Modern filler systems and efficient mixing techniques for improved elastomers

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Innovation in Rubber Design 2016
December/7th – 8th/2016
London, UK
Requirements on elastomers for extrem conditions

- Temperatur resistance
- Life time
- Media resistance
- Lightweight construction
- Strength
- Elasticity

- Environmental exposure
- REACH
- Emissions
- Smell
- Fire behavior
- Migration

Adapted specific elastomer materials
Elastomers - Adapted Materials

Tools for improvement of elastomer properties

Polymer

Additives/Plasticizers

Crosslinking

Filler-Polymer systems

Polymer-Filler interaction

Dispersion
**Fillers - Reinforcement**

- **Degradative Fillers**
  - Grinded CaCO₃, mica, talc
- **Dilution Fillers**
  - Clays
- **Semi-Reinforcing Fillers**
  - Precipitated CaCO₃
  - TiO₂, ZnO
  - Si Aluminates
  - Ca Silicates
  - Hydrated Silica
  - Anhydrous Silica
- **Reinforcing Fillers**
  - Carbon blacks

**Particle Size (nm)**

- $10^5$
- $10^4$
- $10^3$
- $10^2$
- $10^1$

**Fillers - Reinforcement**

- **Graphene (exp. graphite)**
  - $h = 5-8$ nm
  - $d = 2-25$ nm
- **Carbon blacks (CB)**
  - 20 – 50 nm
- **Silica**
  - 15 nm
- **Carbon – Nanotubes (CNT)**
  - Aspect/ratio 10 nm/µm

**Additional Information**

- TIE-GmbH
Carbon fillers - Carbon blacks

Graphitic crystallites
WAXS-measurements

Turbostratic organisations
of graphitic layers

Amorphous carbon
Raman spectroscopy

AFM-measurements show roughness

Heidenreich, 1975

Hess, 1972

Alexander, 1936

La
Lc
Carbon Fillers

Rolled graphene sheets
Single C-Polymer?
C-molecule?

- Bending of C-bonds
- Pyramidalization angle
- Miss-alignment of π-Orbitals
- Higher electron density on external surface of CNTs
- Increasing surface activity

Tube Curvature → Surface Activity

Carbon Nanotubes (CNT)

**SWCNTs:**
- Single cylinder,
- Diameter: 0.7 to 1.5 nm
- Differences in axial/radial organization of C-atoms

**MWCNTs:**
- Ø 1 – 50 nm
- Length: appr. 100 nm – μm region
- high aspect ratio

**Main process:**
*Catalytic Vapor Deposition – metal catalysts*

**Electronic Properties**
- Armchair, zigzag, chiral

**Main process:**
*Catalytic Vapor Deposition – metal catalysts*

**Image:**
- TEM-micrograph of MWCNTs, magnif. 50000x
  (G. Schwerdt, DIK)
Characterization of specific surface

Volumetric static gas adsorption:
BET-Isotherme using 1-butene (model substance)

Systems: N121, N347, EB 262, ES 204, Silica MP 1165, VN 2, CNT-NC 7000

$V = \text{volume adsorbed molecules}$

$V_m = \text{monolayer, volume adsorbed molecules}$

$N = \text{adsorbed molecules}$

$N_m = \text{monolayer, adsorbed molecules}$

**BET:**

$$\frac{p}{(p_0 - p)N_m c + cN_m} = \frac{1}{N_m c} + \frac{c - 1}{N_m} \cdot p$$

Equipment: BEL Sorp max.
Parameter: Temp. 267 K;
$p < 100 \text{ kPa}$

Reduced activity
Distribution of surface energy $Q$ - BET-Isotherm

Static gas adsorption: 1-butene

Systems: N121, N347, EB 262, ES 204, Silica MP 1165, VN 2, CNT-NC 7000

Equipment: BEL Sorp max.
Parameter: Temp. 267 K; $p < 100$ kPa

\[ \Theta(p, T) = \frac{N}{N_m} = \int_0^\infty \theta(p, T, Q) \cdot f(Q) dQ \]

