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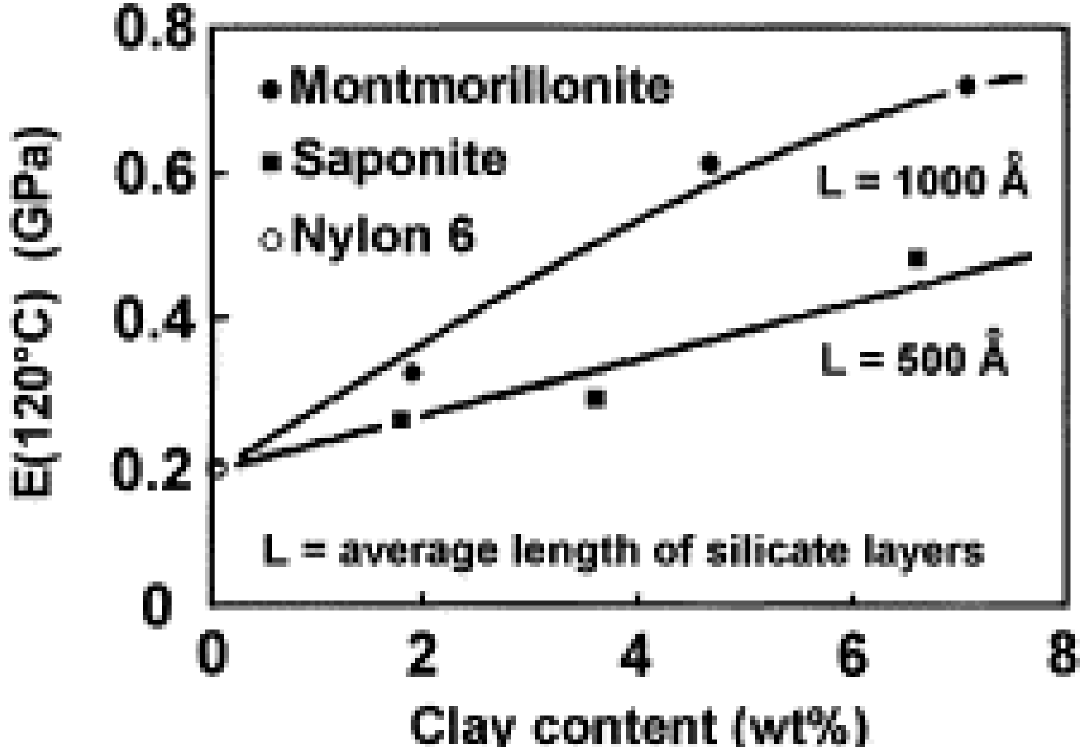
Υβριδικά οργανικά-ανόργανα νανοσύνθετα υλικά και εφαρμογές τους

Πολύκαρπος Πίσσης
ΕΜΠ
Τομέας Φυσικής

Polymer nanocomposites (PNCs)

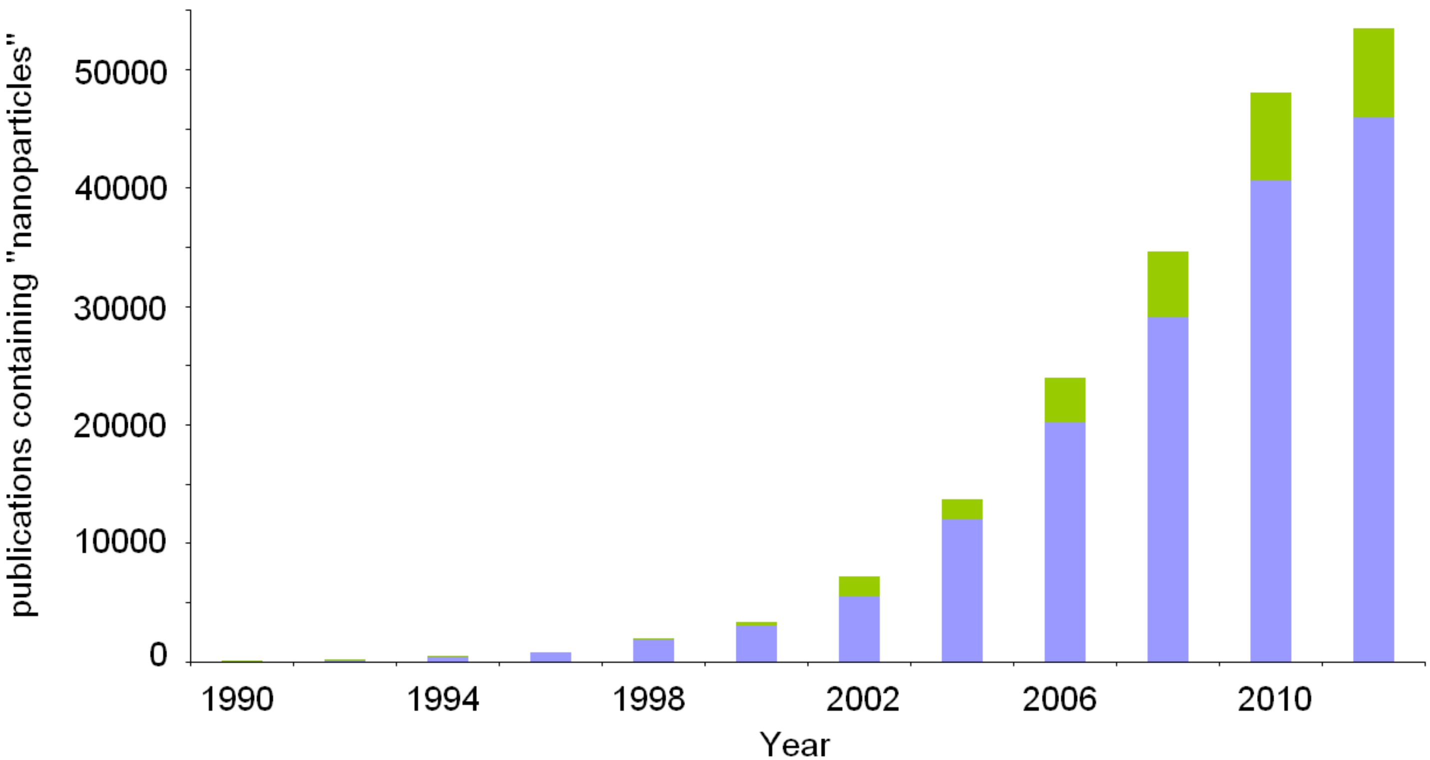
First report on improvement of polymer properties by incorporation of nanofillers
A. Okada, M. Kawasumi, T. Kurauchi, O. Kamigaito, Polym.Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 28 (1987) 447
(from the Toyota research group)



Dependence of tensile modulus *E* at 120°C on clay content for organo-modified montmorillonite and saponite-based nanocomposites
Y. Kojima et al., J. Mater. Res. 6 (1993) 1185-9

Growing interest in PNCs

Publications (blue) and patents (green) containing the word "nanoparticles" per year



Composite materials (composites)

Materials made of two or more constituent materials with significantly different properties
Characteristics different from the individual components
The individual components remain separate and distinct within the composite

Concrete is a mixture of cement and aggregate, giving a robust, strong material that is very widely used.

Plywood is used widely in construction

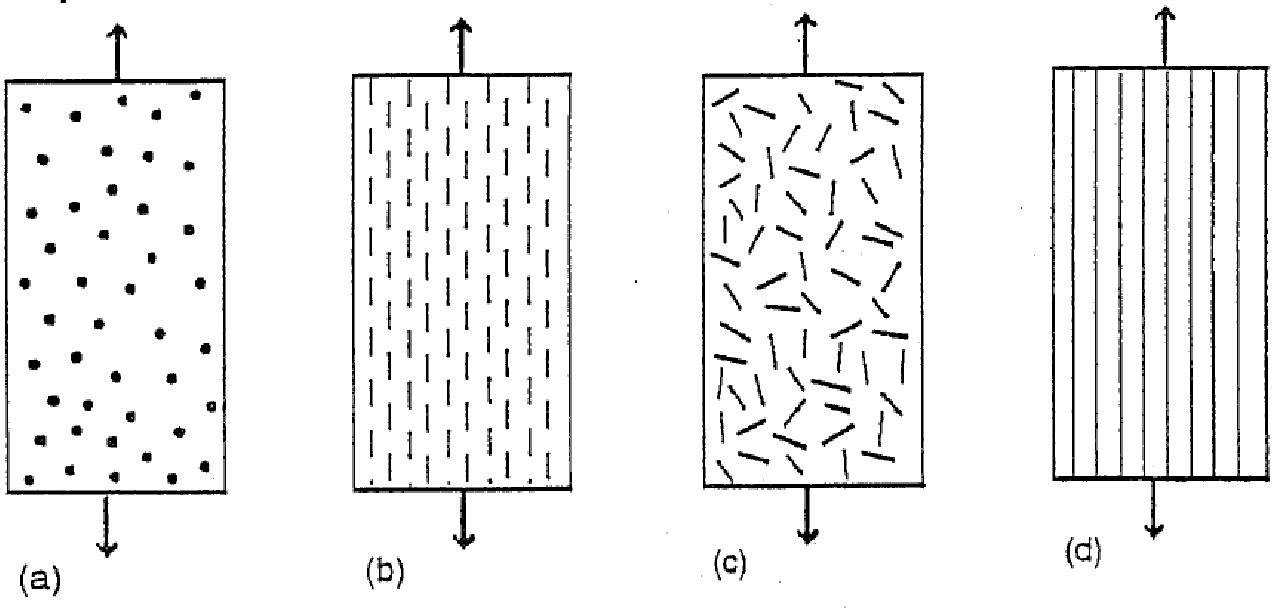
Composite sandwich structure panel used for testing at NASA

Classification of composite materials

matrix and filler

matrix: metal, ceramic, polymer

filler: particulates and fibres



Examples of composites: (a) particulate, random; (b) discontinuous fibres, undirectional; (c) discontinuous fibres, random; (d) continuous fibres, undirectional

History of composites

Bone (hydroxyapatite reinforced with collagen), wood etc in the nature
Straw and mud combined to form bricks for building construction
Plywood (gluing wood by the Ancient Mesopotamians, 3400 BC)
Cartonnage layers (linen or papyrus soaked in plaster, death masks, Egypt, ~2100 BC)
Concrete, lime mortars (Vitruvius 25 BC)
Bakelite the first fiber reinforced plastic 1907
Carbon and Boron fibers from the 1960s, Glass, Aramid and Kevlar Fibers (FRPs, CFRPs, GRPs etc)

L. Holloway (Ed.), Handbook of Polymer Composites for Engineers, Woodhead Publ., Cambridge (1994)
F. L. Matthews and R. D. Rawlings, Composite Materials:Engineering and Science, Chapman, London (1994)

