Inorganic-Organic Hybrid Materials

Bressanone Sept. 2006 Hybrid Materials
**CLASSICAL COMPOSITES**

Property Improvement:
- mechanical stability
- thermal stability
- photochemical stability

**Hybrid Materials**

Various properties possible depending on precursors and processing

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The goal is to create materials with specific combinations of properties by combining different molecular building blocks in various ratios and by controlling their mutual arrangement at the nanolevel.

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Control over homogeneity:
- precursor selection (functional group)
- reaction conditions: kinetics, solvent, etc.
- interactions between the components

<table>
<thead>
<tr>
<th>Properties</th>
<th>Organic materials (polymers)</th>
<th>Inorganic materials (glass, ceramics)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature of bonds</td>
<td>covalent [C–C], van der Waals, H-bonding</td>
<td>ionic or covalent</td>
</tr>
<tr>
<td>$T_g$</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>low (except polyimides)</td>
<td>high</td>
</tr>
<tr>
<td>Density</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Refractive index</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>elastic</td>
<td>hard</td>
</tr>
<tr>
<td></td>
<td>flexible</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td>rubbery (depending on $T_g$)</td>
<td>brittle</td>
</tr>
<tr>
<td>Hydropobicity</td>
<td>hydrophilic or hydrophobic</td>
<td>hydrophilic</td>
</tr>
<tr>
<td>Electronic and magnetic properties</td>
<td>insulating to conductive non-magnetic</td>
<td>insulating to semiconductors magnetic</td>
</tr>
<tr>
<td>Processability</td>
<td>at low temperatures and pressures (molding, casting, etc.)</td>
<td>at high temperatures and/or pressures (sintering, glass forming)</td>
</tr>
</tbody>
</table>
Nanolego

Form
Function
Geometry of the linkage
Connectivity
Kind of linkage

Inorganic Building Blocks

Si
O
O
O
Si
O
O
O
Ti
O
O
O
O

Mechanical, optical, electrical, magnetical properties

Connecting Blocks

Reduction of the crosslinking density, coupling sites between inorganic / organic components

Organic Building Blocks

Functional groups, crosslinking, polymerizability

Flexibility, elasticity, processability

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Nanolego: Linking the Building Blocks

Polymerization / Polycondensation

Sol-Gel-Process

Self-Organization

Na$_4$SiO$_4$ + H$^+$

Zn(NO$_3$)$_2$ + HO

+$\text{H}_2\text{NN}$ H 2

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Nanolego: Critical Issues

- Homogeneous distribution of the building blocks in the material
- Stable distribution: no microphase separation
- Interaction between the two components
- Structure-property relationships
- Inclusion of functionalities
- Tailoring of
  - molecular structure ↔ nanostructure ↔ microstructure
  (= hierarchical structure design)
**Precursors**
- Molecular precursors
- Clusters (nano-building blocks, NBB)
- Alkoxyisilyl-substituted organic polymers
- Pre-formed nanostructures

**Classes of sol-gel hybrid materials**
- Physically entrapped components
- Functionalized inorganic networks
- Interpenetrating networks
- Dual networks

**Molecular Precursors**

**Network Modifiers** (non-reactive organic groups)

\[
\begin{align*}
\text{(RO)}_3\text{Si} & \quad \text{(RO)}_3\text{Si} - \text{CH}_3 \\
\text{(RO)}_3\text{Si} & \quad \text{(RO)}_3\text{Si} \quad \text{(RO)}_3\text{Si}
\end{align*}
\]

**Precursors with Functional Organic Groups**

- Polymerizable organic groups
  \( \Rightarrow \) inorganic-organic hybrid polymers
- Groups with other organic functions

\[
\begin{align*}
\text{(RO)}_3\text{Si} & \quad \text{(RO)}_3\text{Si} \quad \text{HS-Si(OR)}_3 \\
\text{(RO)}_3\text{Si} & \quad \text{(RO)}_3\text{Si} \quad \text{(EtO)}_3\text{Si} \\
\text{(RO)}_3\text{Si} & \quad \text{(RO)}_3\text{Si} \quad \text{NO}_2 \\
\text{(EtO)}_3\text{Si} & \quad \text{NH}_2 \\
\text{(RO)}_3\text{Si} & \quad \text{NH}_2 \\
\text{(RO)}_3\text{TiO}_3 & \quad \text{Co-phthalocyanine}
\end{align*}
\]
Nano Building Blocks: Polyhedral Oligomeric Silsesquioxanes (POSS)

Unreactive organic (R) groups for solubilization and compatibilization. → One or more reactive groups for grafting or polymerization.

