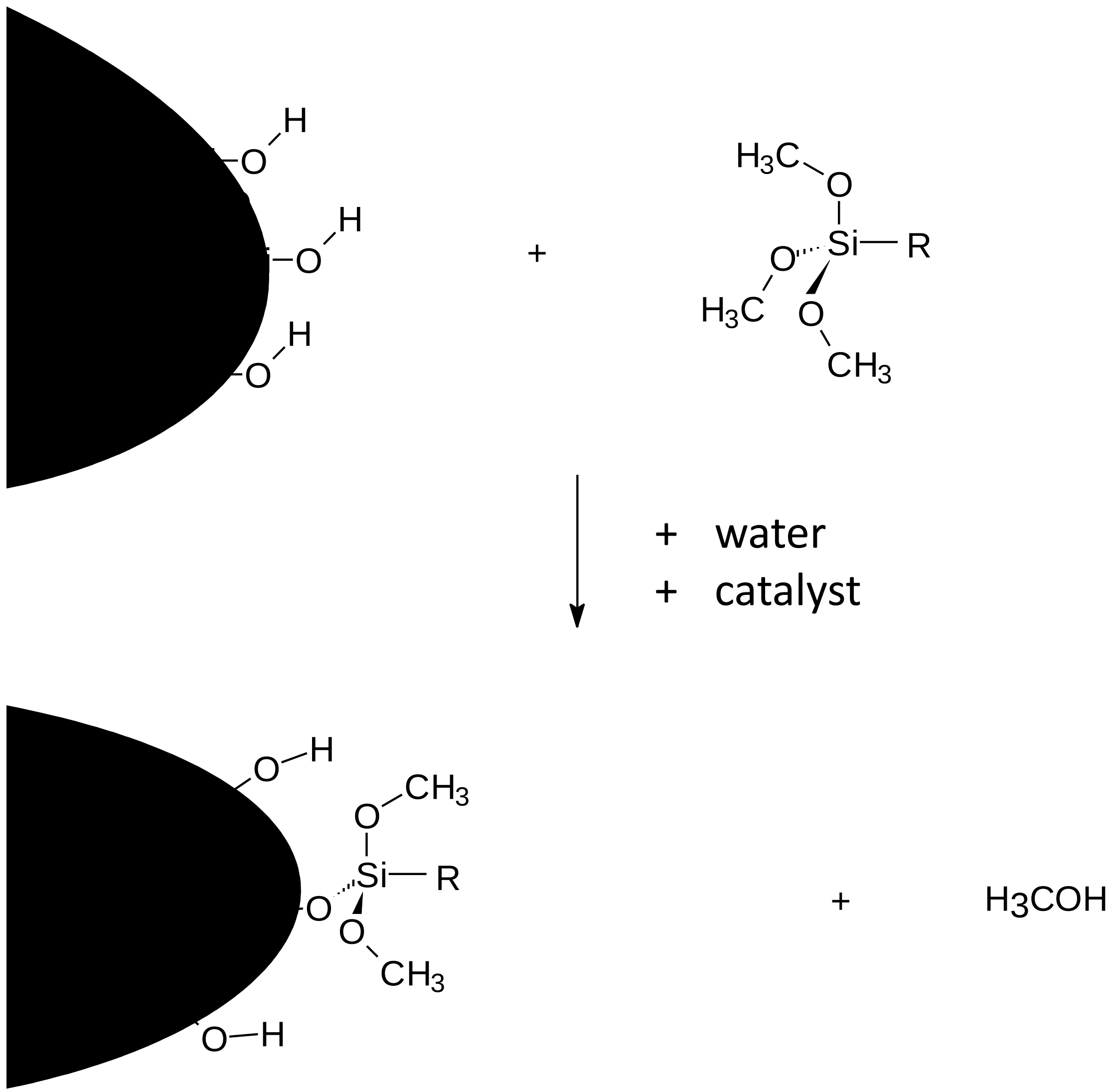
<u>compatibilisation step</u> to overcome the interaction forces between the primary particles (by <u>smsm-principle</u>)