Graphitic Planes (sp²)
Crystallite Edges
Amorphous Carbon (sp³)
Slit Shaped Cavities

CNT: Low surface energy,

$N$ = adsorbed molecules
$N_m$ = monolayer, adsorbed molecules

Characterization of CNT/CB – Surface energy

Inverse Gaschromatography (IGC)

Test component: e.g. pentane
Retention time \( t_r = t_r2 - t_r1 \)
Retention volume \( V_r = t_r \times F \times j \)
Spec. retention volume \( V_{r*} = V_r / m \)

\( t_r \) = Retention Time (min), \( F \) = Carrier gas flow rate (ml/min),
\( j \) = Pressure correction factor, \( m \) = mass of the filler (g),
\( P_i \) = Inlet pressure (Bar), \( P_o \) = Outlet pressure (Bar)
Characterization of CNT and CB by IGC

Test components:
- Pentane
- Hexane
- Heptane
- Acetone
- Acetonitrile

Surface energy:
\[ \gamma_s = \gamma_s^d + \gamma_s^{sp}, \text{ with } \gamma_s^d, \gamma_s^{sp} \text{ disp. / polar part} \]

\[ \gamma_s^d = \frac{\Delta G_{CH_2}}{4N^2} \cdot \frac{a_{CH_2}^2 \cdot \gamma_{CH_2}}{a_{CH_2}} \]

\( a_{CH_2} \): area covered by a \(-CH_2-\) unit;
\( \gamma_{CH_2} \): surface free energy of a surface composed entirely of \(-CH_2-\) units; \( N \) = Avogadro’s number

Free sorption energy:
\[ \Delta G = R \cdot T \cdot \ln(V_r^*) \]

Surface energy for CNTs and CBs
Test component: pentane

Higher interaction
Reinforcement in elastomers

Phys./chem. filler-rubber interaction

Hydr. effect: \( \eta = \eta_0 \cdot (1 + 2.5 + \phi + 14.1 \phi^2) \)

\[ G = \nu \cdot k \cdot T \]

\( \nu = \text{network density} \)

\( \phi = \text{filler vol.- fraction} \)


S. Shiga, M. Furuta, RCT, 58, (1985), 1/22
### Used materials and compounds

<table>
<thead>
<tr>
<th></th>
<th>phr</th>
<th></th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NBR (28 % ACN)</strong></td>
<td>100</td>
<td><strong>EPDM (50 % ext. oil)</strong></td>
<td>100</td>
</tr>
<tr>
<td>CNT NC7000</td>
<td>0-10</td>
<td>CNT NC7000</td>
<td>0-10</td>
</tr>
<tr>
<td>CB (N550)/N772</td>
<td>0-60</td>
<td>CB (N550)</td>
<td>0-50</td>
</tr>
<tr>
<td>ZnO/st.-acid</td>
<td></td>
<td>Paraff. oil</td>
<td>10</td>
</tr>
<tr>
<td>S/CBS</td>
<td></td>
<td>ZnO/st.-acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>S/ZBEC/TBzTD/MBT/CBS</td>
<td></td>
</tr>
<tr>
<td><strong>FKM</strong></td>
<td>100</td>
<td>Hybrid systems:</td>
<td></td>
</tr>
<tr>
<td>CNT NC7000</td>
<td>0-10</td>
<td>CB / CNT ratios in phr:</td>
<td></td>
</tr>
<tr>
<td>CB (N 990)</td>
<td>0-60</td>
<td>0 – 60 / 2 – 15</td>
<td></td>
</tr>
<tr>
<td>Carnauba wax</td>
<td>1</td>
<td>depending on polymer</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DHBP /TAIC</td>
<td></td>
<td></td>
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</tbody>
</table>