Nanosopic size Si-Si distance = 0.5 nm R-R distance = 1.5 nm.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Nano Building Blocks: Functionalized Metal Oxide Clusters

Zr₆O₄(OH)₄(methacrylate)₁₂

Ti₁₀O₁₆(OEt)₁₂(OPr)₈
(same with OCH₂CH₂OC(O)C(Me)=CH₂)

{(BuSn)₁₂O₁₄(OH)₆}²⁺·2 methacrylate⁻

covalent interaction

electrostatic interaction

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Bridged Alkoxy Silanes

Alkoxy Silyle Substituted Organic Polymers
Consequences of Introducing Organic Substituents

- Reduced degree of crosslinking of the inorganic network
- Polarity changes (changes in hydrogen bonding)
- Reactivity change of the remaining alkoxide groups
  (electronic and steric effect of the organic substituents)

These effects are an inevitable consequence of the organic modification
Degree of Crosslinking

\[ \text{Si(OR)}_{4+n}R_n \]
\[ n = 1-3 \]

- \( \text{Si(OR)}_3R \)
- \( \text{Si(OR)}_2R_2 \)
- \( \text{Si(OR)}R_3 \)

Polyhedral Oligomeric Silsesquioxanes

Influence on Reaction Rates

Example:

\[ (\text{RO})_3\text{Si} \cdot \cdot \cdot \text{Si(OR)}_3 \]

0.6 M in methanol, 25°C
The dashed line is pH vs. gel time for \( \text{Si(OMe)}_3 \) (2.0 M in methanol, 60°C).
Influence on Reaction Rates

Precursors
- Molecular precursors
- Clusters (nano-building blocks, NBB)
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- Pre-formed nanostructures

Classes of sol-gel hybrid materials
- Physically entrapped components
- Functionalized inorganic networks
- Interpenetrating structures
- Dual networks
**Types of Inorganic-Organic Hybrid Materials by Sol-Gel Processing**

**Class I materials:**
weak interactions

Physically entrapped molecules, particles, etc.

Interpenetrating inorganic and organic networks

**Class II materials:**
strong interactions

Modification of the gel network by organic groups

Dual inorganic and organic networks connected by covalent bonds

**Entrapped Biomolecules**

Additives
- Polymers
- Surfactants
- Protein stabilizers
- Fillers

Biomolecules
- Proteins
- DNA
- Cells

Precursor sol

\[ (R)_{2}Si(OR)_{3-n} + H_{2}O \rightarrow (R)_{2}Si(OR)_{3-n}/OH_{n} + nROH \]

Hydrolysis

\[ 2(R)_{2}Si(OR)_{3-n}/OH_{n} \rightarrow (R)_{2}Si(OR)_{3-n}/OH_{n} - Si(OR)_{3-n}/H_{2}O \]

Condensation

Polycondensation

Gelation

Sol-gel formation with entrapped biomolecules

Aging

Condensation and Polycondensation continue for days accompanied by solvent evaporation and Sol-Gel shrinkage

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NO-releasing glucose biosensor
(cleaved NO suppresses degradation by bacteria)

Glucose oxidase in MeSi(OEt)_3 Gel

Glucose oxidase in polyurethan

M.H. Schoenfisch et al., 2004

Entrapped Inorganic Particles: Dental Filling

pyrogenic silica
(= 40 nm)

standard dental glass particles
(= 0.7 µm)

Fraunhofer ISE
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**Entrapped Inorganic Particles: Controlled Release**

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*in SiO₂*
**Heterogenization of Homogeneous Catalysts**