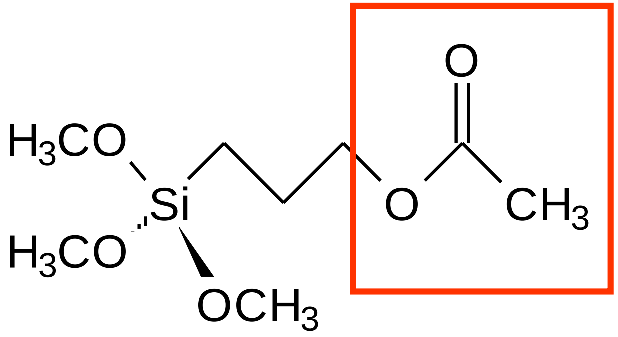
well separated primary particle

surface modification layer to protect primary particles against re-agglomeration

Specific surface modification of SiO_2 nanoparticles using alkoxysilanes

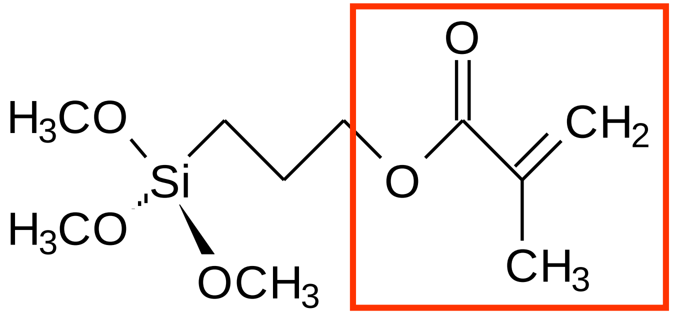


Compatibilisation by surface modification of the SiO_2



APTS

compatible

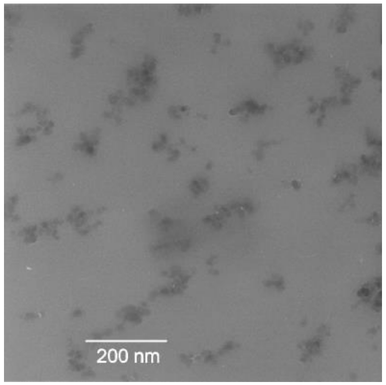


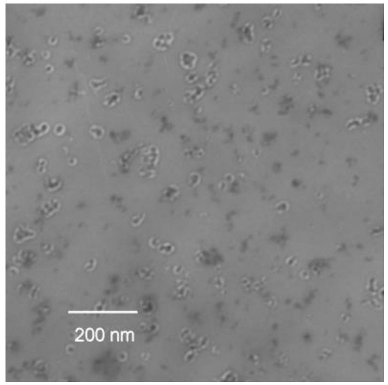
MPTS

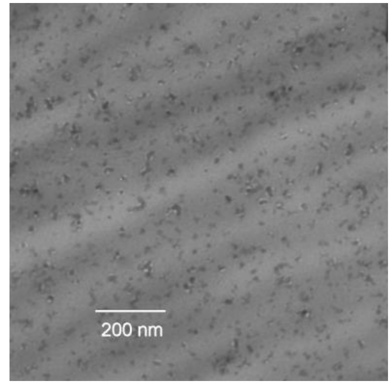
compatible + polymerisable

TEM – analysis on ultramicrotomed specimen from PMMA / SiO_2 nanocomposites

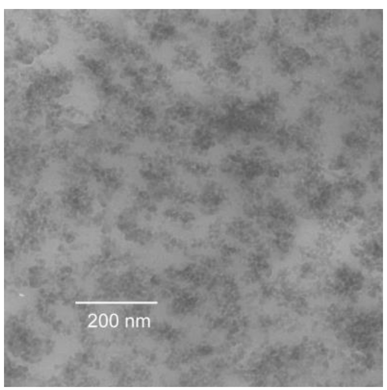
2 Vol.%

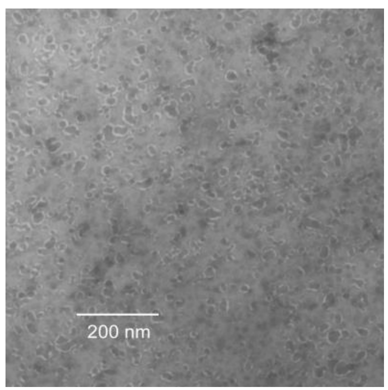


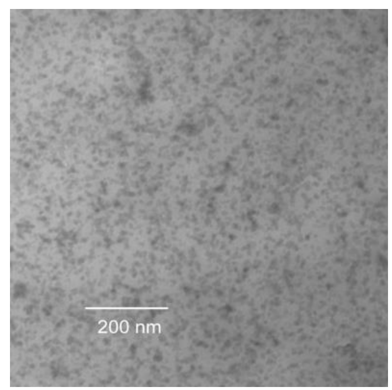




unmodified SiO_2 | APTS / SiO_2 | MPTS / SiO_2







5 Vol.%

morphology on ultramicrotomed specimen

unmodified SiO_2:
agglomerates > 100 nm

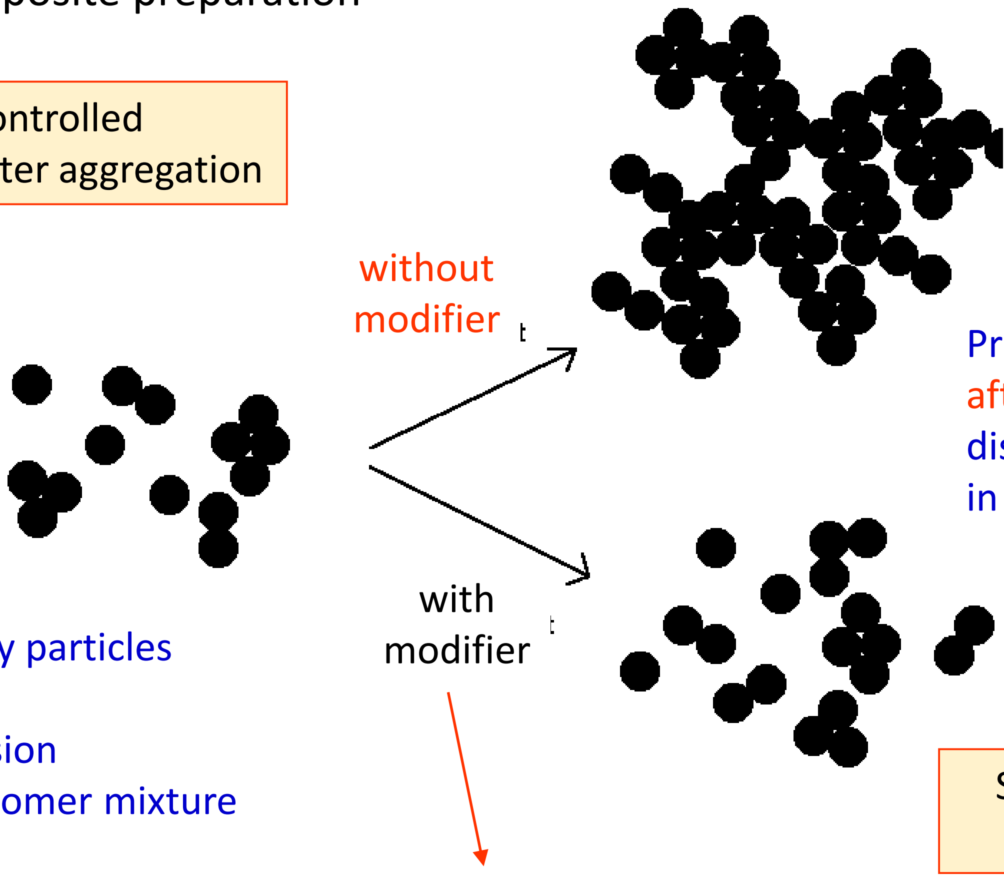
APTS/MPTS – SiO_2:
agglomerates consisting of 2-3 primary particles
< 30 nm

Compatibilisation concept
= valuable

Structural model after SAXS – analysis

Investigation of the agglomerate formation mechanism of the SiO_2 –particles
During composite preparation

Diffusion controlled
cluster-cluster aggregation

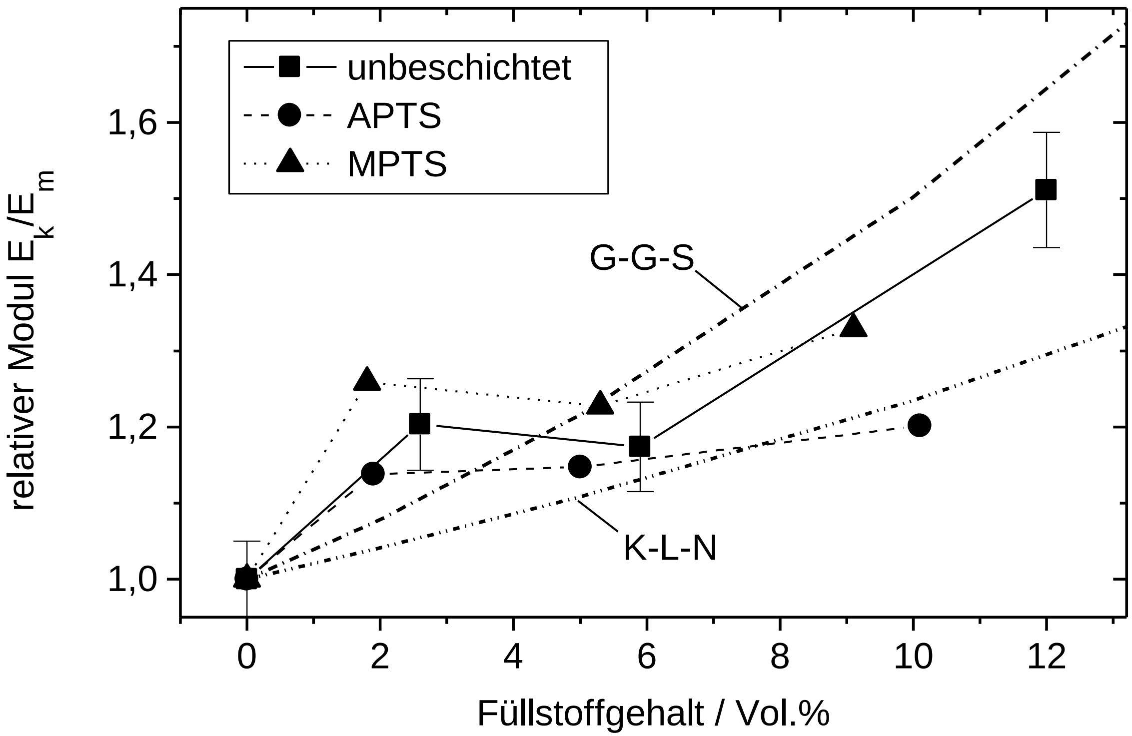


State is frozen during
polymerisation

minimisation of the interfacial free energy

Elastic modulus of P(MMA-co-HEMA) / SiO_2 nanocomposites (3-point bending)

10 nm SiO_2 with different surface modification



Elastic modulus according to classical mixing rules

Model calculations

G-G-S: Guth-Gold-Smallwood

$$E_K = E_M \left(1 + (1+A)\frac{\phi}{\phi_{max}} + 14{,}1\phi^2 \right)$$

K-L-N: Kerner-Lewis-Nielsen

$$\frac{G_K}{G_M} = \frac{1 + AB\phi_F}{1 - B\psi\phi_F}$$ with

$$B = \frac{(G_F / G_M) - 1}{(G_F / G_M) + A}$$ and

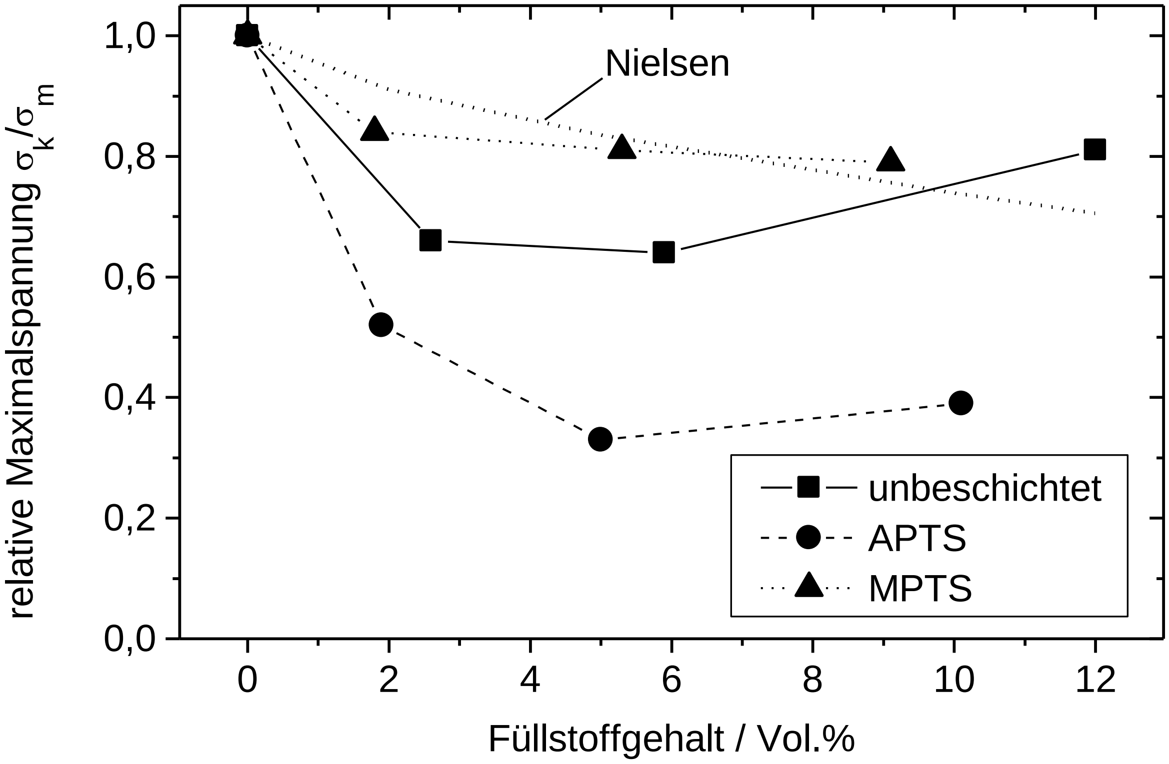
$$\psi\phi_F = \left[1 + \left(\frac{1-\phi_{max}}{\phi_{max}^2} \right) \phi_F \right] \phi_F$$