**EPDM:** Keltan 9565 Q, high molecular type, 62.5 % ethylene

**Hybrid systems:**

1. **Internal mixer (Haake Rheomix),**
   Rotor speed. Var. (50; 75; 100 rpm)
2. **Two roll mill (Curing system)**

**TAIC:** Triallylisocyanurate (70 % active content)
**DHBP:** 2.5-Di-methylhexane-2.5-di-tert. butyl peroxide (45 % active content)
Mixing optimization

Mixing sequence:

2 min.: filler
5-6 min.: ZnO/Stearic acid

Two roll mill:
4-5 min. CBS/S

Parameters:
• mixing time
• rotor speed

Laboratory Mixer (Polylab)
Chamber- Vol.: 300 ml
Filling: 70 %
Compound: 6 phr CNTs/NBR/ZnO/St.-acid

Increasing rotor speed:
Increase in torque and temperature
Mixing of Compounds - CNT vs. CB

Mixing conditions
Temp. 50 °C
Rotor speed 50 rpm
Mixing time 15 min.

Mixing steps
1) 0 min. polymer
2) 3 min. CNTs/CB N550
3) 6 min. ZnO+ Stearic acid (3 phr each)
4) 15 min. Stop

Two-roll mill
1) Sulfur (2 phr)
2) CBS (2 phr)

- CNTs require higher torque than CB (higher energy input with CNTs) at same temperature
- Temp. increases more with CNTs than with CB, 10 phr CNT: 150 °C vs. CB: 135 °C
Mixing optimization - Variable CNT-concentration

Laboratory Mixer (Polylab)
Chamber- Vol.: 300 ml
Filling: 70 %
Compound: 6 phr CNTs

Concerning temperature and torque profiles
best parameter: 15 min. and 50 rpm
**Morphological Characterization**

System: FKM/1.5 Vol-% CNTs- nanocomposites, Prepared: Lab-Mixer

Preparation/Specimen:
- Ultramicrotome
- Diamant knifes.
- Cryo-sections (100 nm).
- Magnification: 31,500 x

- TEM: Zeiss Libra 120
  Acc. voltage: 120 kV,

Clusters of CNTs
Some agglomerates
No difference from 50 to 60 rpm
Rheological Properties of FKM-systems

Rubber Process Analysis (RPA)

Alpha Technologies RPA 2000
Frequency: 1 Hz
Amplitude: 0.3 to 400 %
Temperature: 80 °C
Sample mass: approx. 5 g.

Low additional content of CNT (hybrid systems): 15 / 5 for CB/CNT ~ 40 phr CB ~ 10 phr CNT

FKM-CNT

FKM-CB (N990)

FKM-CB (N990)/CNT

10 phr CNT
Rheological Properties – Payne effect

Rubber Process Analysis (RPA)

Alpha Technologies RPA 2000
Frequency: 1 Hz
Amplitude: 0.3 to 400 %
Temperature: 80 °C
Sample mass: app. 5 g.

- CNTs affects higher increase of $G'$ than CB
- CNT shows higher Payne effect - anisotropy (for example at 5 Vol.%)

FKM/-, NBR/- and EPDM/CNT

Related storage modulus $\frac{G_f}{G_u}$ - difference at 1 % and 400 % strain

- CNTs affects higher increase of $G'$ than CB
- CNT shows higher Payne effect - anisotropy (for example at 5 Vol.%)
Vulcanization behavior – Mixing parameters

System: NBR/CNT (6 phr)

Equipment: Rheometer MDR 2000 E

\[ \Delta S \cong G = \nu_e \cdot R \cdot T \]

Temp.: 160 °C
Deformation-angle: +/-1,5 °
Frequence: 1 Hz

No significant influence of mixing parameters on crosslinking level
Vulcanization behavior as $f(c_{\text{filler}})$

Results:
- Vulcanization time ($t_{90}$) is reduced by CNTs, (higher thermal conductivity)
- $\Delta S$ is increased slightly by CNTs – different behavior at percolation limit
  
  (20 dNm vs. 17 dNm)

Rheometer:
- Temp.: 160 °C
- Deformation-angle: +/-1,5 °
- Frecuence: 1 Hz 
  
  (DIN 53529)

NBR/CB N550

NBR/CNT

$T_{90}$ (min) vs. $S_{\text{max}}-S_{\text{min}}$ (dNm)

$C_{\text{NT}}$ (phr) vs. $T_{90}$ (min.)