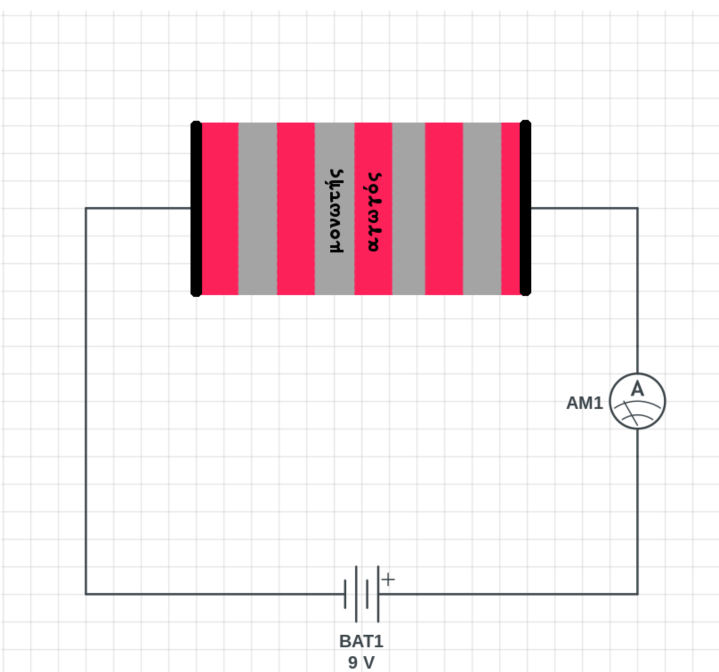
Properties of composite materials

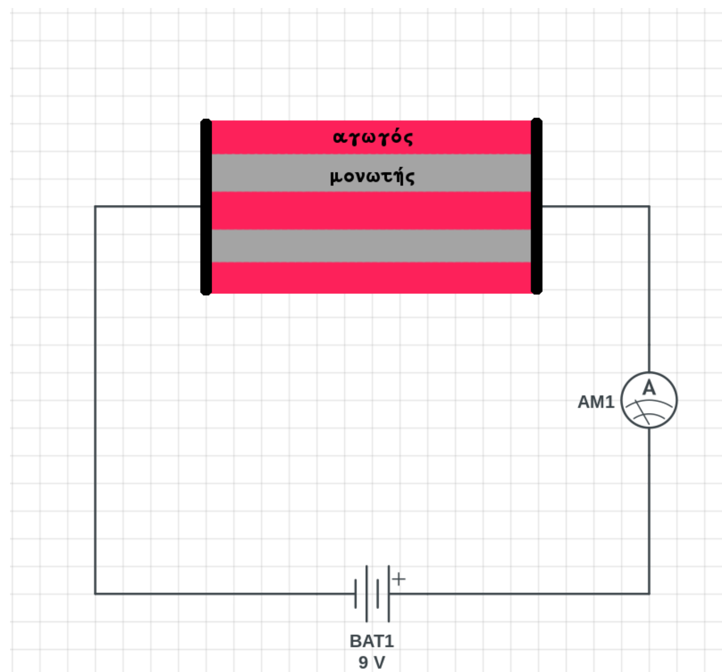
How to calculate the properties of a composite in terms of the properties of the constituting phases?

1. Additive properties $\rho_{tot} = \rho_1 V_1 + \rho_2 V_2$

1. Properties calculated by using effective medium theories (EMT)

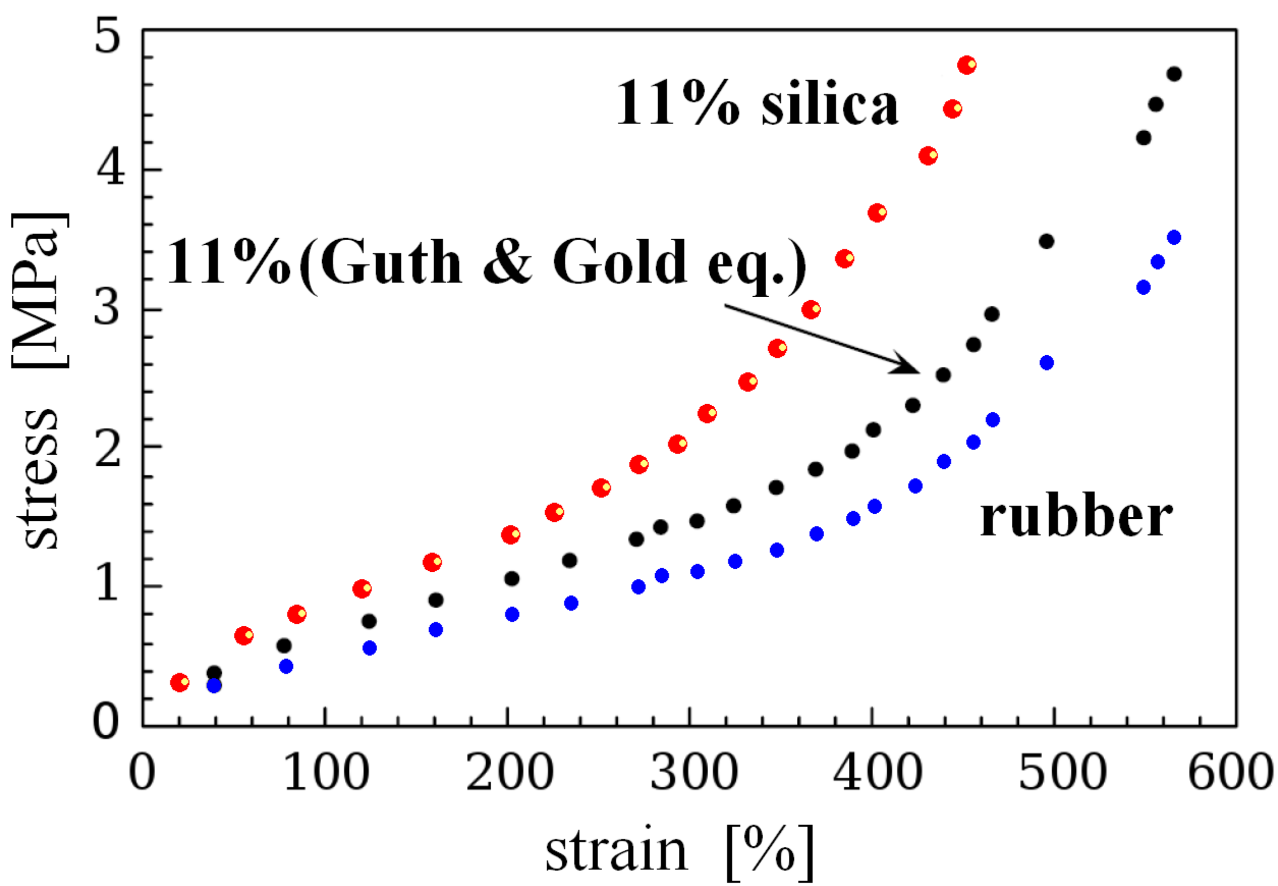
$$\sigma_{tot} = \sigma_{tot}(\sigma_1, \sigma_2, p_2, d, \text{μορφολογία})$$





Properties Improvement in PNCs

Natural Rubber / Silica, Mechanical properties



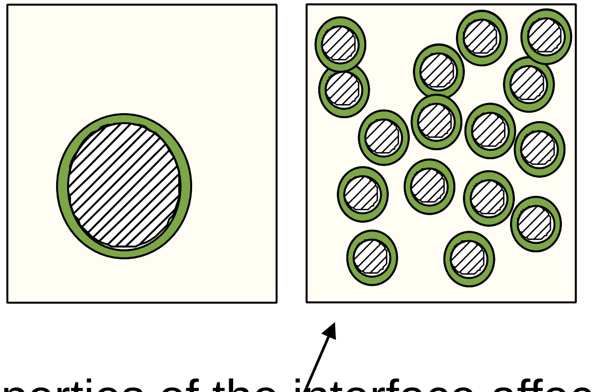
Guth & Gold equation:

$$G = G_0(1 + 2.5\varphi + 14.1\varphi^2)$$

L. Bokobza, J. P. Chauvin, Polymer 46, 4144-4151, 2005.

Effects of interfaces (1)

Polymeric chains close (a few nm) to a solid surface: changes in
- structure (density, chain configuration)
- phase transitions
- molecular mobility

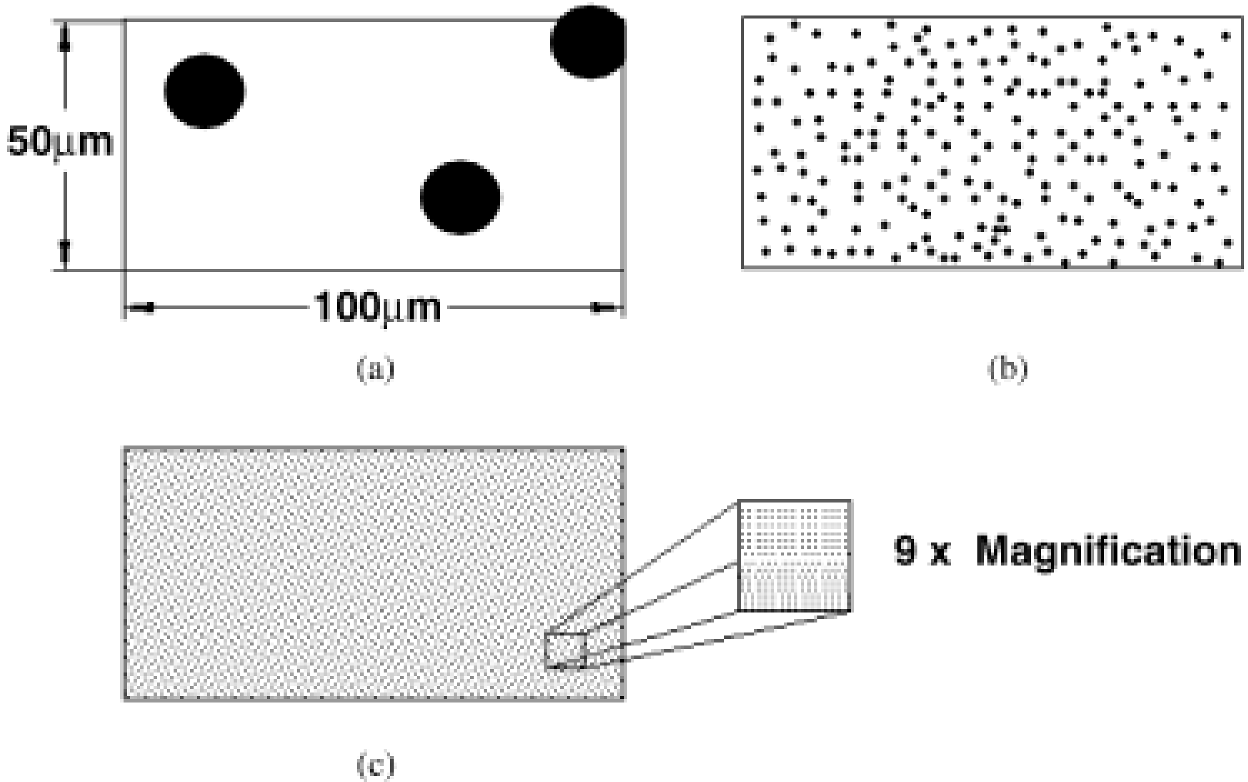


The properties of the interface affect
or dominate over the bulk properties

- new properties or combination of properties interesting for applications
- (fundamental physics) effects close to interfaces become bulk properties