$E = 2G\,(1 + \mu)$

APTS: compatibilised
MPTS: chemical bonding

Maximum strength of P(MMA-co-HEMA) / SiO_2 nanocomposites (3-point bending)

10 nm SiO_2 with different surface modifications



Model calculation
Nielsen theory

$$\frac{\sigma_K}{\sigma_M} = 1 - 1{,}21\,\phi_F^{2/3}$$

APTS: compatibilised
MPTS: chemical bonding

Maximum strength for composites with crosslinked nanoparticles remains
On the same level as predicted for spherical particles

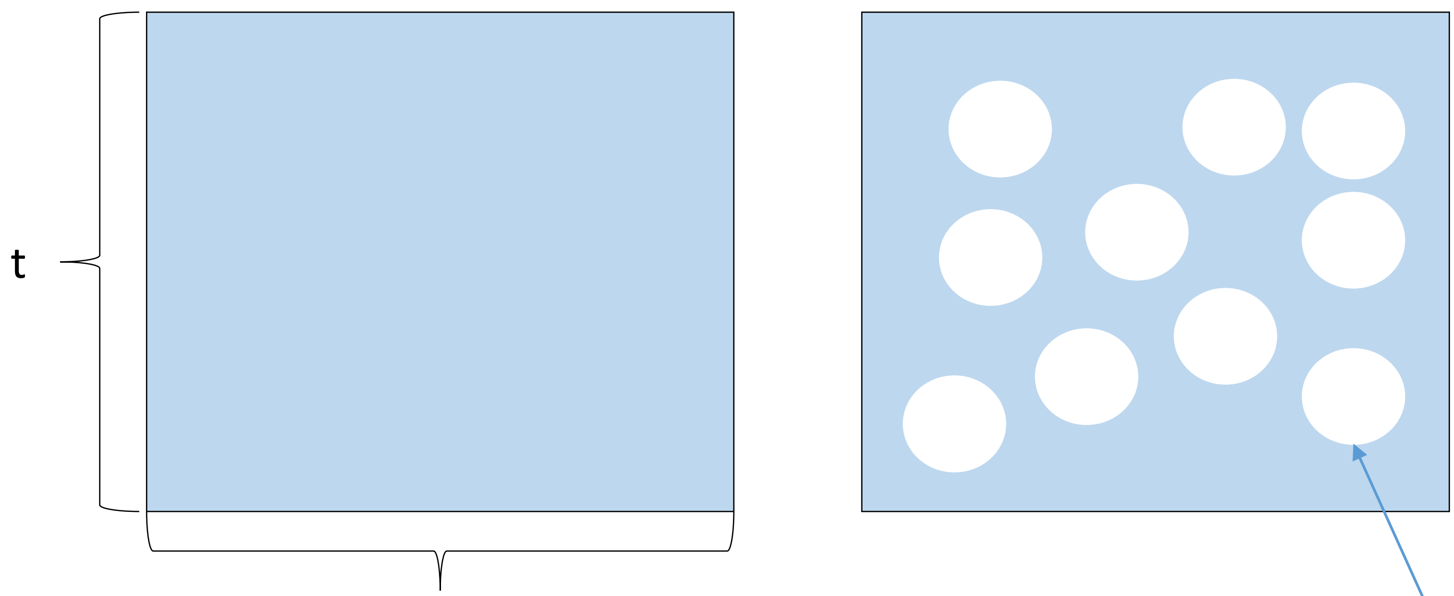
Model calculation for strength of composites

$$\frac{\sigma_C}{\sigma_M} = 1 - 1{,}21\,\phi_F^{2/3}$$

Nielsen model

σ_C: maximum strength composite
σ_M: maximum strength matrix

reduction of load bearing cross-section by presence of spherical particles

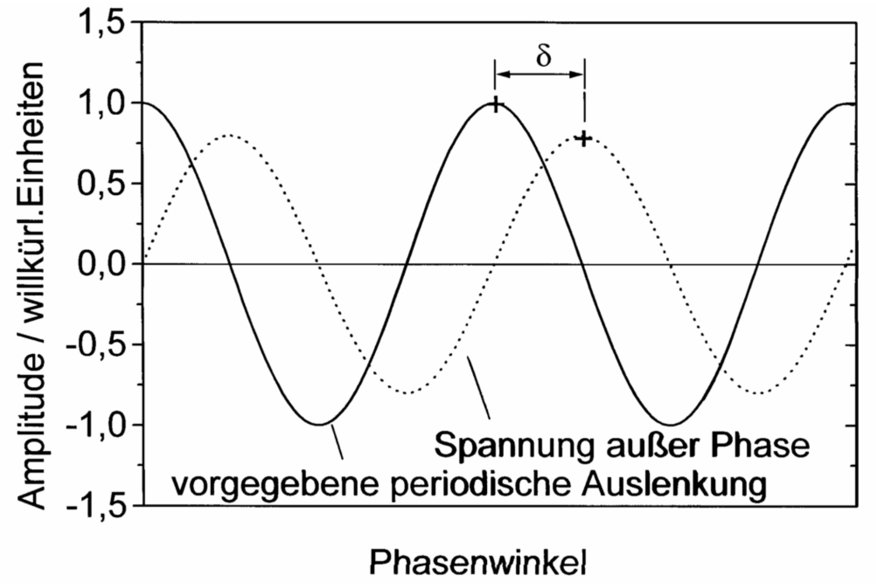


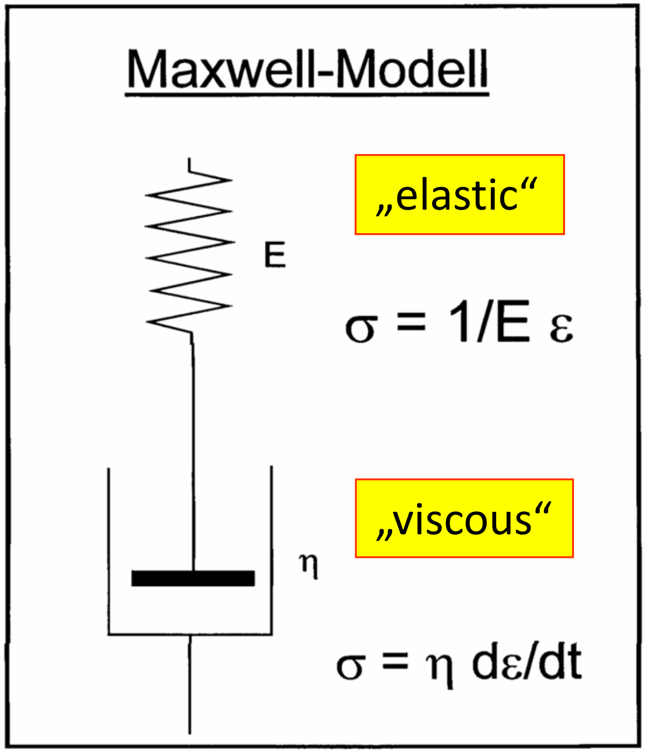
load bearing
cross-section area = (w * t)