**Classical approach**

\[
\begin{align*}
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n \quad \text{RO} \\
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n \\
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n
\end{align*}
\]

**Sol-gel approach**

\[
\begin{align*}
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n \quad \text{RO} \\
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n \\
\text{RO} & \quad \text{Si} \quad \text{A} \quad \text{ML}_n
\end{align*}
\]

- Classical approach
- Sol-gel approach

**Heterogenization of Catalysts by Sol-Gel Processing**

**Examples:**

- More active in the hydroisolation of 1-hexene than Rh(CO)(PR$_3$)$_2$Cl
  - U. Schubert et al., 1989
- Synthesis of N,N-diethylformamide from CO$_2$, H$_2$, and diethylamine
  - A. Baiker et al., 1999
- Catalyst for the oxidation of 3,5-di-tert-butylcatechol to the quinone
  - M. Louloudi et al., 1998

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Coatings with Optical Properties

Photochromism: **fast** for optical switches, for eye protection, privacy shields
**slow** for optical data storage, energy conserving coatings, etc...

**Example:** Spirooxazine derivative

Embedding in sol-gel coatings:
For sufficient photochromism: dye concentration > 25 wt% → mechanical stability of sol-gel film is deteriorated.

Grafting of the dye to the sol-gel matrix → higher chromophore concentrations can be achieved without affecting the mechanical integrity of the sol-gel matrix

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- Dual networks
Sequential two-step process:
Second network is formed in the first

Examples:
- Generation of the organic polymer in the pores of an inorganic porous material (in channels of zeolites or mesoporous materials, between sheets of a layered lattice, such as a clay mineral) ⇒ rigid inorganic moiety with a regular pore or channel structure in the nanoscale
- Inorganic structures form and interpenetrate an organic polymer (difficulties: incompatibility between the moieties ⇒ phase separation)

Interaction via hydrogen bonds to silanol groups of the forming silica

Organic polymers with hydrogen bonding ability:

- poly(VP)
- poly(DMAA)
- poly(VA)
- poly(VAc)
- poly(MMA)
- poly(HEMA)

Si(OR)$_4$ and/or RSi(OR)$_3$ $\text{H}_2\text{O}$, [Katal]

No macro phase separation
Resulting materials: high degree of homogeneity and optical transparency

Important reaction parameter: pH
Change of crosslinking density and interaction with polymer using RSi(OR)$_3$/Si(OR)$_4$ mixtures
Nanostructured hybrid polymer

Poly(isopren-block-ethyleneoxide) swollen in THF/CH$_3$Cl

Sol from GLYMO and Al(O$^t$Bu)$_3$ (H$_2$O/HCl)

$\text{O}_3\text{Si}(\text{RO})_3\text{Si}_3\text{O}_\text{O}$

Interpenetrating Networks

Addition of tetrakis(2-(acryloxy)ethoxy)silane improves homogeneity

TEM images of the nanocomposites:

Increasing Sol-Gel Catalyst Concentration $\Rightarrow$ Faster Reaction

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Nanocomposites: Polymer-Clay

Layered solid

Layered solid

Exfoliated layers

+ Monomer (Polymerization)

+ Polymer

+ Monomer (Polymerization)

or

+ Polymer

Nanocomposites: Polymer-Clay

Layered inorganic material

Polymer intercalated between the galleries

Exfoliated with partly structural ordering

Completely exfoliated inorganic structure
Nanocomposites: Polymer-Clay

"Macro"-composite: $\ell = 1 \, \mu m$

- Reinforcement
- Interfacial Region
- Bulk
- $0 < z < R_i$
- $z > R_i$

"Nano"-composite: $\ell = 1 \, nm$

- 1 nm thick montmorillonite sheet in epoxy resin
- 3 layers

Nanocomposites: Intercalation of Polymers in Pores

Direct Intercalation

Polymer + Porous Host

Problems:
- Pore diameter ↔ size of Polymer
- Diffusion of polymer
- Usually only end of polymer sits in pore but not the whole chain
Monomer is intercalated into the pores (vapor, liquid), then polymerization.