G. C. Papanicolau et al., Coll. Polym. Sci., The concept of the boundary interface in composite mechanics, Coll. Polym. Sci. 256 (1978) 625-30
G. C. Papanicolau et al., Compos. Interf. 14 (2007) 131-52

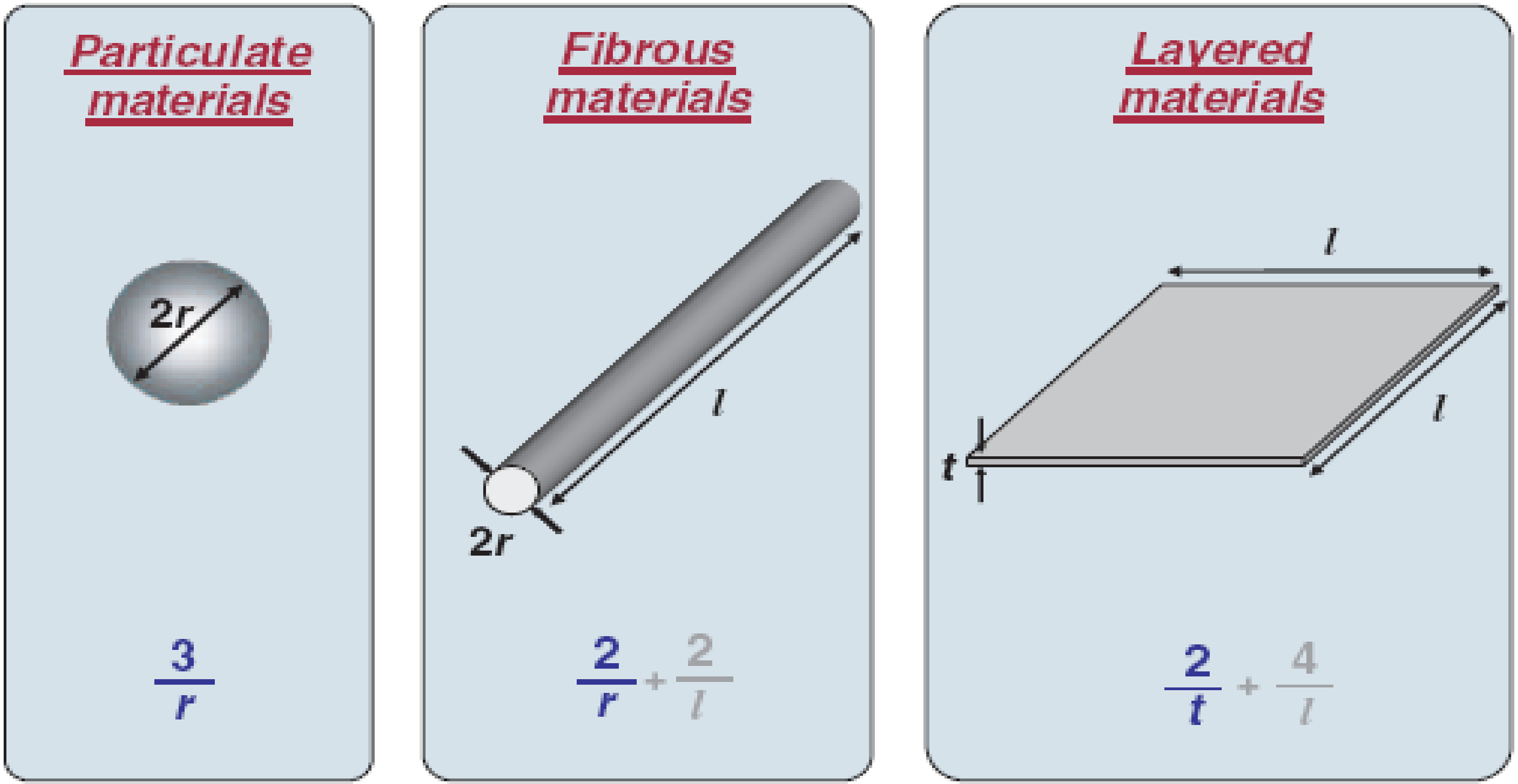
Effects of interfaces (2)



Schematic drawings of microstructural appearance of typical-particulate vs. fine-particulate vs. nano-particulate composites based on electronic microscopic observations: (a) 3 vol% of particles with 10 μm diameter (2.86 particles within a volume of 50 000 cubic μm); (b) 3 vol% of particles with 1 μm diameter (2860 particles within a volume of 50 000 cubic μm); and (c) 3 vol% of particles with 0.1 μm (100 nm) diameter (2.86 million particles within a volume of 50 000 cubic μm)

M. Z. Rong et al., Polymer 42 (2001) 3301-4

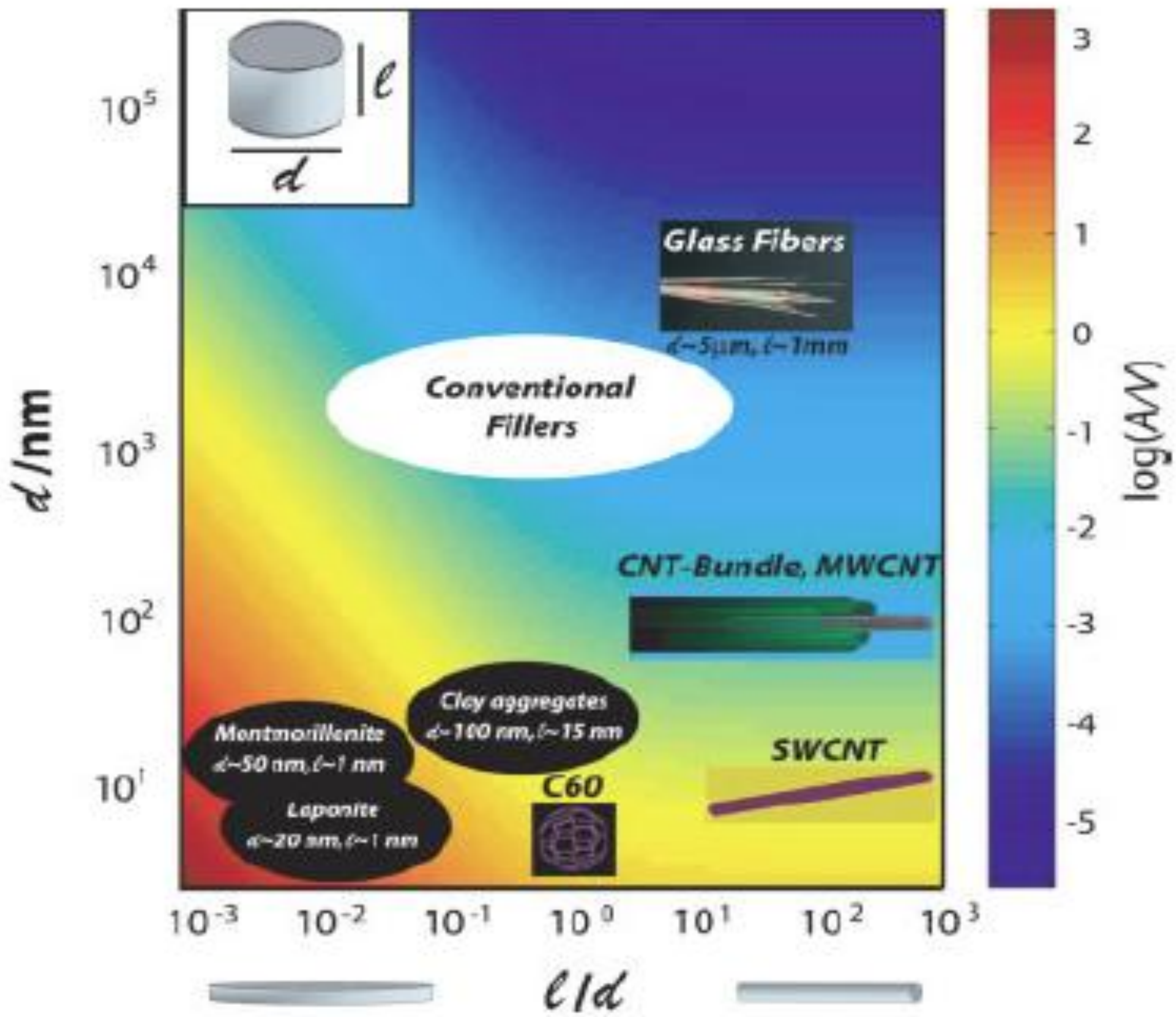
Effects of interfaces (3)



Common particle reinforcements/geometries and their respective surface area-to-volume ratios

E. Thostenson et al., J. Compos. Sci. Techn. 65 (2005) 491-516

Effects of interfaces (4)



Calculated interfacial area per volume of particles (in 1/nm), assuming a right – circular cylindrical particle shape,
for different particle diameters and aspect ratios

M. R. Bockstaller et al., Adv. Mater. 17 (2005) 1331-49

Synthesis-processing (1)

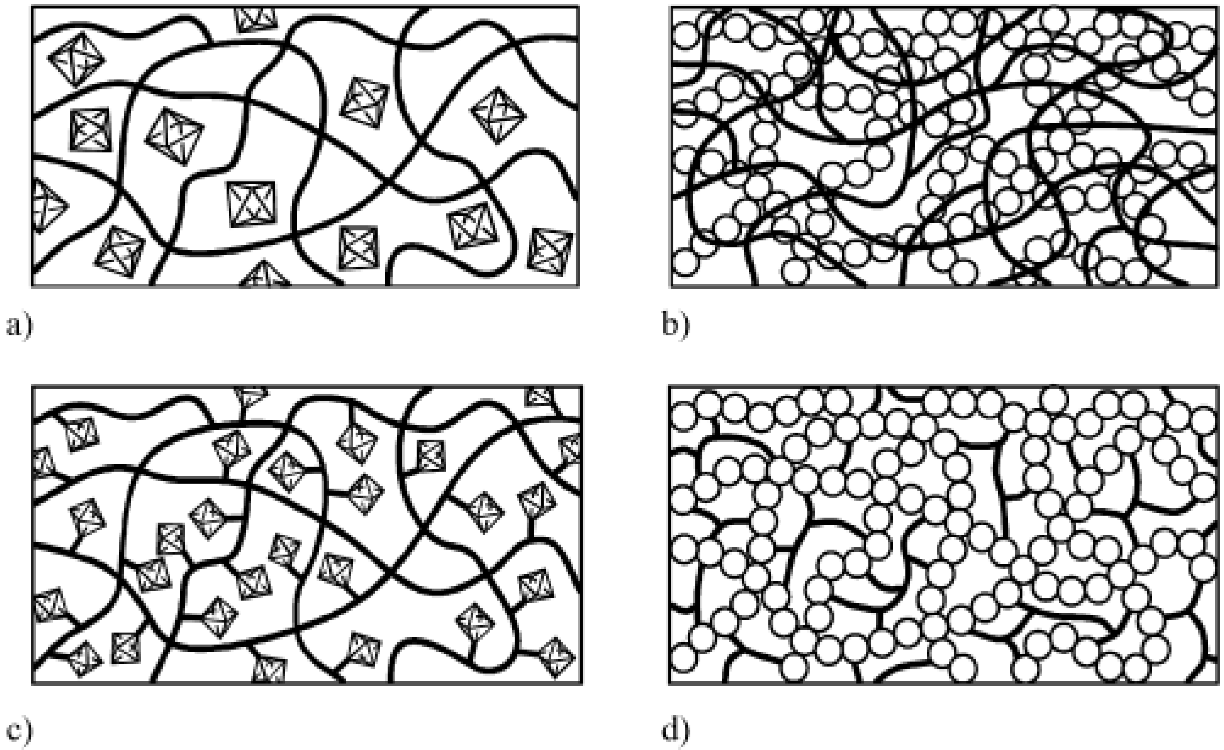
Two approaches for device fabrication where nanoparticle properties can be exploited