load bearing
cross-section area = (w * t) - $A_{particles}$

Dynamic mechanical thermal analysis (DMTA): principle

Polymers = visco – elastic materials

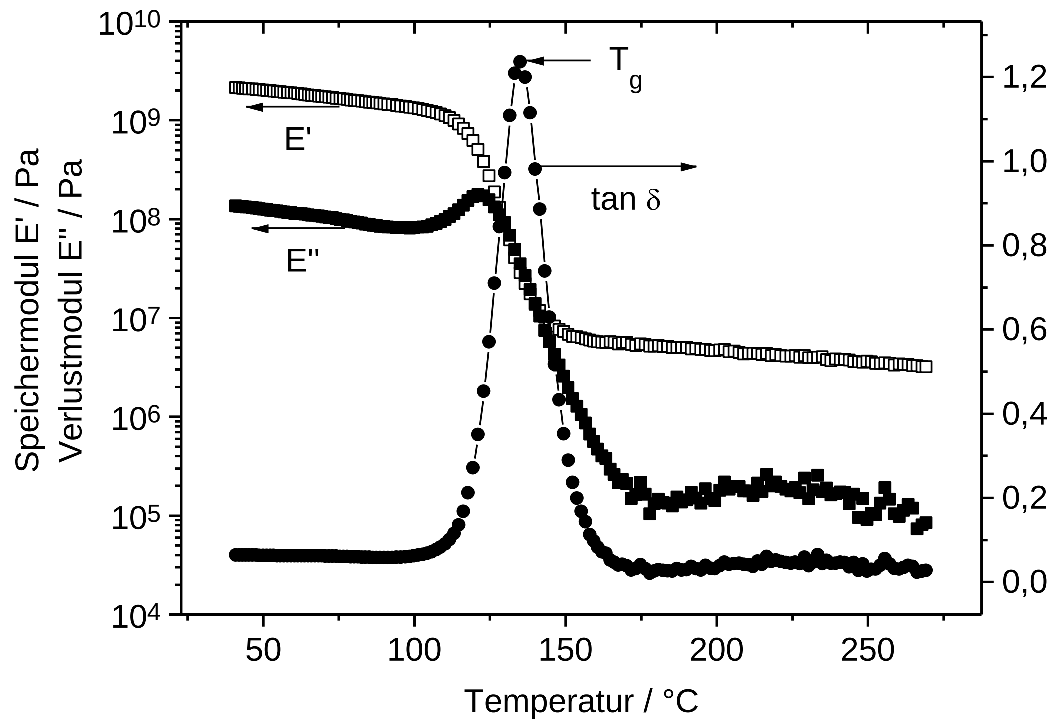




$E'' = \tan\delta * E'$

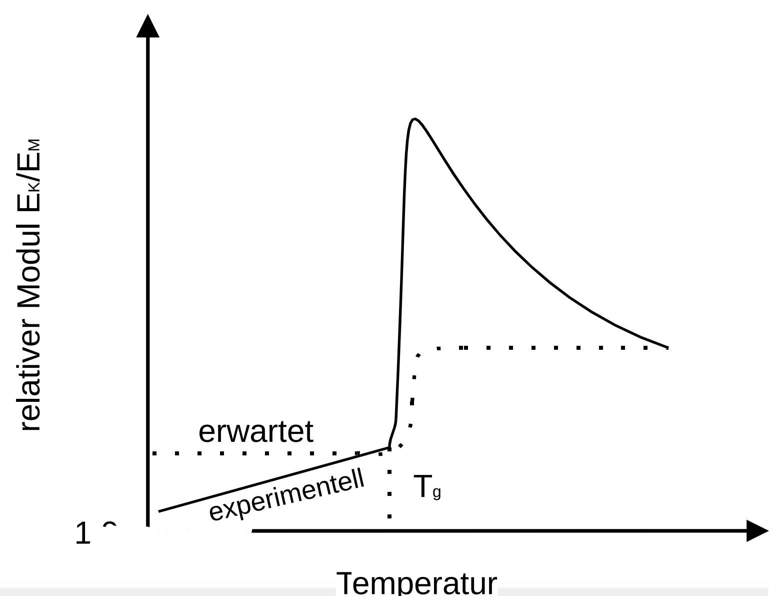
storage modulus E‘: elastic components
tan d: damping behaviour
loss modulus E‘‘: viscous components

Generelles dynamisch mechanisches Verhalten bei einem Thermoplasten (ungefüllt und gefüllt)

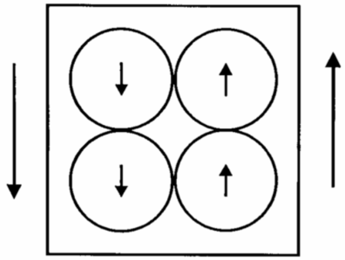


ungefülltes Polymethylmethacrylat (PMMA)