T. Aida et al. 2000

Fig. 23 A proposed mechanism for the formation of Eternis polyethylene with ionically-maneuvered mesoporous silica fiber (5437).

T. Bein et al. 1992

Fig. 24 Illustration for free radical polymerization of acrylonitrile within the mesoscopic channels of MCM-41 and subsequent pyrolysis to form a conducting carbon nanowire.

T. Aida et al. 2000
## Precursors

Molecular precursors  
Clusters (nano-building blocks, NBB)  
Alkoxylysilyl-substituted organic polymers  
Pre-formed nanostructures

## Classes of sol-gel hybrid materials

Physically entrapped components  
Functionalized inorganic networks  
Interpenetrating structures  
**Dual networks**

### Dual Network Structures

#### Preparation strategies

- Concomitant formation of the inorganic and organic structures
- Stepwise formation of the organic and inorganic networks  
  - from pre-formed organic structures  
  - from pre-formed inorganic structures

#### Options

- Chemical composition of the inorganic component(s)  
- Chemical composition of the organic component(s)  
- Proportion of the inorganic/organic components  
- Curing method (thermal / photochemical)  
- Dimension of the inorganic / organic components (molecular, nanometer, extended)
Concomitant Formation of Inorganic and Organic Network

Typical procedure

- **Precursors**
  - Metal Alkoxides
  - Metal Salts
  - + water (ev. catalyst or additives)
  - - alcohol

- **Hydrolysis Condensation**
- **Sol**
- **Gelation**
- **Gel**
- formation of inorganic network
- **Hardening (thermal or uv)**
- **Hybrid Polymer**
- formation of organic network

**Many Examples:**

Coatings Section

**Often used precursors**

\[
\begin{align*}
&\text{(RO)₃Si} & \text{(RO)₃Si} \\
&\text{O} & \text{O} \\
&\text{O} & \text{O} \\
&\text{O} & \text{O} \\
&\text{O} & \text{O}
\end{align*}
\]

+ Si(OR)₄, Zr(OR)₄, Al(OR)₃, etc.
+ acrylate, epoxide monomers, etc.

increase of “inorganic / organic ratio”

decrease of “inorganic / organic ratio”
Concomitant Formation of Inorganic and Organic Network

Sequential formation of the organic network

photo-initiator, hv

UV-polymerization of methacryl groups

ΔT

thermal polymerization of epoxy groups

Concomitant Formation of Inorganic and Organic Network

**Figure 3**: Comparison of a monolithic composite (left) with a conventional glassy plug (right). Cylinders have the same inner diameter and the same inner diameter and the same outer diameter. The thickness of the composite is approximately 0.5 mm.
Coating or forming of ORMOCER® (with chromophor as UV initiator)

Direct 3D-laser writing (2-photon polymerisation with femtosecond laser pulses)

Development of the structure (removal of uncured ORMOCER®)

Requirements for hardening:
- precise focussing
- 2-photon process
- polymerisation in Ormocer® layer (O₂ protection)
- chromophor as initiator

**ORMOCER®** = Organically modified Ceramics

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Photochemical Crosslinking (3D Laser Lithography)

CAD File Layer model 'Venus of Milo' in ORMOCER® (REM)

**I am made from ORMOCER®!**
Photochemical Crosslinking (3D Laser Lithography)

1. inorganic condensation
2. organic polymerization

acrylic monomer + polymer (incomplete polymerization)

inorganic condensation between fully polymerized polyacrylate

Low shrinkage by the use of prepolymerized materials

Hybrid Polymers from Pre-Formed Organic Polymers
Hybrid Polymers from Pre-Formed Organic Polymers

Hybrid Materials applying Dendrimers

Porous Materials using Dendrimers as Templates

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Hybrid Polymers from Pre-Formed Inorganic Structures

T_g vs- Composition Relationship for POSS-POSS-Methacrylate/MMA Copolymers

T_g transitions measured via TMA

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Improved properties through controlled reinforcement of polymer chains at the molecular level