1. “top-down” approach
photolithography, electron-beam lithography (microelectronics)

2. “bottom-up” approach
self-assembly processes, control of structural arrangement of nanoparticles and of morphology

Synthesis-processing (2)

For a given composition, properties are determined to a large extent by the final morphology



Different kinds of inorganic-organic composite materials

a) Embedding of the inorganic moiety into the organic polymer

b) Interpenetrating networks (IPNs)

c) Incorporation of inorganic groups by bonding to the polymer backbone

d) Dual inorganic-organic hybrid polymer

G. Kickelbick, Prog. Polym. Sci. 28 (2003) 83-114

Synthesis-processing (3)

1. Mixing with preformed particles
2. Sol-gel techniques
3. Using nanobuilding blocks

Synthesis-processing (4)

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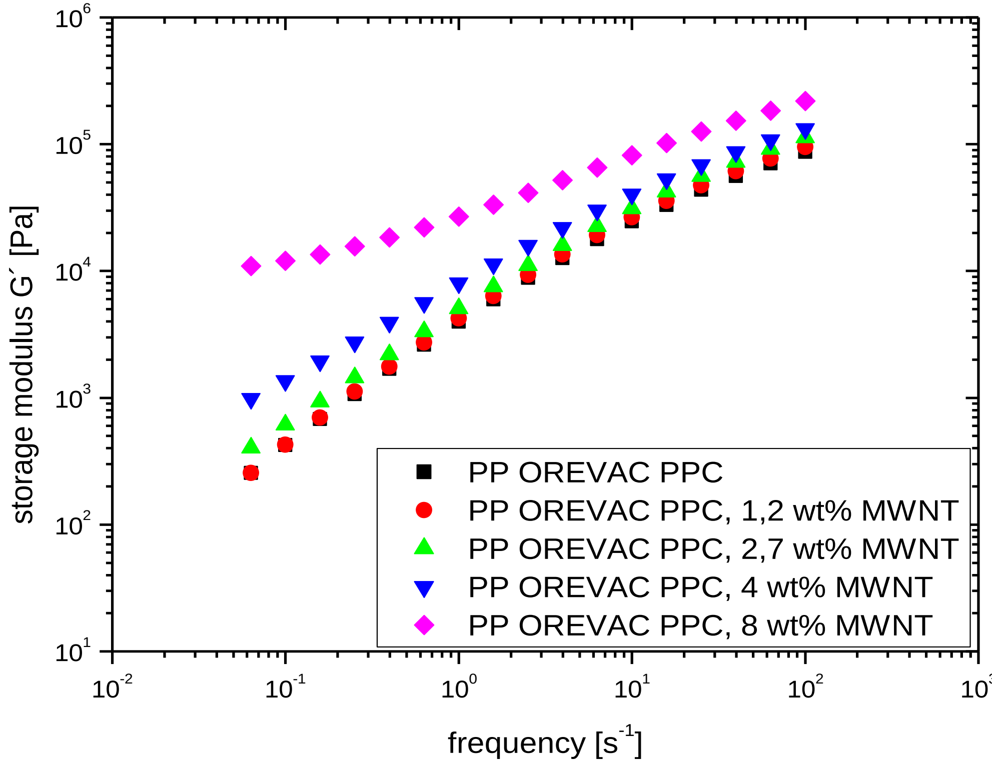
Mixing with preformed particles

Rheological measurements – MA PP/MWCNT series



Storage modulus (Fig.) and viscosity increase with CNT addition. At 190°C first clear rheological indication of percolation is seen starting at 8 wt% MWNT. At 4 wt% already a small increase in η* and G' at low frequencies can be observed. This concentration is much higher than detected in electrical measurements (already percolated at 2.7 wt%)

Synthesis-processing (5)

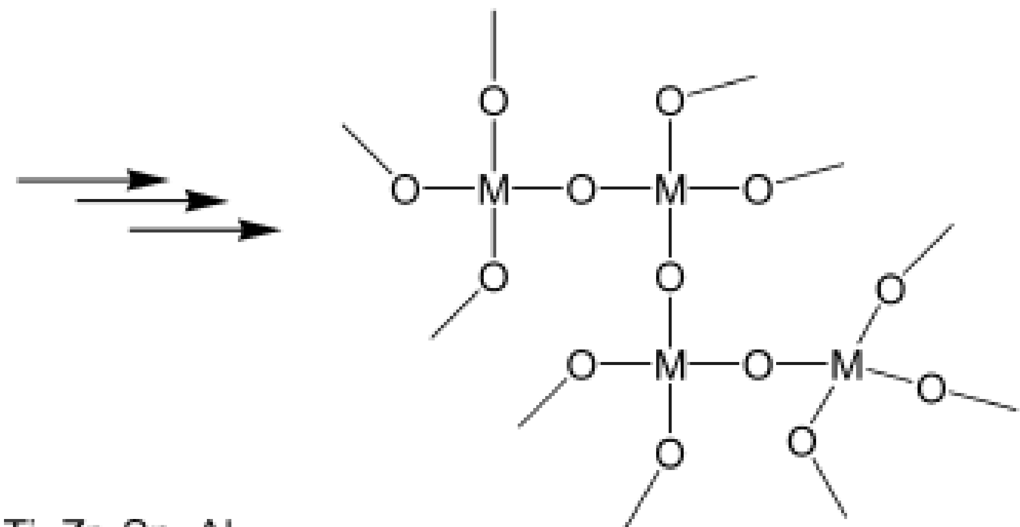
Sol-gel techniques

Hydrolysis:

$$M(OR)_n \xrightarrow{H_2O} M(OR)_{n-m}(OH)_m + HOR$$

Condensation:

$$2\ M(OR)_{n-m}(OH)_m \longrightarrow (RO)_{n-m}(HO)_mM{-}O{-}M(OR)_{n-m}(OH)_m$$



M = Si, Ti, Zr, Sn, Al, ...
R = Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu, ^{s}Bu, ...

Formation of metal oxide frameworks by sol-gel techniques

G. Kickelbick, Prog. Polym. Sci. 28 (2003) 83-114

Synthesis-processing (6)

Using nanobuilding blocks

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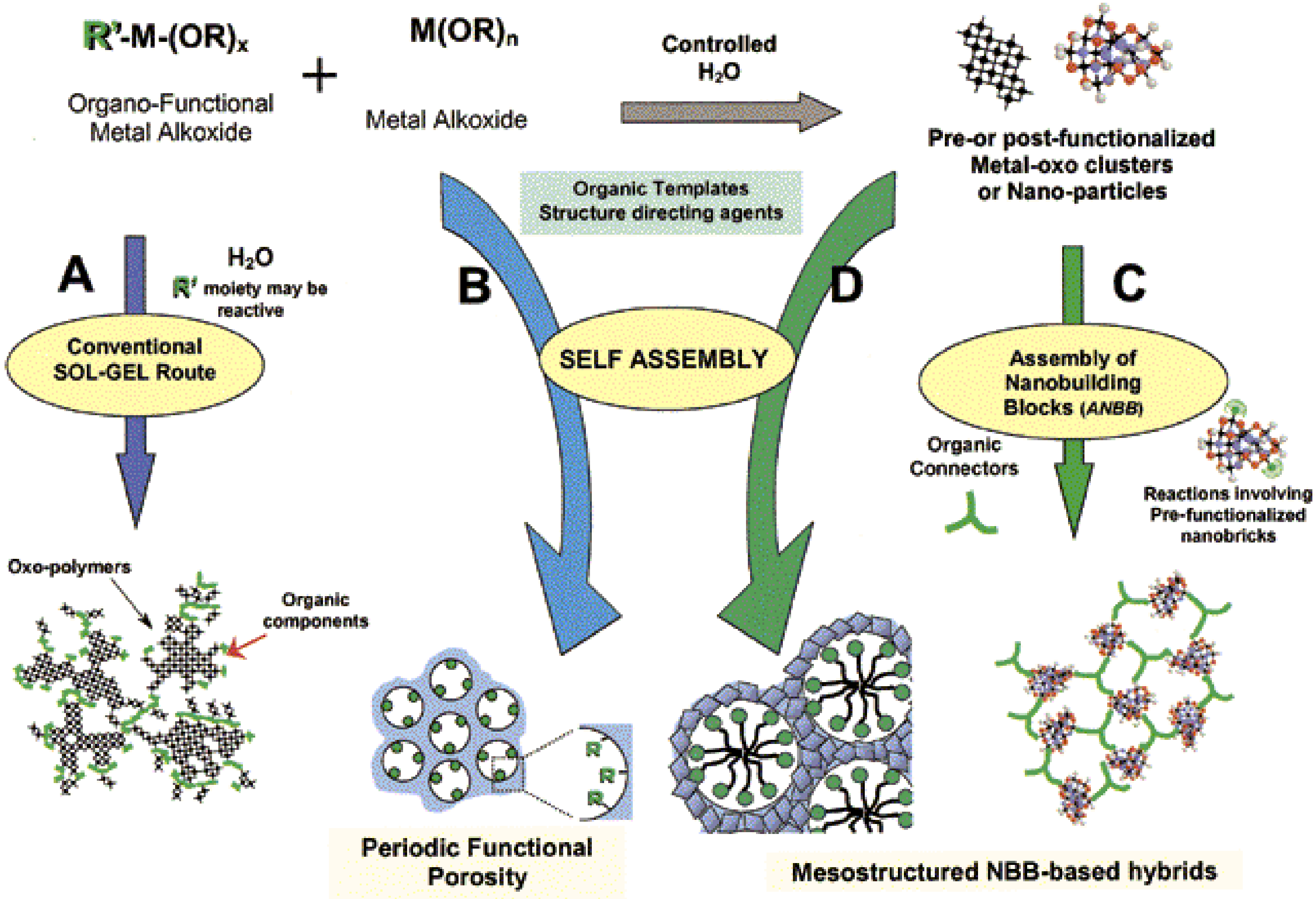

Different paths for obtaining hybrid materials. Conventional sol-gel route (path A), use of templates capable of self-assembly (paths B, D), assembly of nanobuilding blocks (paths C, D)