gefüllter Thermoplast

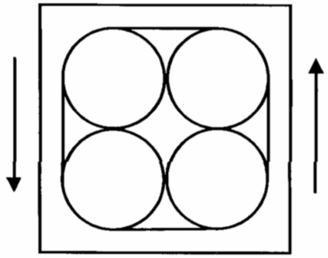


Dynamic mechanical thermal analysis (DMTA) for polymers filled with particles



Below Tg

flexible agglomerates



above Tg

rigid agglomerates

relative storage modulus

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

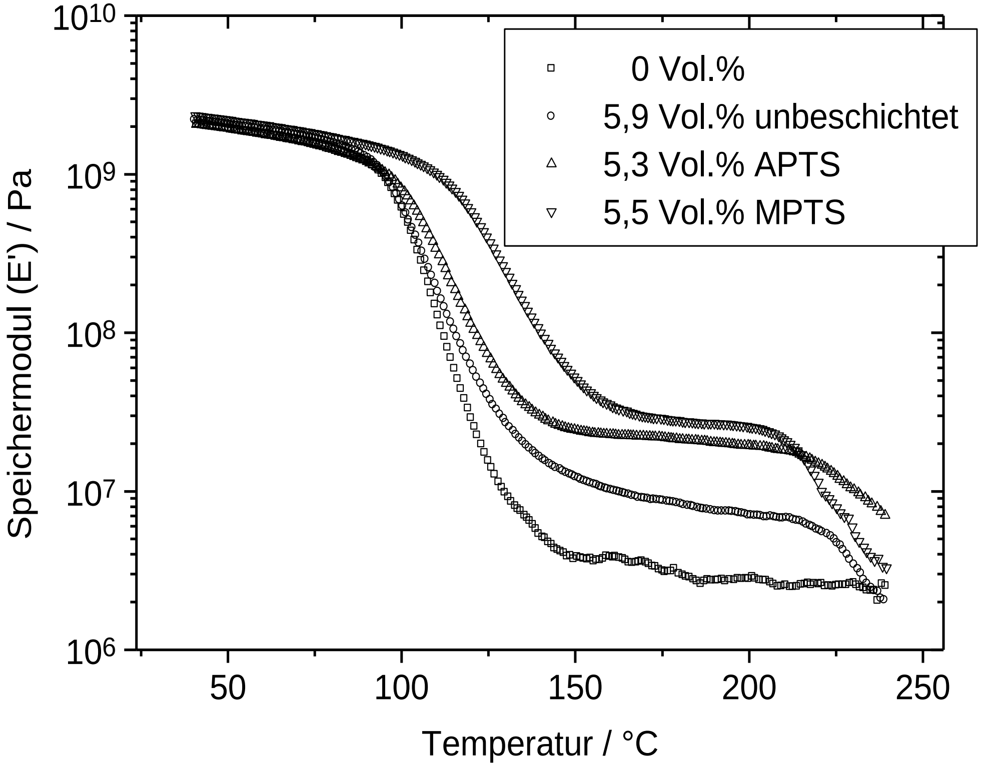
reduced mechanical damping

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

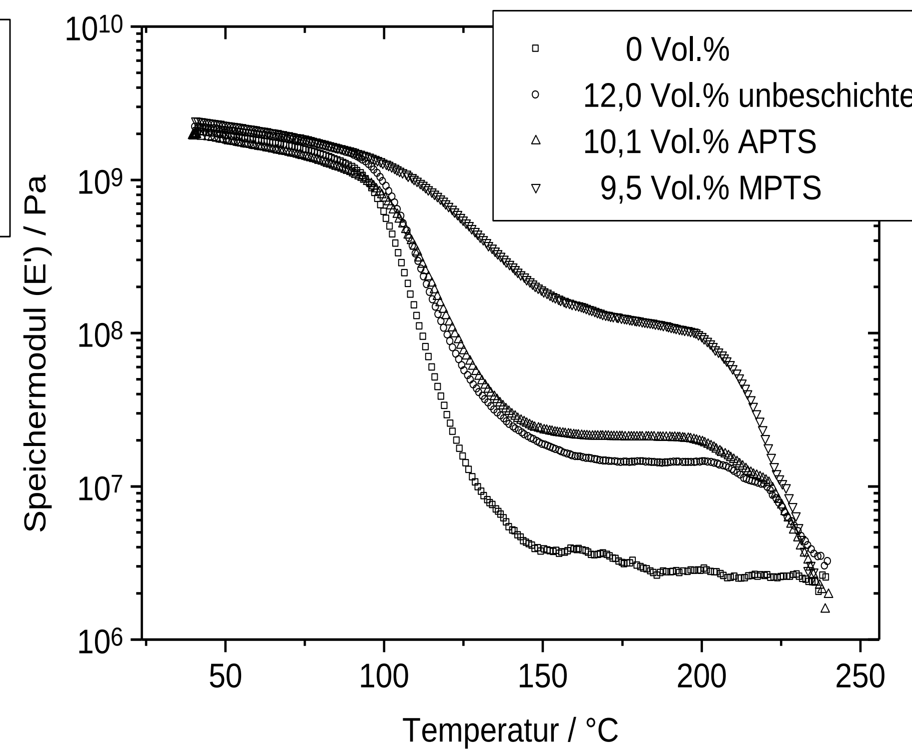
$\Delta_{red} < 1$	matrix = immobilised
$\Delta_{red} = 1$	matrix = unaffected
$\Delta_{red} > 1$	additional damping mechnisms