Property enhancements via POSS observed in POSS-copolymers and blends:
- Increased $T_{dec}$
- Increased $T_g$
- Reduced flammability
- Reduced heat evolution
- Lower density
- Disposal as silica
- Extended temperature range
- Increased oxygen permeability
- Lower thermal conductivity
- Thermoplastic or curable
- Enhanced blend miscibility
- Oxidation resistance
- Altered mechanics
- Reduced viscosity

POSS for fire retardant materials

Traditional Polymer

POSS Polymer

www.hybridplastics.com
Hybrid Polymers from Pre-Formed Inorganic Structures

Polymerizable Metal Oxo Clusters

Zr$_6$O$_4$(methacrylate)$_{12}$ for free radical polymerization

Zr$_6$O$_4$(5-norbornene-2-carboxylate)$_{12}$ for ROMP

Polymerizable groups X

Polymerizable Metal Oxo Clusters

Hybrid Polymers from Pre-Formed Inorganic Structures

Metal Oxo Clusters as Initiators for ATRP

multifunctional initiator + monomer + catalyst + solvent

e.g. Ti$_6$O$_4$(OCCBrMe$_2$)(OiPr)$_8$

Polydispersities <1.5.
90% of the chain ends still active after isolation

G.Kickelbick et al.

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Combination of polyoxometallates (electrochromism, photochromism, conductivity, redox activities) + conjugated molecules and polymers ⇒ electrically active organic materials (light emitting diodes, field-effect transistors, solid-state lasers)

Monofunctionalization of $\text{Mo}_6\text{O}_{19}^{2-}$

\[
[\text{Mo}_6\text{O}_{19}^{2-}] + \text{Ph}_3\text{P} = \text{Na}_2 \xrightarrow{90\degree C, 4\text{h}} [\text{Mo}_6\text{O}_{19}^\text{(Na)}_2]^{2-} + \text{Ph}_3\text{P} = \text{O}
\]

\[
[\text{Mo}_6\text{O}_{19}^{2-}] + \text{ArNCO} \xrightarrow{150\degree C, 24\text{h}} [\text{Mo}_6\text{O}_{19}^\text{(Ar)}_2]^{2-} + \text{CO}_2
\]

\[
[\text{Mo}_6\text{O}_{19}^{2-}] + \text{ArNH}_3 \xrightarrow{180\degree C, 24\text{h}} [\text{Mo}_6\text{O}_{19}^\text{(Ar)}_2]^{2-} + \text{H}_2\text{O}
\]

Examples:

**Hybrid Polymers from Pre-Formed Inorganic Structures**

Z. Peng et al. 2004

**Figure 1. X-ray crystal structures (Envision drawing) of three $[\text{Mo}_6\text{O}_{19}\text{(Mo}_{10}\text{O}_{40})^{1-}]$ anions, a) 1a, Ar = 2,6-dimethyl-4-toluidine; b) 1b, Ar = 2,6-dimethyl-4-ethylphenyl; c) 1c, Ar = 4-(2,6-dimethyl-4-ethylphenyl).**

**Scheme 1. Ph-containing coupling reactions of side-functionalized homo-polyesters with ethylphenyl.**

**Scheme 4. Synthesis of conjugated polymers with POMs as side-chain pendants.**

Z. Peng et al. 2004
**Hybrid Polymers from Pre-Formed Inorganic Structures**

### Magnetic Polymers

$\text{Mn}_{12}O_{12}(OOC-\text{CH}=\text{CH})_{16}$

Radical polymerization

$+ \text{CH}_2=\text{CMe-COOMe}$

PMMA crosslinked by $\text{Mn}_{12}$

Superparamagnetic

$\text{Mn}_{12}^*$

- total cluster spin $S = 10$
- ($4 \text{ Mn}^{IV}, S = \frac{3}{2} + 8 \text{ Mn}^{III}, S = 2$)

### Hybrid Polymers from Pre-Formed Inorganic Structures

- Preparation of nanoparticles
- „Stöber-Process“
- $\text{Si(OEt)}_4 + \text{NH}_2\text{OH}$

Surface modification

Initiators at the surface, e.g.

Polymerization from the functionalised surface

G.Kickelbick et al.

AFM