C. Sanchez et al., Chem. Mater. 13 (2001) 3061-83

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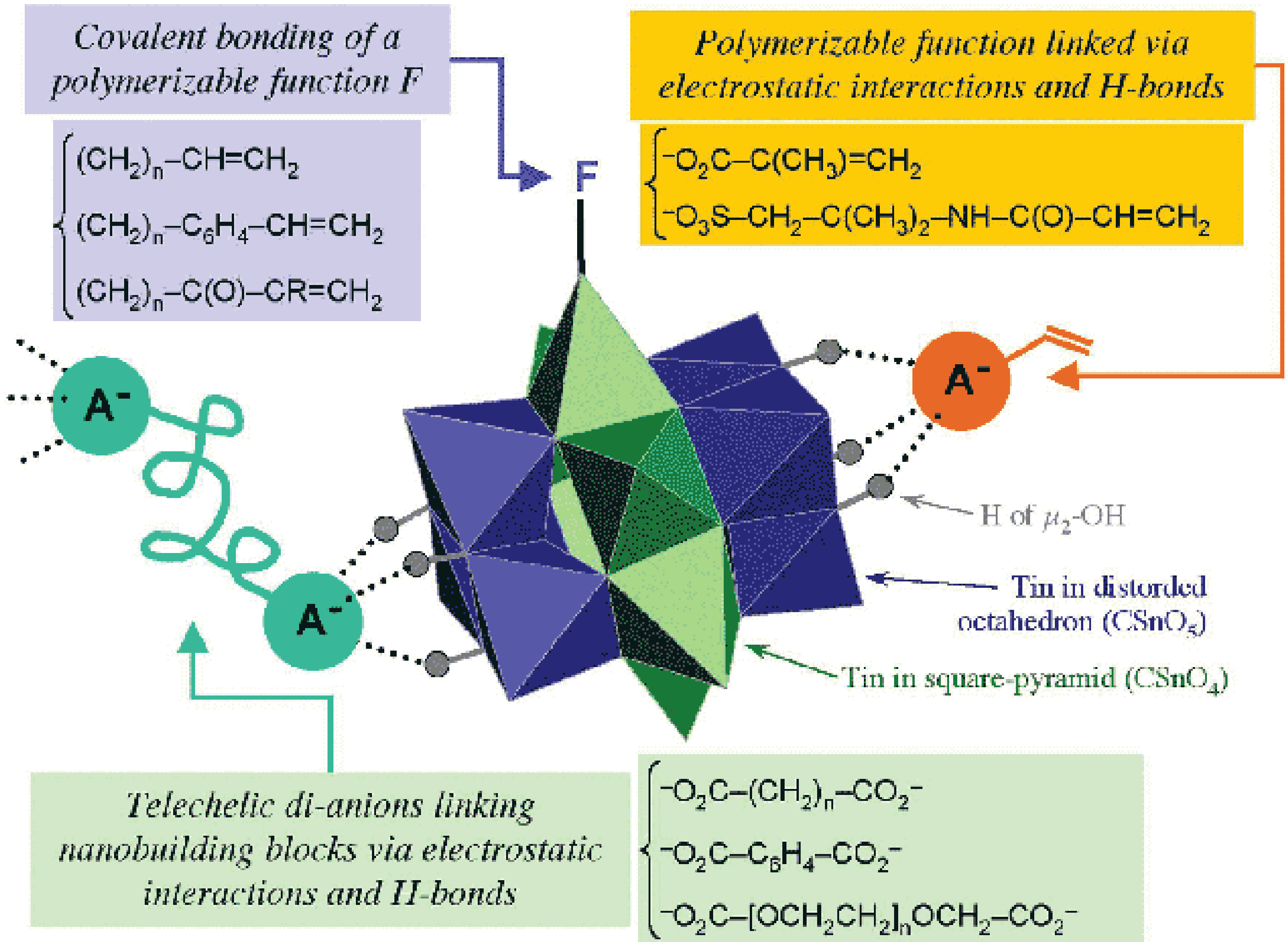
Synthesis-processing (7)

Using nanobuilding blocks



Schematic representation of the various possible strategies that can be used to assemble functionalized tin-12 clusters

C. Sanchez et al., Chem. Mater. 13 (2001) 3061-83

Synthesis-processing (8)

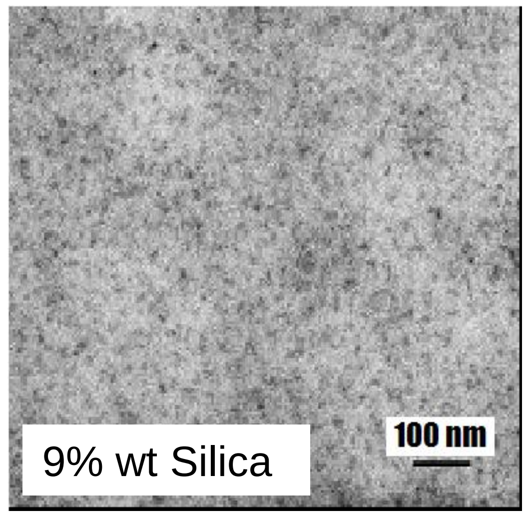
Morphological characterization

PDMS/silica & PDMS/titania

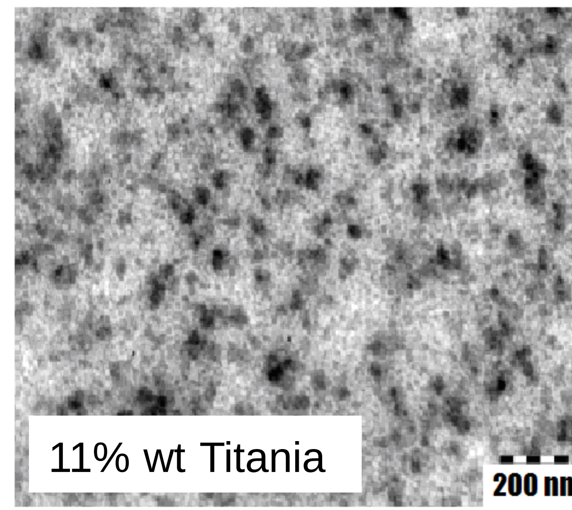
Preparation by *Sol-Gel techniques* – optimization of preparation conditions

Precursors:

- *TEOS* $Si(OC_2H_5)_4$, for silica
- *Titanium(IV) n-butoxide* $Ti(OC_4H_9)_4$, for titania



diameter ~ *10nm*



diameter ~ *20 - 40nm*

- rather diffuse interfaces in the case of silica, better defined in the case of titania
- for higher silica content probably interpenetrated polymer-silica structure, titania particles are almost connected in a branched network structure even at low filler content

P. Klonos *et.al*. *Polymer 51* (2010) 5490–9.

Applications (1)

Timing belt covered with injection molded nylon-6/clay nanocomposites
M. kawasumi, J. Polym. Sci. Part A Polym. Chem. 42 (2004) 819-24

Applications (2)

(a) (b)

Thermoplastic polyolefine nanocomposites, applications for automotive part
F. Hussain et al., J. Compos. Mater. 40 (2006) 1511-75

Applications (3)

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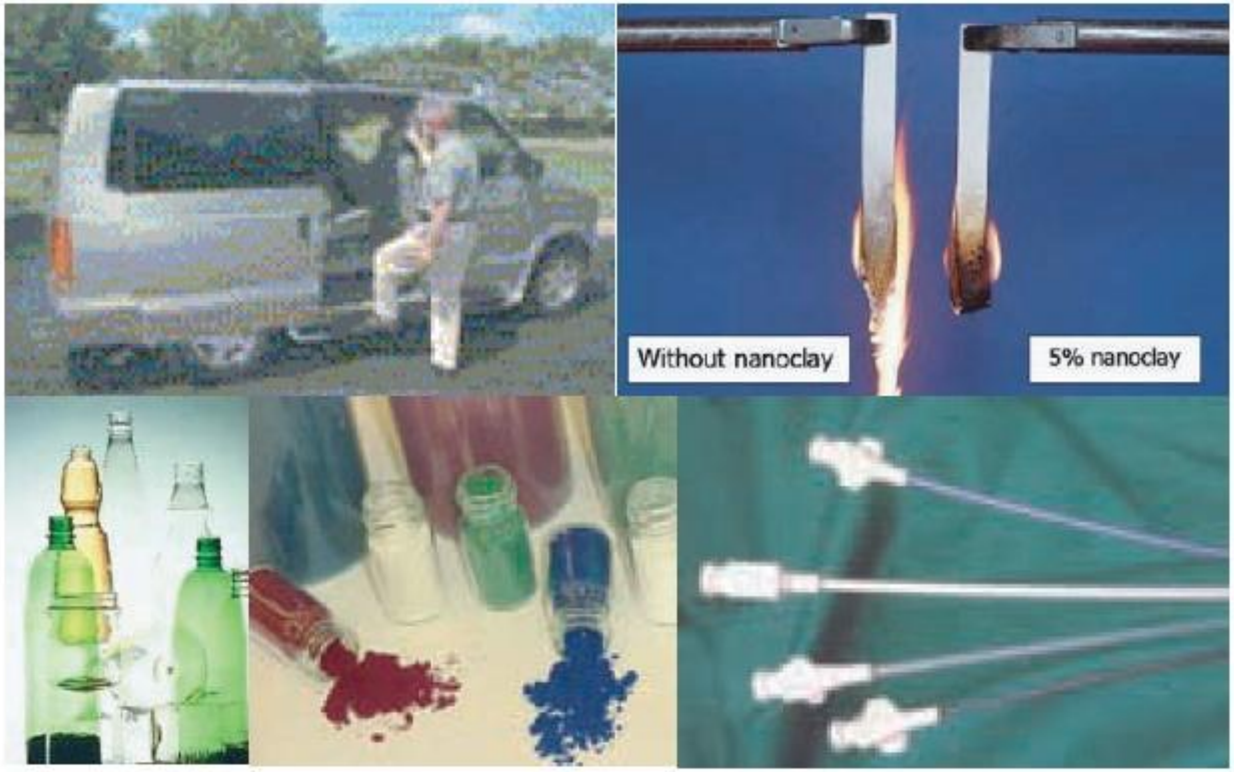

Fig. 13. Selected commercial products made from clay-based polymer nanocomposites.