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

5 vol.-% 10 nm SiO_2



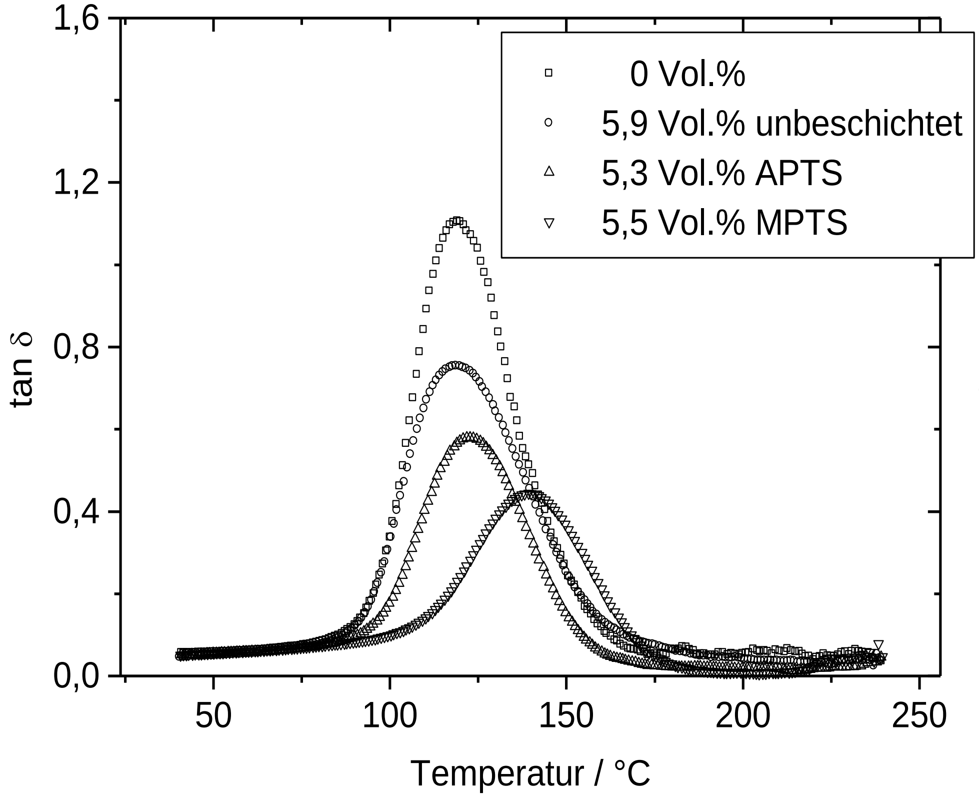
10 vol.-% 10 nm SiO_2



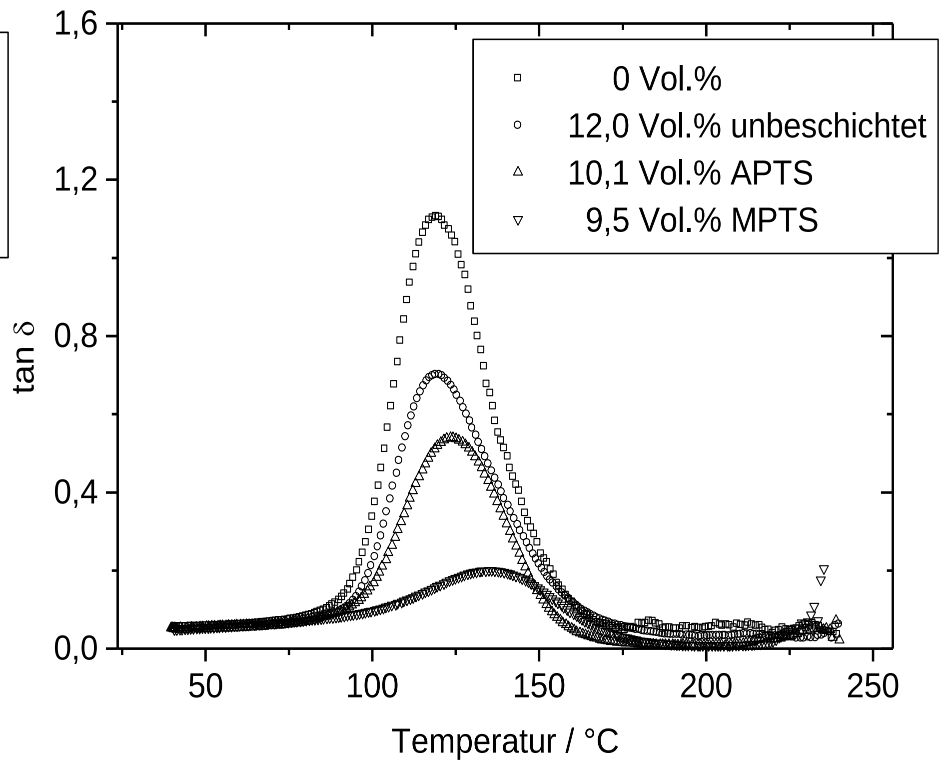
Significant rubbery plateau

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

5 vol.-% 10 nm SiO_2



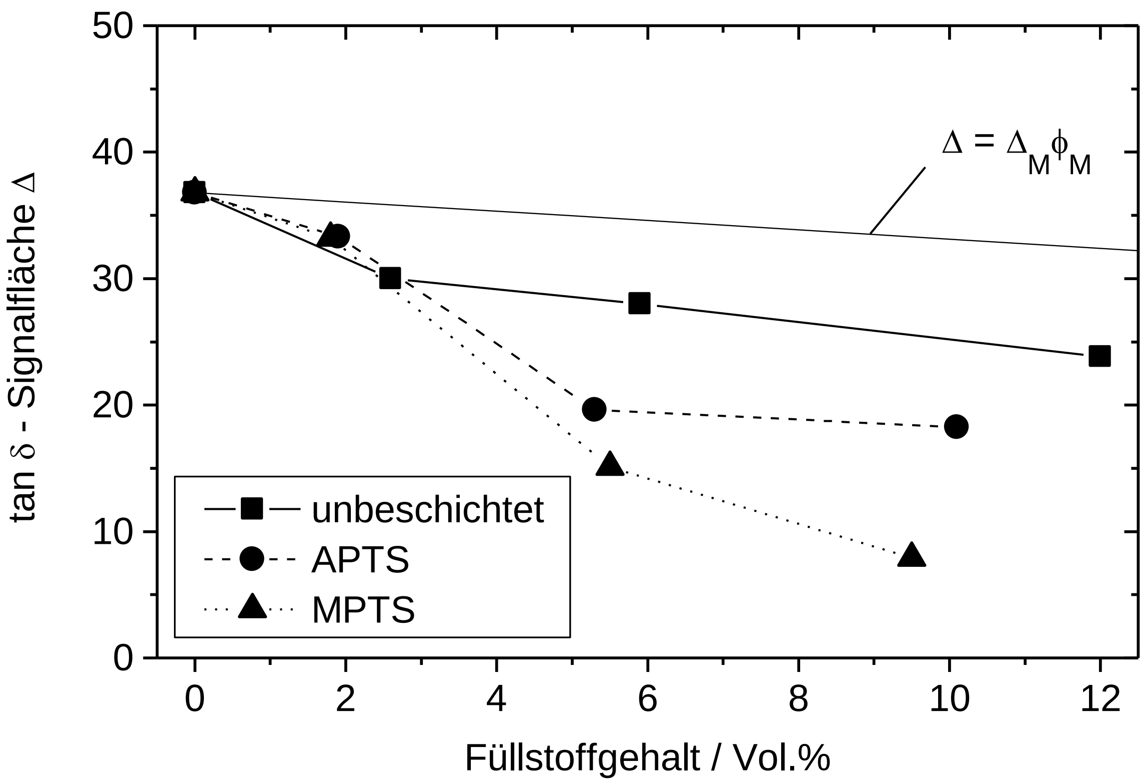
10 vol.-% 10 nm SiO_2



→ Strong cross linking tendency of the nanoparticles

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

10 nm SiO_2 with different surface modifications



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

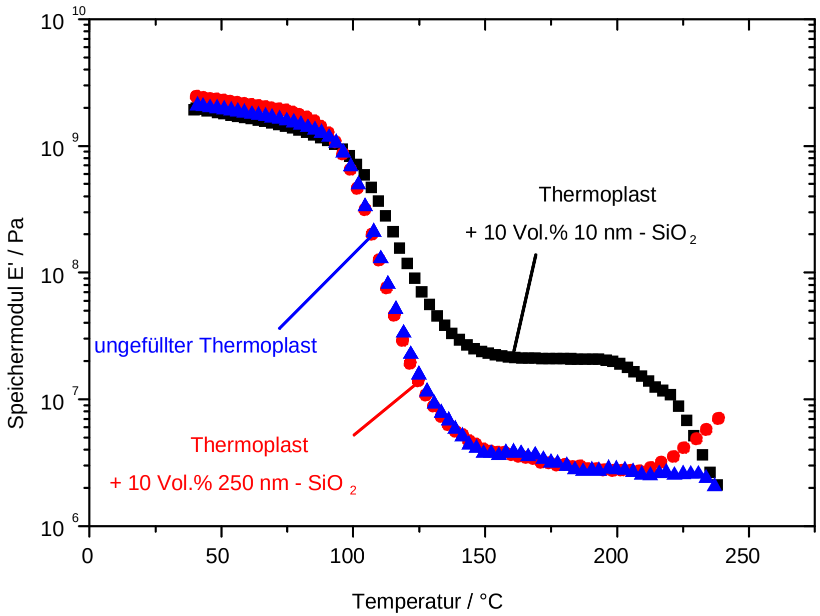
Model calculation
Δ: simple mixing rule

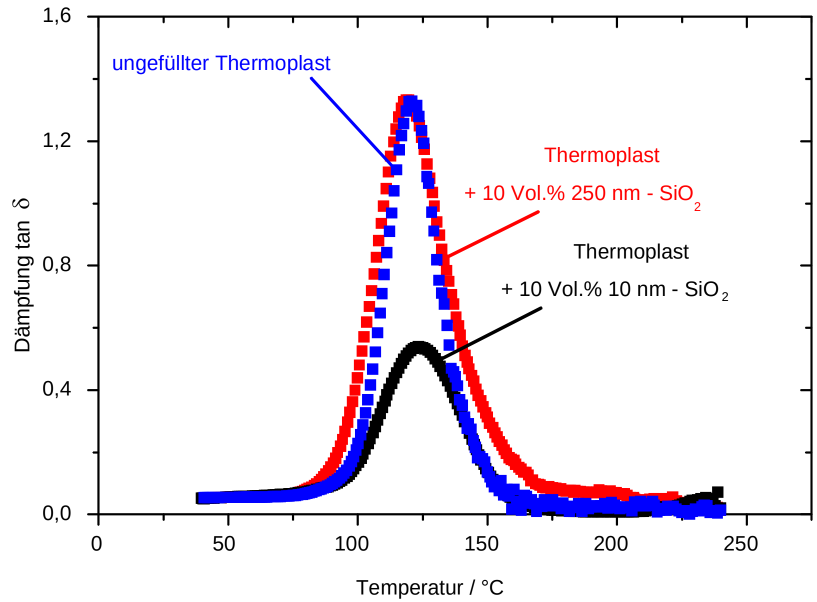
APTS: compatibilised
MPTS: chemical bonding

Indications for immobilised polymer matrix

Information about the interface in polymer matrix nanocomposites ?

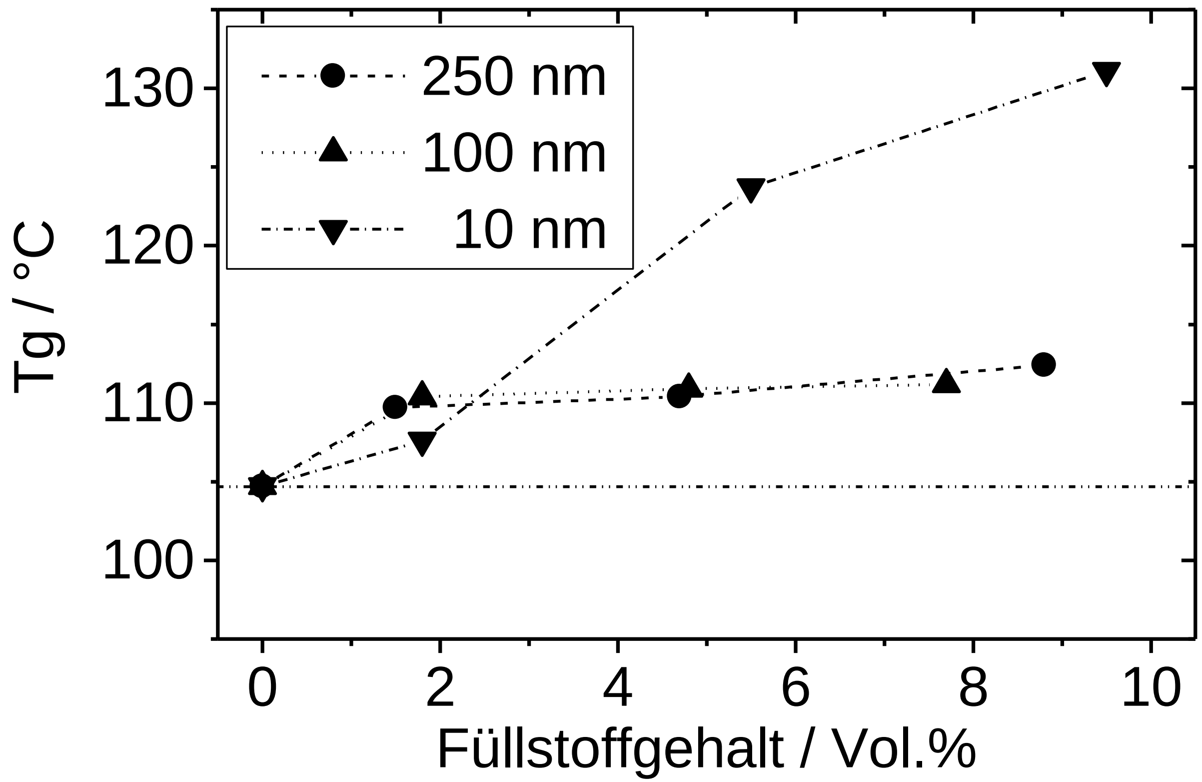
Dynamic mechanical thermal analysis (DMTA)





- 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

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



Particle size 10 nm: significant increase of Tg

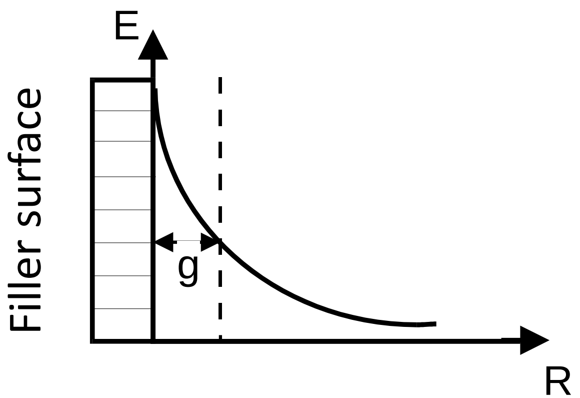
Potential: Plastics with increased temperature stability