$S_{\text{max}}-S_{\text{min}}$ (dNm) vs. $C_{\text{CB}}$ (phr)
Vulcanization behavior of FKM-systems as \( f(c_{\text{filler}}) \)

Rheometer:
Temp.: 160 °C
Deformation-angle: +/-1.5 °
Frequency: 1 Hz
(DIN 53529)

FKM/CNT

At 5 phr
\[ \Delta S_{\text{CNT}} = 27.0 \text{ dNm} \]
\[ \Delta S_{\text{CB}} = 13.3 \text{ dNm} \]

Higher \( c_{\text{CNT}} \): Increase in \( \Delta S \), higher as at NBR (reinforcing effect)
Mechanical Properties

Stress Strain –measurements acc. to DIN 53504
S2-specimen
Speed: 200 mm/min
Zwick-testmachine

- CNTs reinforce at low concentrations much more than CB
- Elongation at break decreases above percolation (2 to 4 phr)
- At 10 phr $\sigma_{\text{CNT}} = 12.0 \text{ MPa}$, $\varepsilon_{\text{CNT}} = 209 \%$
  $\sigma_{\text{CB}} = 8.5 \text{ MPa}$, $\varepsilon_{\text{CB}} = 363 \%$
**Mechanical Properties**

Stress Strain –measurements acc. to DIN 53504

S2-specimen

Speed: 200 mm/min

Zwick-testmachine
Reinforcing Factor CNT vs. CB

From stress-strain measurements:

Related modulus at 100 % Reinforcing Factor = \( \left( \frac{\sigma_F}{\sigma_0} \right)_{100\%} \)

RF\text{FKM}: 4 : 1.5 Vol.% CNT/17 Vol. % CB
RF\text{NBR}: 4 : 3.2 Vol.% CNT/19 Vol. % CB
RF\text{EPDM}: 2 : 5.0 Vol.% CNT/15 Vol. % CB

For the same reinforcing effect
The loading of CB has to be factor 5-6 higher than for CNT
Polymer-Filler Interaction

Swelling experiments: Kraus Equation

Specimen: 2 mm discs, 1 g
Swelling medium: MEK
Temperature: 20 °C
Equilibrium: 24 h

\[
\frac{V_{ro}}{V_{rf}} = 1 - m \left( \frac{\phi}{1 - \phi} \right)
\]

\[
C = \frac{m - Vr_0 + 1}{3(1 - Vr_0^{1/3})}
\]

\(V = \) equilibrium volume fraction, filled/unfilled
\(m = \) polymer-filler interaction parameter
\(C = \) Kraus constant
\(\phi = \) filler volume fraction

<table>
<thead>
<tr>
<th>Interaction parameter</th>
<th>FKM/CNT</th>
<th>NBR/CNT</th>
<th>NBR/CB</th>
<th>EPDM/CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m)</td>
<td>2.3</td>
<td>1.6</td>
<td>0.3</td>
<td>0.7(^1))</td>
</tr>
<tr>
<td>(C)</td>
<td>12.2</td>
<td>3.8</td>
<td>1.5</td>
<td>2.5(^1))</td>
</tr>
</tbody>
</table>

\(^1)\)EPDM-values are corrected by the extender oil content
Electrical Conductivity

Dielectric spectroscopy

 Principle: Orientation of dipoles in presence of altering current (AC)