Zeng et al., J. Nanosci. Nanotechnol. 5 (2005) 1574-92

Applications (4)

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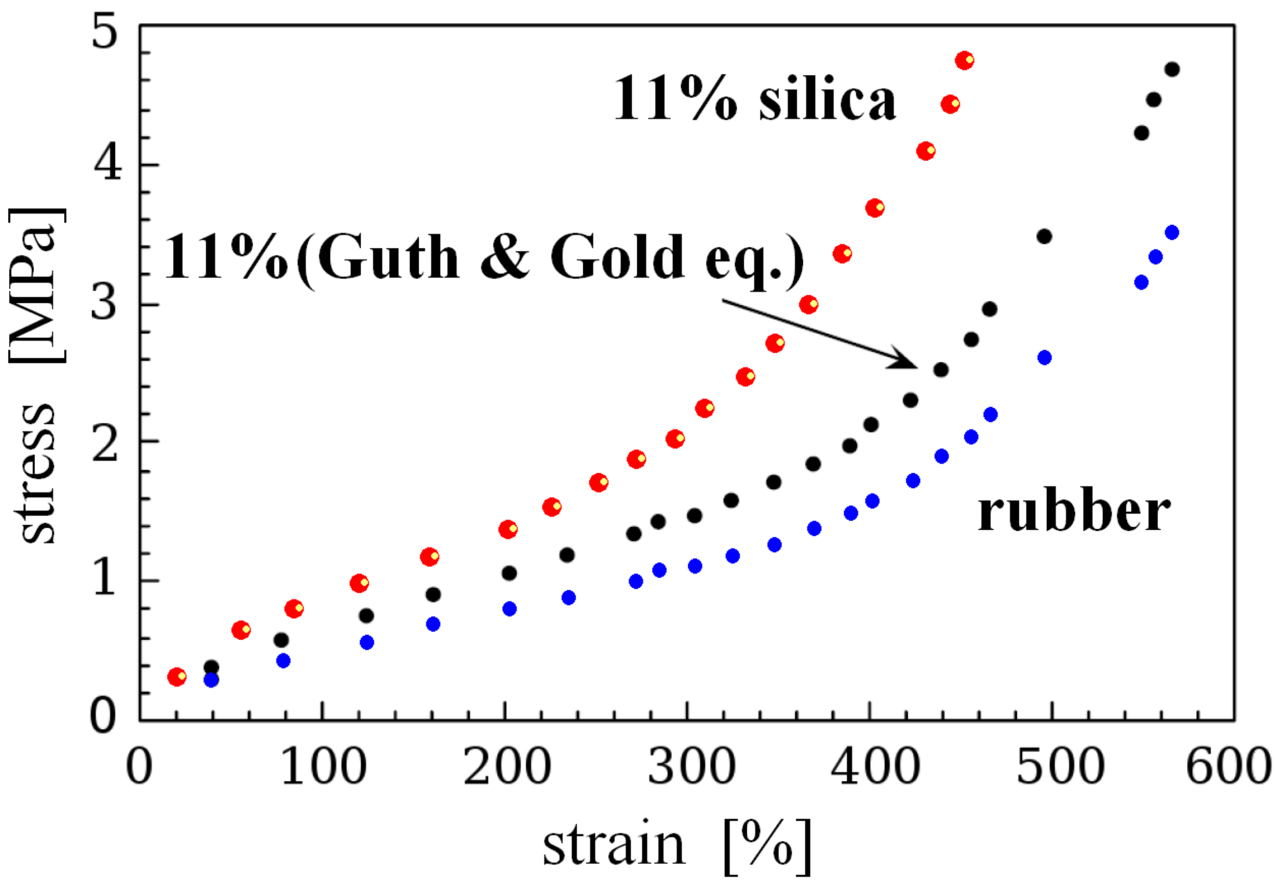
Properties Improvement: Mechanical properties



Guth & Gold equation:

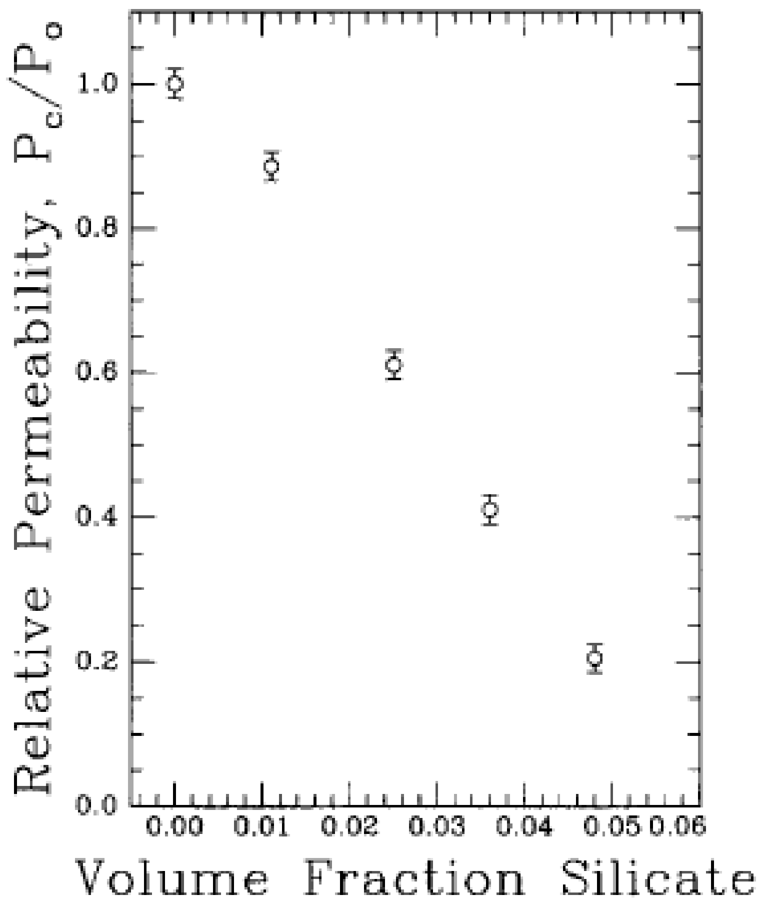
$$G = G_0(1 + 2.5\varphi + 14.1\varphi^2)$$

$$G = G_0 \,.\, X \,.\, Y$$

L. Bokobza, J. P. Chauvin, Polymer 46, 4144-4151, 2005.

Applications (5)

Properties Improvement: Barrier properties



Water permeability in poly(ε-caprolactone)/clay nanocomposites

P. B. Messersmith, E. P. Giannelis, J. Polym. Sci. Part A Polym. Chem. 33 (1995) 1047-57

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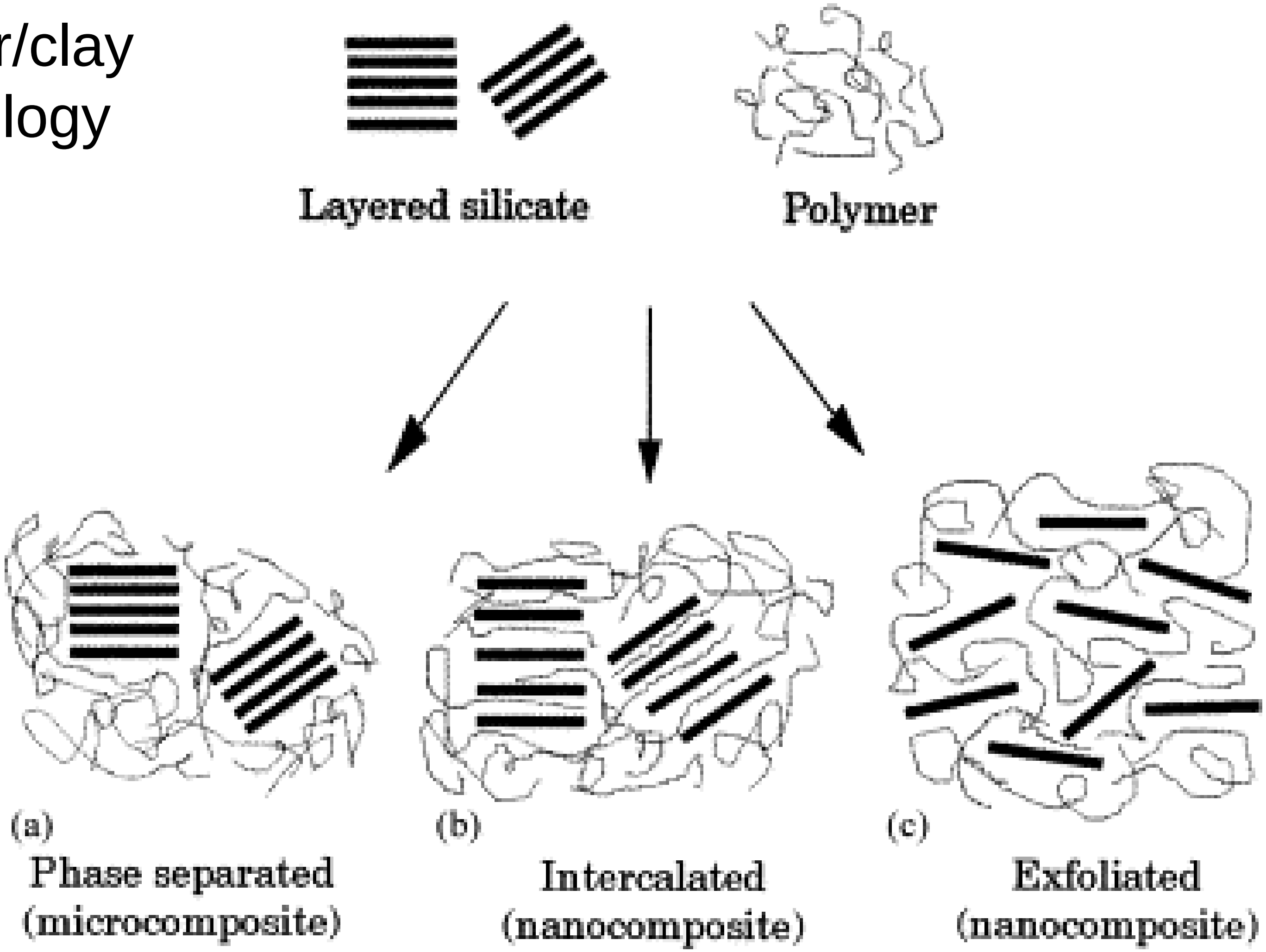
Applications (6)

Properties Improvement: Barrier properties

polymer/clay morphology



M. Alexandre, P. Dubois, Mater. Sci. Eng. 28 (2000) 1-63

Applications (7)
Properties Improvement: Barrier properties

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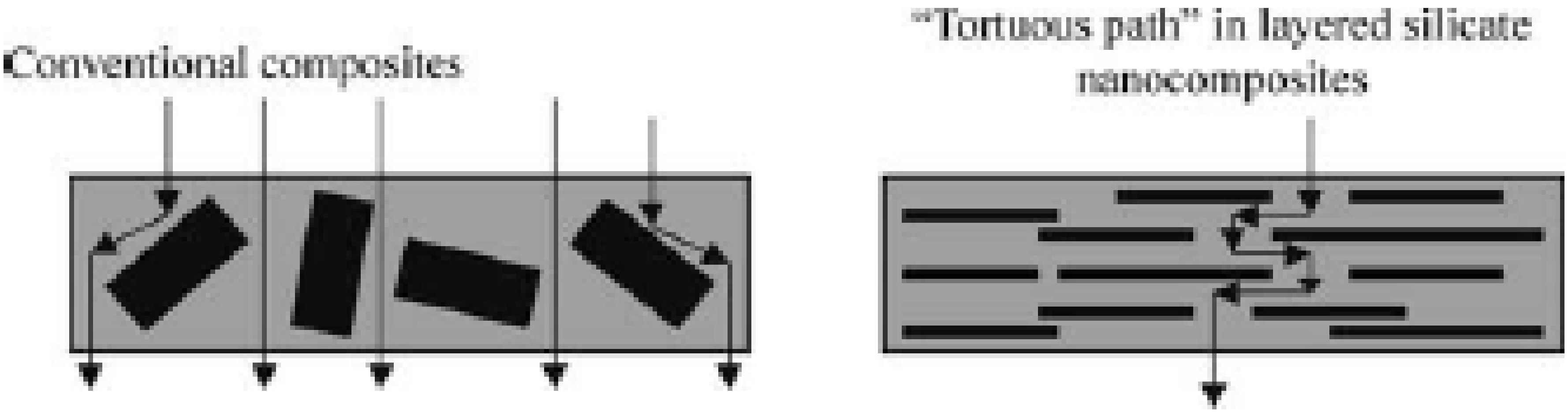
Permeablity = Solubility X Diffusion Coefficient