Morphology and glass transition temperature

requirement: precise determination of the glass transition temperature

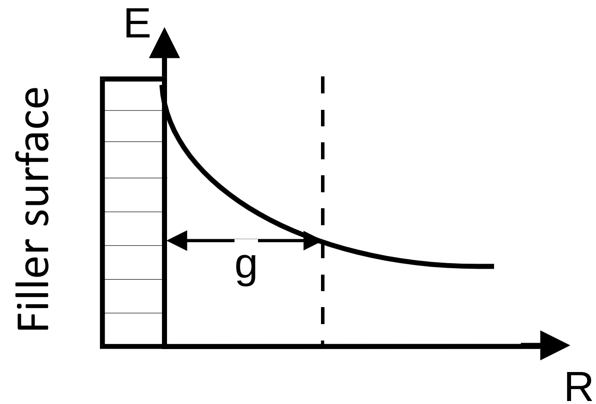
<u>Glass transition temperature</u>
= indicator of the change in the thermodynamic properties
of the polymer matrix in presence of the filler particles

Energy distribution of the polymer molecules close to the particle surface



weak particle / matrix interaction

Tg almost unaffected

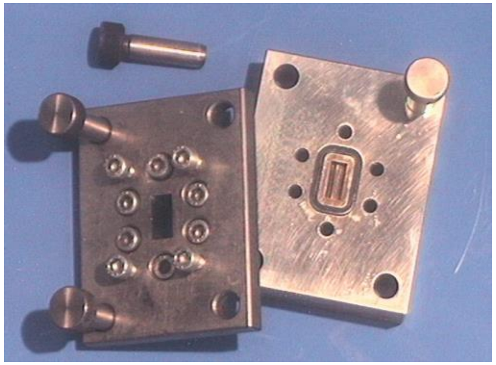


strong particle / matrix interaction

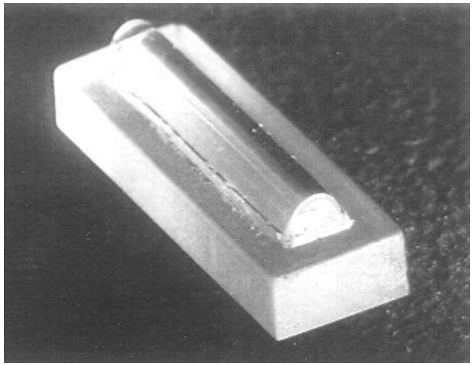
Tg ↑ (hindered chain mobility)

Optical components from Nanomers

Aspheric Laser focusing lenses

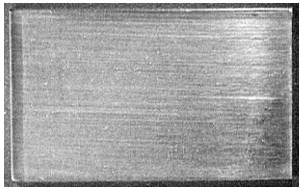


mould for cylindrical lens



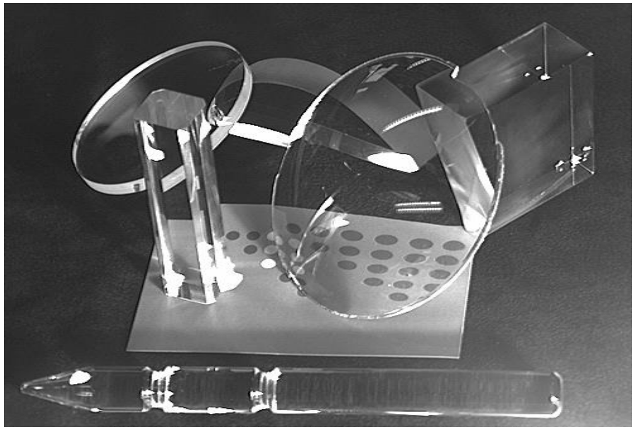
Nanomer lens

after 250 cycles steel wool test



PMMA

Nanomer



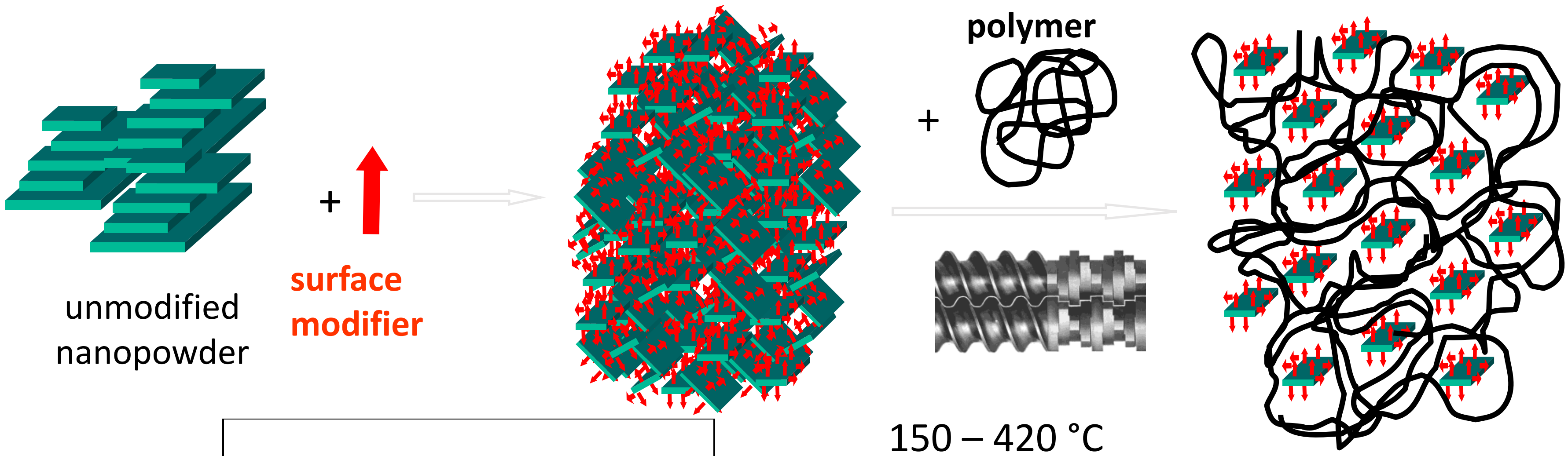
Tailor able optical, mechanical and thermal properties

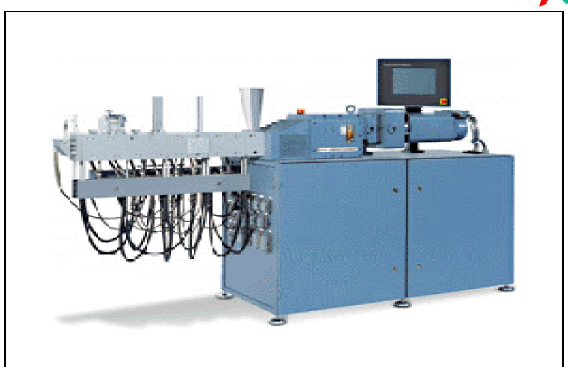
High precision moulding process (replication) at low cost

Polymer matrix nanocomposites by compounding (twin screw extruder)

Nanopowder with surface modification:

Interfacial free energy between nanoparticles can be be overcome by the shear forces of the extruder





