Polymere Nanoverbundwerkstoffe –
Chancen, Risiken, Potentiale

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Influence of particle size

- Particle size: 10 μm (Fibre), 1 μm (Talcum), 10 nm (Nanotubes)
- Volume content: 30% (Fibre, Talcum), 3% (Nanotubes)
- Number of particles: $\sim 10^6$ (Fibre), $\sim 10^{10}$ (Talcum), $\sim 10^{15}$ (Nanotubes)
- Interface: $\sim 0.1$ m² (Fibre), $\sim 1$ m² (Talcum), $\sim 100$ m² (Nanotubes)
- Aspect ratio: $\sim 20$ (Fibre), $\sim 100$ (Talcum), > 1000 (Nanotubes)
Carbon Nanotubes

- Structural differences according to manufacturing
- Purity, defect density & aspect ratio
- Influences on mechanical properties
Dispersion method

Three-Roll-Mill 120 S from Exakt GmbH
- Rollers made of alumina (Al$_2$O$_3$) or steel
- Gap-size: ~ 5 µm

Dispersions

- SWCNT exhibit highest SSA (Specific Surface Area) of all nano-fillers
- SWCNTs show mixture of small agglomerates and good dispersed CNTS
- CB dispersed into aggregate structure (~150 nm)
- Partly dispersed into primary particles (~30 nm)
Dispersion

- MWCNT-NH$_2$ – best dispersion results
- Very few agglomerates observed
- MWCNT-NH$_2$ show sufficient matrix adhesion
- CNTs sticking out of cutted films are covered with matrix

- MWCNT – good dispersion results
- Very few agglomerates observed
- Tendency to form loose aggregates after dispersion
DMTA – Glass Transition Temperature


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Nanocomposites:
⇒ Improved stiffness
⇒ Enhanced strength
⇒ Increased fracture strain

Functionalisation effect

Stress-Strain Diagramme of Epoxy-CNT


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Fracture toughness

- Similar influence on toughness at 0.1 wt.%
- Toughness ($K_{IC}$) increases by ~ 45%
  at 0.5 wt.-% DWCNT-NH$_2$
  (0.65 -> 0.94 MPa·m$^{1/2}$)

⇒ Identification of toughening mechanisms

Cracks artificially induced due to vacuum drying after etching

- Surface-cracks (~2µm)
- Bridging of DWCNT-NH$_2$ via (500 – 1000 · d)
- Bridging-mechanism observed

Functionaldised MWCNTs (Jeffamine®) in Epoxy

Telescopic pull-out

Matrix

50 nm

25 nm


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TEM – dispersion in ternary systems

Dispersion at the primary particle level

- No formation of TiO$_2$ networks
- Attachment of TiO$_2$ to MWCNTs

Interpenetration of particle networks

- No dispersion at the primary particle level
- Formation of MWCNT and SiO$_2$ domains


Rheological investigations

Steady Rate Sweep

Binary systems
- ▲ 0.95 vol.-% MWCNT
- ◇ 0.47 vol.-% MWCNT
- ▽ 0.95 vol.-% SiO₂
- ▼ 0.95 vol.-% TiO₂

MWCNT:
Strong thixotropy (dense network)

SiO₂:
No thixotropy (but network!)

TiO₂:
No thixotropy (less interactions)
Rheological investigations

**Steady Rate Sweep**

Same amount of TiO$_2$/SiO$_2$ added:

- **For TiO$_2$:**
  No change of MWCNT-network
  (Dispersion on primary particle level)

- **For SiO$_2$:**
  Change in MWCNT-network formation
  Less interparticle interactions

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<th>SiO$_2$</th>
<th>TiO$_2$</th>
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<td>vol.-%</td>
<td>0.47</td>
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- **Underproportional superposition**
- **Additive superposition**

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Fracture toughness - $K_{IC}$

Binary systems
- Increase of 15% independent of type of particle
  → Equal mechanisms?
- MWCNT: Doubling of filler content
  → insignificant increase in $K_{IC}$
  → Maximum in increase in $K_{IC}$

Ternary systems
- Increase of 30%
  → Addition of the increase in $K_{IC}$ of each type of particle
Electrical properties of CNT/Epoxy composites

Electrical conductivity

Log conductivity [S/m]

Log volume fraction [%]

catalytically-grown carbon nanotubes
Carbon black

Young's modulus 1 [TPa]
Strength 50 – 150 [GPa]
Diameter 3 [nm] SWCNT
10 – 15 [nm] MWCNT
Length 1 [µm] – 1 [mm]
Piezoresistivity - (ir)reversible uniaxial strain

Results in agreement with previous works and theories on RRNs.

Differences explainable through RRN models:

- many interconnects to/from one particle
- few tunneling resistors between contacts
- very sensitive toward orientation change of particles
- relatively stable tunneling resistors
- few interconnects to/from one particle
- many tunneling resistors
- insensitive toward orientation change of particles
- relatively unstable tunneling resistors

Tensile tests – elastic regime

Good linear approximation for MWCNT nanocomposites up to 1.5% strain
- Advantageous for technical exploitation and integration
- MWCNT nanocomposites exhibit “k-factor“ of ~4.3 and ~2.95

Thermal conductivity

Idealised CNT

- Perfect graphitic structure
- Theoretically high thermal conductivity of 6600 W/mK for SWCNTs at RT (based on perfect graphite structure and neglecting boundary effects)

Phonon mechanism dominates conduction of thermal energy

- Defects cause phonon scattering
  ⇒ The larger the number of defects, the larger the defect-scattering losses
- Interfacial boundary scattering
  ⇒ The larger the interface, the larger the boundary scattering losses
Manufacturing of GFRPs

Manufacturing of composites with nanocomposite matrix via VARTM

multiaxial non-crimp-fabric ECR-Glass

-\([0/\pm 45/90/-45]_{as}\)
-\([- (0/90), (90/0)]_s\)

Homogeneous filler distribution over entire specimen


Interlaminar shear-strength - ILSS

- Investigation of interlaminar shear-strength (ILSS) via „short-beam“ 3-Point-Bending-Test

Shear-strength

\[ S_H = \frac{3}{4} \frac{F_{\text{max}}}{bd} \]

- Increased ILSS from 31,8 to 34,8 MPa (+9%) (CB)
- Increased ILSS from 31,8 to 37,8 MPa (+19%) (DWCNT-NH₂)


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Cyclic tensile tests - Analysis

Decrease of sample stiffness correlates with increase in resistance

Spontaneous drops in stiffness → local damage (e.g. rupture of fibre bundles)

Correlate with sudden increase in resistance

Assessment of state of fatigue damage

Specimen under dynamic tensile load
GF-NCF-EP+0.3wt.% MWCNT
R measured in z-direction

Acknowledgements:

European Commission
Bundesministerium für Bildung und Forschung BMBF
Deutsche Forschungsgemeinschaft DFG
Deutscher Akademischer Austauschdienst DAAD