Formation of tortuous path in PLS nanocomposites
S. Sinha Ray, M. Okamoto, Prog. Polym. Sci. 28 (2003) 1539-1641

Food packaging
- Nanoclays (to reduce gas permeability)
- Silver nanoparticles (antimicrobial properties)

Applications (8)

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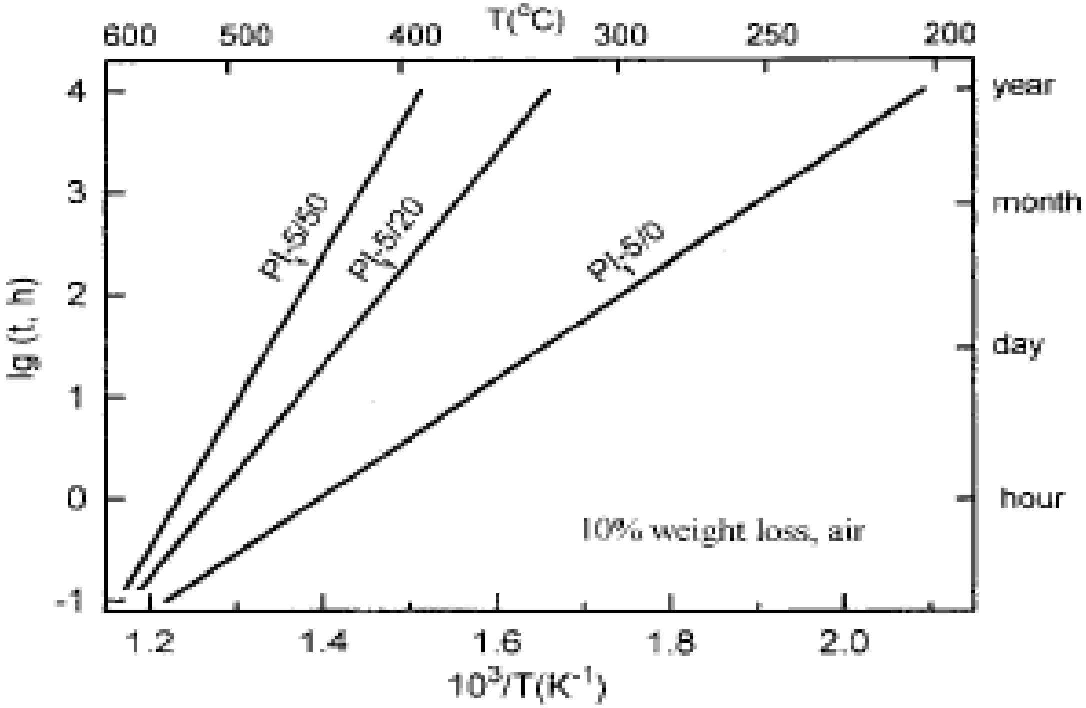
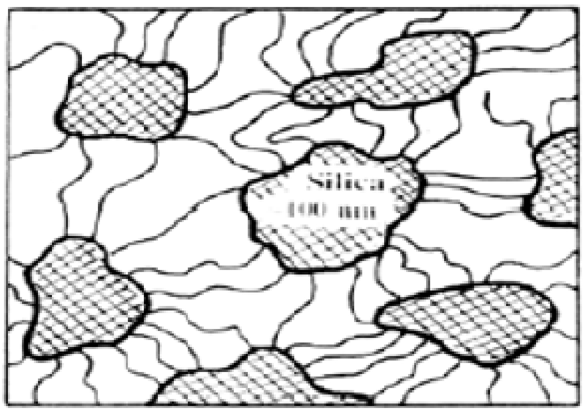
Properties Improvement: Thermal stability





Morphology, schematically (on the basis of SEM images)

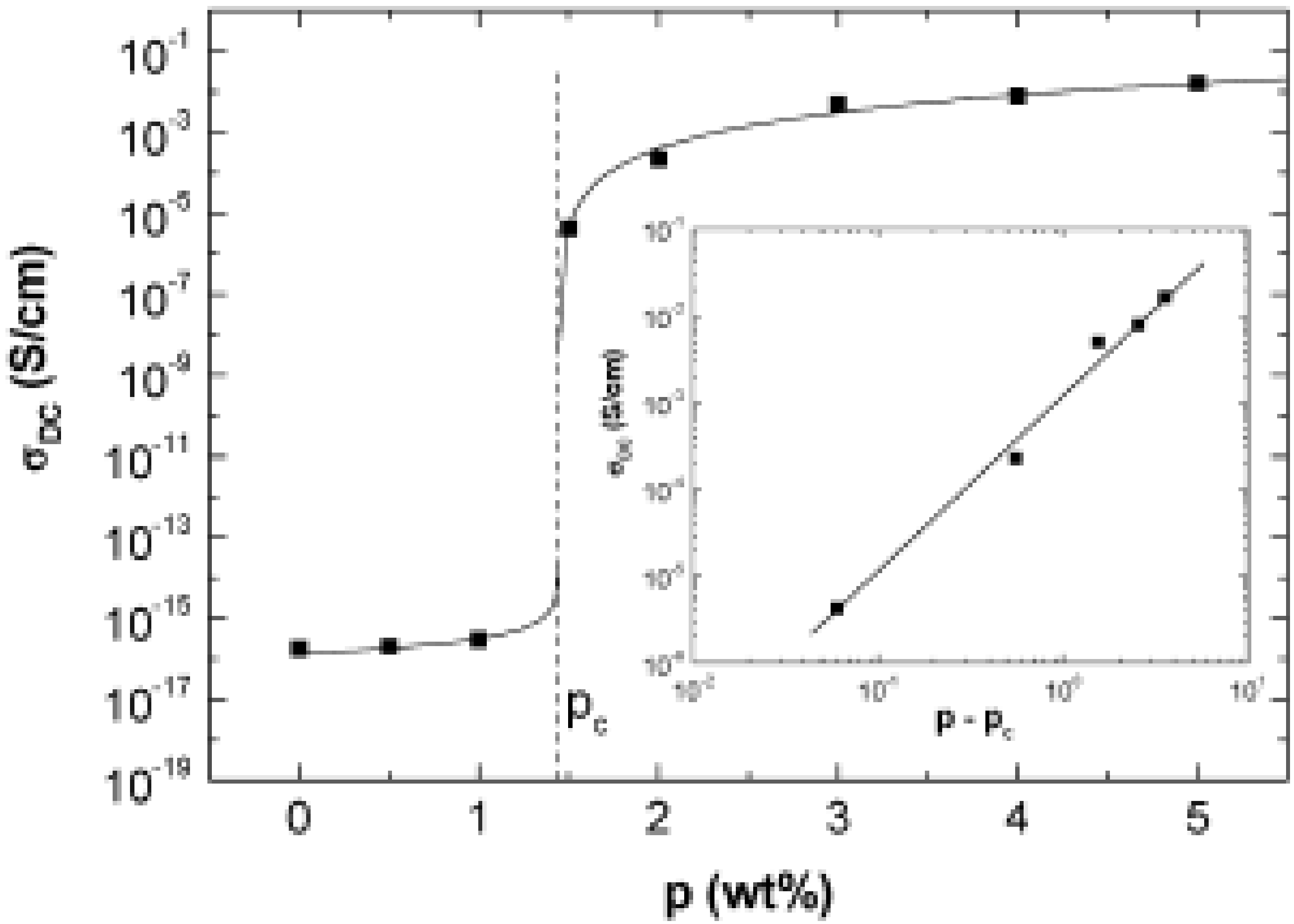
Predicted thermal longevity in polyimide/silica nanocomposites calculated from thermogravimetric data

V. A. Bershtein et al., J. Polym. Sci. Part B Polym. Phys. 40, 1056-69 (2002)

Applications (9)

Properties Improvement: Electrical properties

Here we make use of the good properties of the filler



MWCNTs in PC
Evaluation of dc conductivity in terms of percolation
$\boldsymbol{\sigma_{dc}(p) \sim (p - p_c)^t}$

P. Poetschke et al., Polymer 44 (2003) 5023-30

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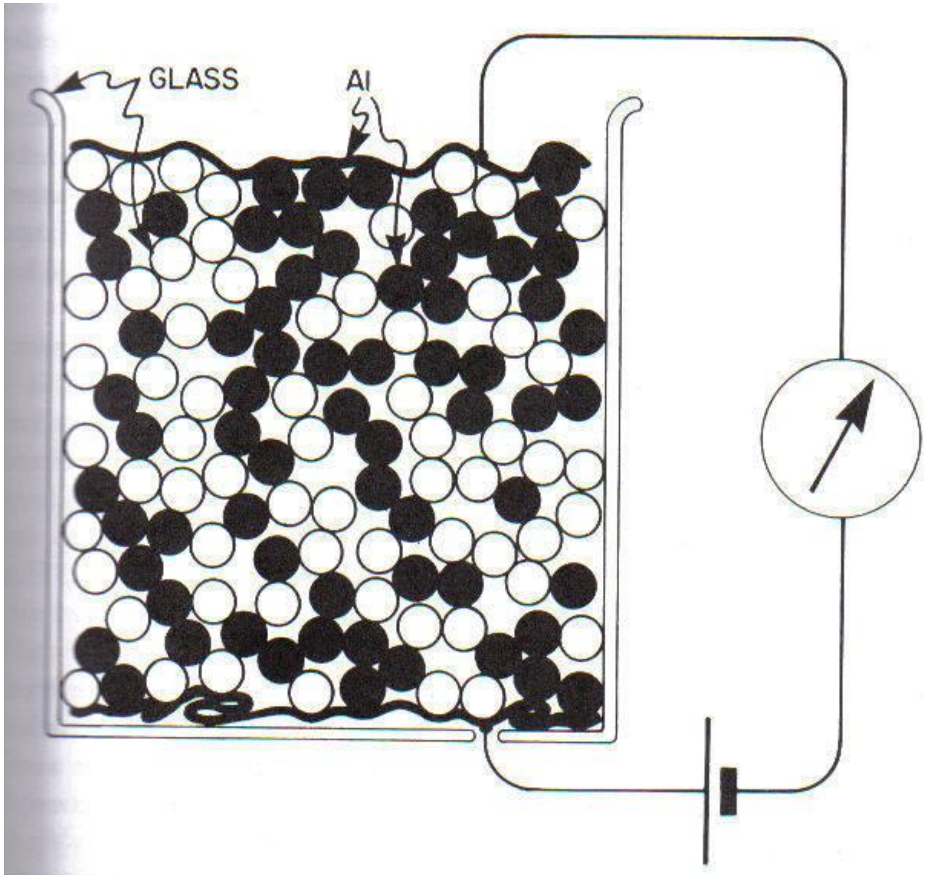
Applications (10)
Properties Improvement: Electrical properties