Extruder-Geometrien in der Technik

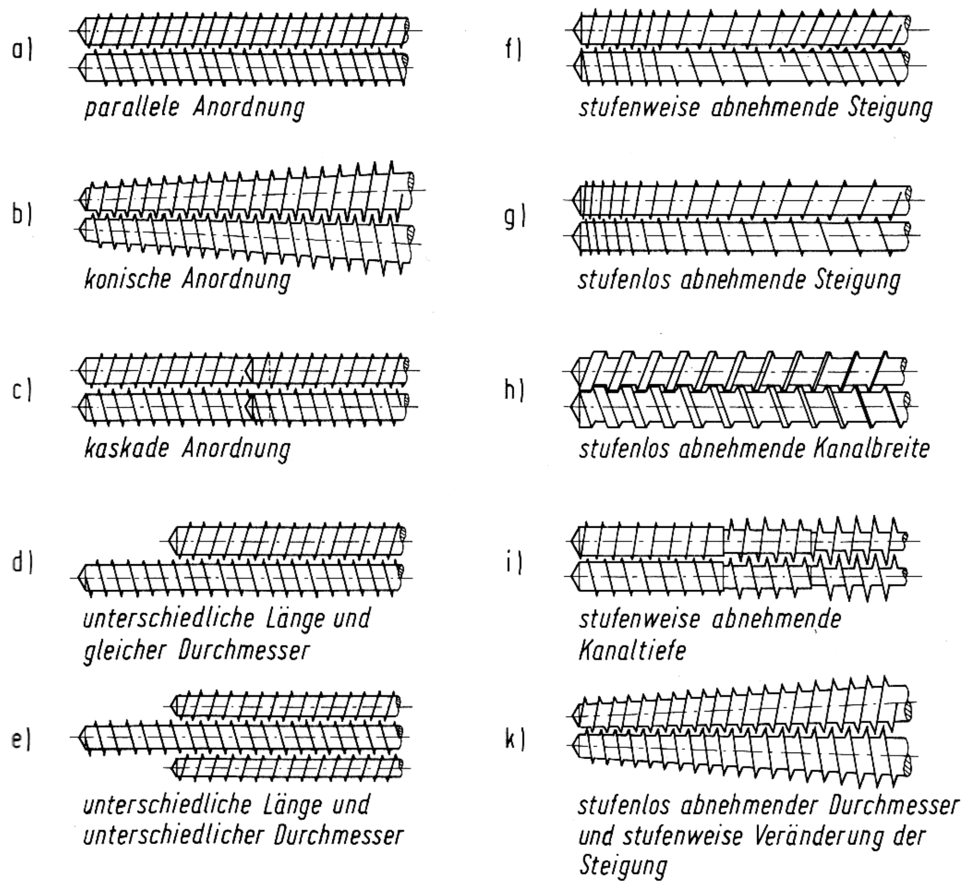


Bild 3.67. Anordnungen und Geometrien von Doppelschnecken

…für jedes Dispergierproblem eine technische Lösung

Compounding techniques at INM

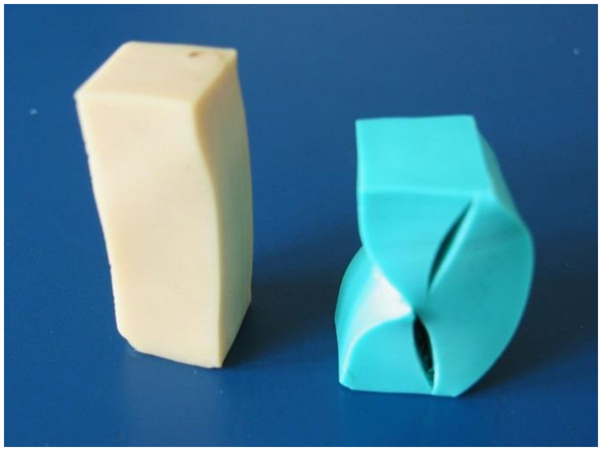
single screw extruder

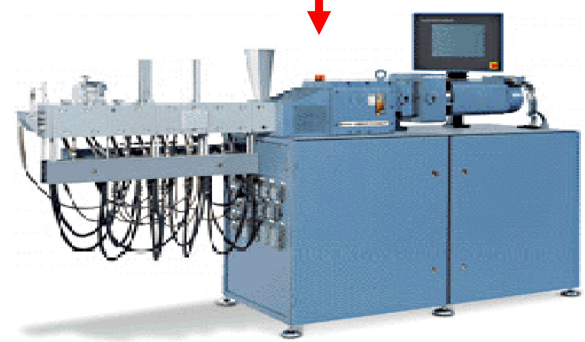
kneader

foil extruder

Polymermatrix nanocomposites

thermoplastic nanocomposites by compounding





PU specimen
+ 5 wt.% 8 nm-ZrO_2

PU specimen
unfilled

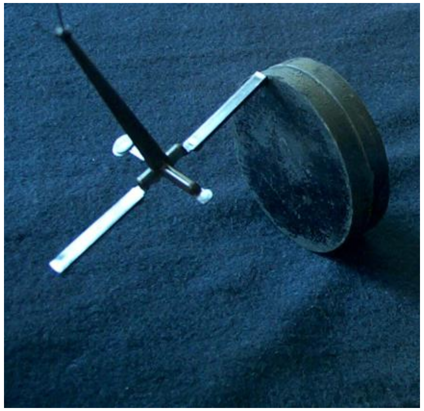
pressure experiment: 100 MPa at 23 °C

WO 2004/110926 A1 (12.06.2003)

- isotropic properties via spherical ZrO_2 nanoparticles
- strong reinforcement at low degrees of filling

Further properties of compounds

Magnetic nanocomposites



Injection moulded part
polypropylene with
1 wt.-%
Fe_2O_3-nanoparticles

Potential:
Heating of polymers
„Disbond on command"
„Polymerisation on command"

IR - absorbing nanocomposites

System	TLT [%]	TSET [%]
Polycarbonat	86,3	83,6
PC / ITO (0,8Gew%)	68	45

PC - nanocomposite + 0,8 wt.-% ITO
(foil thickness: 1 mm)

→ Fulfils requirements for automotive
IR-protective glass

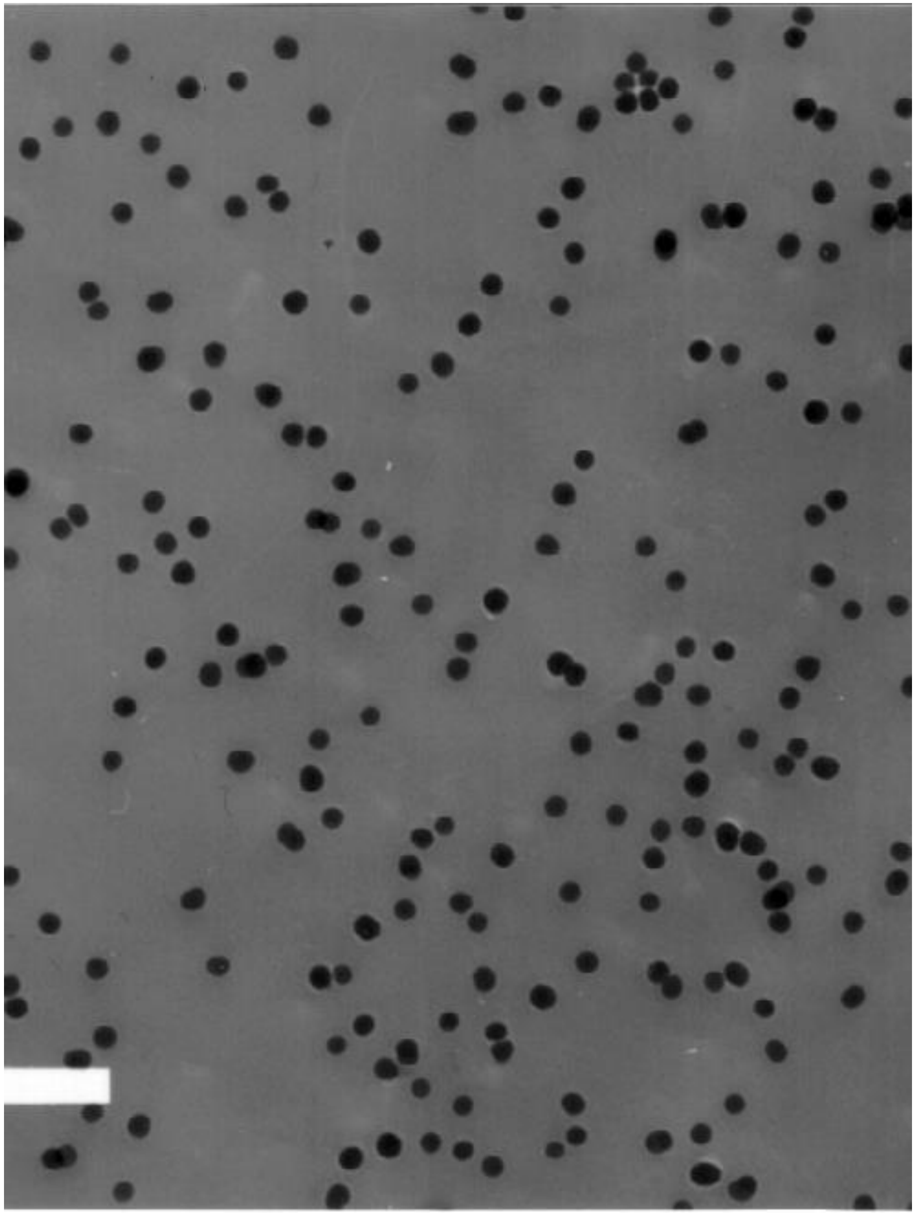
TLT: Total Luminous Transmittance
TSET: Total Solar Energy Transmittance

Schlussfolgerungen, Ausblick

- Chemischer Ansatz zu (Nano)Kompositen bietet viele Variationsmöglichkeiten um Materialeigenschaften einzustellen
- Verbessertes Verständnis des Versagens- und Mikrodeformationsverhaltens nach wie vor wünschenswert
- Multiphasen-Komposite lassen ungewöhnliche visko-elastische Eigenschaften erwarten (Smarte Komposite)
- Jede Menge Potential für Anwendungen vorhanden

New Ideas. New Materials.

INM



THANK YOU VERY MUCH FOR YOUR ATTENTION

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