Percolation
in 3D



R. Zallen, The Physics of Amorphous Solids, Wiley, New York, 1983

Applications (10)

Properties Improvement: Electrical properties

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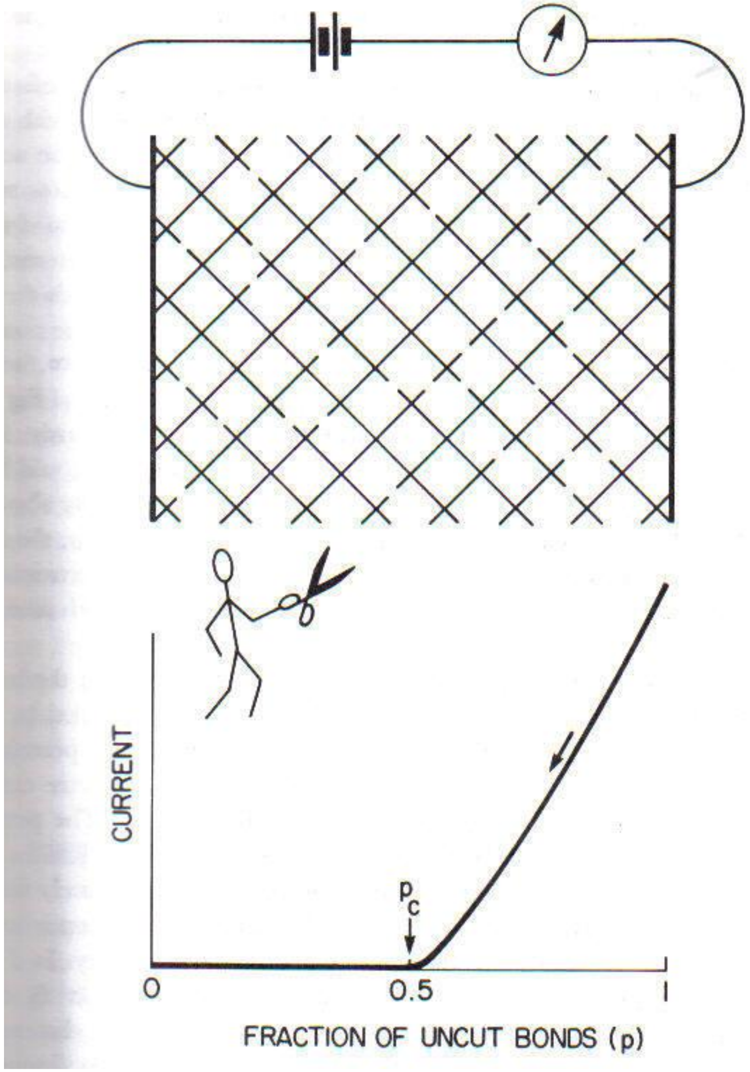
Percolation
in 2D



R. Zallen, The Physics of Amorphous Solids, Wiley, New York, 1983

Applications (11)

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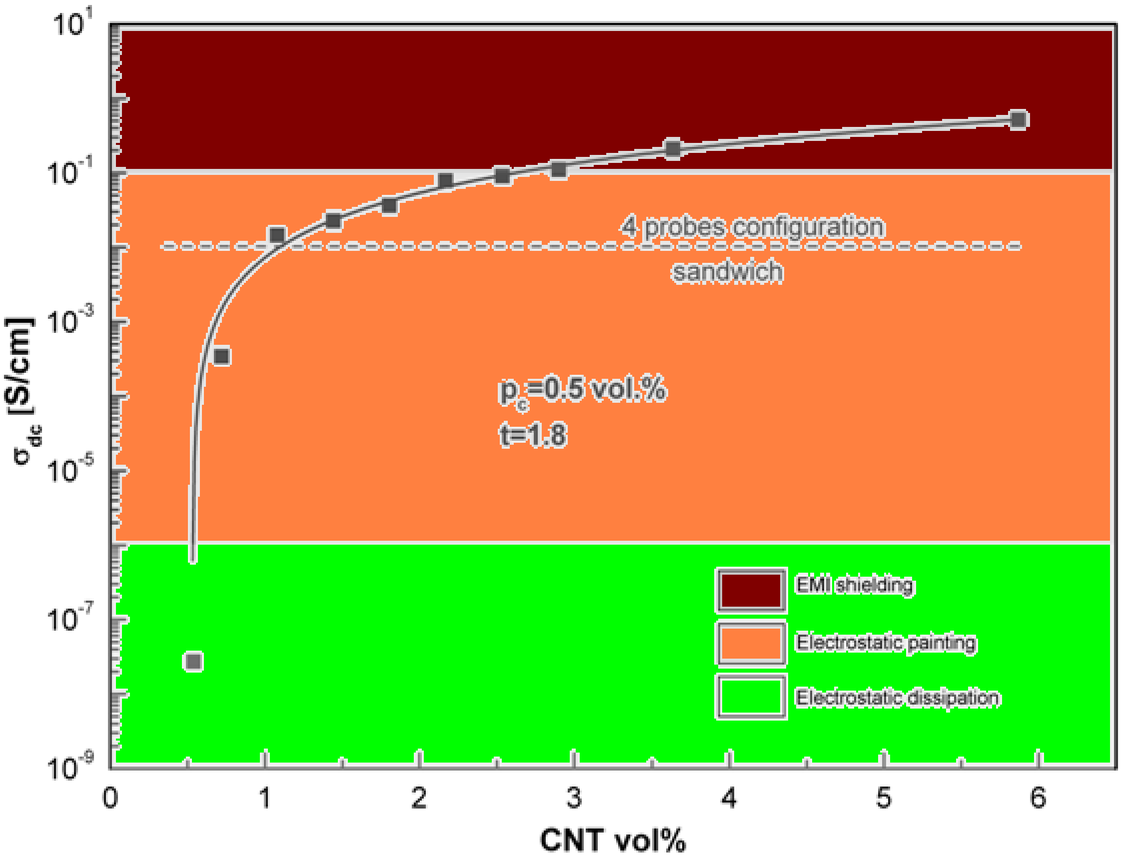
Properties Improvement: Electrical properties

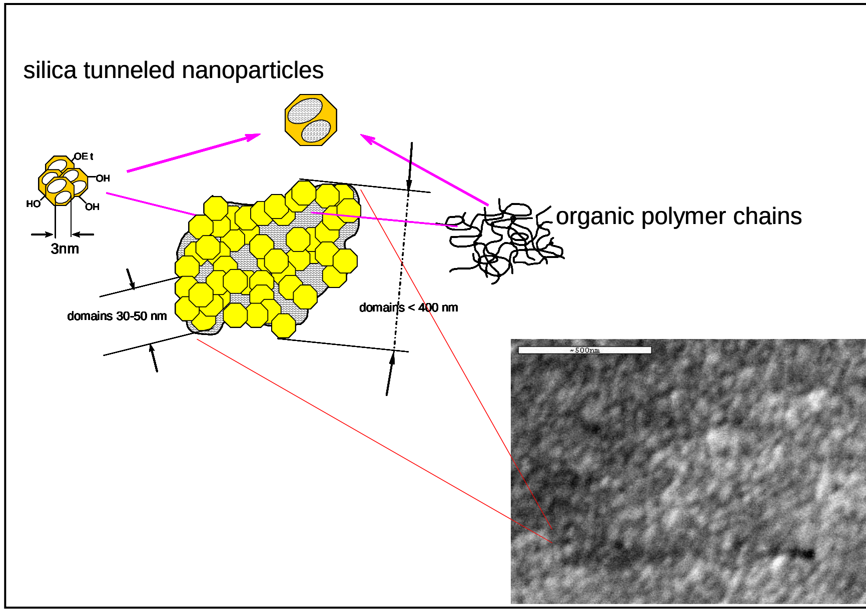
PMMA/MWCNT nanocomposites



E. Logakis et al. Comp. Sci. Technol. 71 (2011) 854-862

Applications (12) PHEA/silica hydrogels

Scaffolds for tissue engineering



1. Polymerisation of PHEA
2. Hydrolysis of TEOS

$$\equiv Si-O-C_2H_5 + H_2O \rightarrow Si-OH + C_2H_5OH$$

3. Condensation

$$\equiv Si-OH + HO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + H_2O$$

and/or

$$\equiv Si-OH + C_2H_5-O-Si \equiv \rightarrow \equiv Si-O-Si \equiv + C_2H_5OH$$

f= 0% to 30% in silica

✓ SEM: excellent dispersion

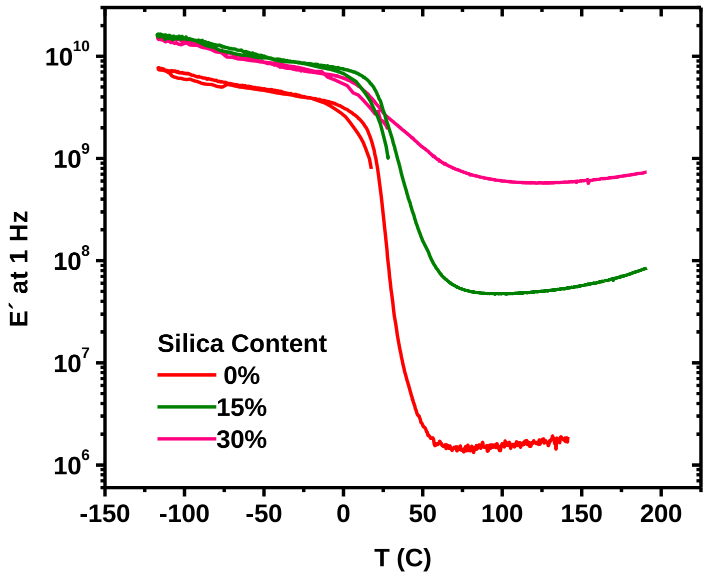
✓ TGA: Nanoparticles form a continuous network

=> An organic and an inorganic network combined

J. A. Gomez Tejedor et al., J. Polym. Sci. Part B Polym. Phys. 46 (2007) 43-54
J. G. Rodriguez Hernandez et al., Eur. Polym. J. 43 (2007) 2775-83

Applications (13) PHEA/silica hydrogels

Dynamic Mechanical Analysis



At 1 Hz: glass-rubbery transition at 10-20 C

- mechanical enhancement by 3 o.o.m. compared to pure PHEA!

J. A. Gomez Tejedor et al., J. Polym. Sci. Part B Polym. Phys. 46 (2007) 43-54
J. G. Rodriguez Hernandez et al., Eur. Polym. J. 43 (2007) 2775-83