Permittivity

\[ \varepsilon^* = \varepsilon' - i\varepsilon'' \]

\(\varepsilon''\) reaches maximum values at Tg

Conductivity

\[ \sigma = \varepsilon_0 \varepsilon'' \omega \]

\[ \sigma'' = \varepsilon_0 \varepsilon' \omega \]

High Resolution Dielectric Analyzer
BDS 40 (Novocontrol GmbH)
\(f = 10^{-1} - 10^7\) Hz

Dielectric Constant \(\varepsilon\)
Free Charge Carriers (Electrons, Ions) Conductivity \(\sigma\)
Dipoles Polar Molecules
Electrode polarisation

Glass Transition
\(\alpha\) - relaxation
\(\beta\) - relaxation
Segment movements

Principle: Orientation of dipoles in presence of altering current (AC)
Electric Conductivity – NBR-systems

Method:
High Resolution Dielectric Analyzer
BDS 40 (Novocontrol GmbH)
f = 10^{-1} – 10^{7} Hz

Parameter: filler content
filler type

*Electrical saturation above elect. percolation threshold*

At 10 phr
\[ \sigma'_{\text{CNT}} = 0.01 \text{ S/cm} \]
\[ \sigma'_{\text{CB}} = 2.5 \times 10^{-10} \text{ S/cm} \]
**Electric Conductivity – FKM-systems**

**Method:**
High Resolution Dielectric Analyzer
BDS 40 (Novocontrol GmbH)
\( f = 10^{-1} – 10^{7} \) Hz

- CNT: high conductivity, \( \text{sp}^{2} \) - structure of C-atoms
- Continuous filler-filler contact network
- High aspect ratio of the CNTs, substitution of CB by small amounts of CNT (hybrid)

Parameter: Filler content
Filler type and combination
Electric Conductivity

Method:
High Resolution Dielectric Analyzer
BDS 40 (Novocontrol GmbH)
f = 10^{-1} – 10^{7} Hz

- Electrical Percolation Threshold: CNTs = 1-2 phr range
- Depending on polymer type:
  - CNTs = 1-2 phr range
  - CB = 10-15 phr range, Factor : < 5 to 6
  - Perculation threshold is < appr. 5 phr (0.6 to 2.8 vol-%)
High conductivity silicon-CNT composites for electrodes

**Objective:**
- Material development for an electrode as implantate to the brain measuring and stimulation of neuronal signals
- Treatment of neurological diseases like Alzheimer's, Morbus Parkinson

**Materials**
- Biological compatible soft silicone rubber PDMS (product Sylgard 184)
  - crosslinking: Pt-catalysed curing system
  - dyn. viscosity: 3500 mPa*s (liquid silicone)

- Highly electrical conductive filler – CNT Nanocyl 7000 (MWCNT)
  (volume resistivity on powder = $10^{-4}$ Ω*cm or conductivity of $10^6$ S/m comparable to Cu or Au)
Mixing of low viscous silicone/CNT-compounds

Using an internal mixer or laboratory stirring system for low-viscosity mixture

Difficulties
- shear thickening while compounding
- motor strength too low
- Bad dispersion

Planetary mixer
- different geometry and principle of mixing
- two mixing tools
- additional scraper (10 rpm)
- High shear forces
- up to 620 rpm
- vacuum bell jar

PC-Laborsystem Dissolver - LPV 1A40
Source: http://www.pc-laborsystem.ch

TEM micrographs: 2 phr CNT in silicone, DIK
Mixing Optimization

**Rotors speed** 4.0 wt% CNT

best result with 300 rpm at 10 min. :  \( \sigma' = 1,1 \cdot 10^{-1} \) [S/cm]

at 1Hz conductivity of silicone:  \( \sigma' = 3,3 \cdot 10^{-15} \) [S/cm]

**CNT-concentration**

- Highest conductivity with 5 wt% CNT:  \( \sigma' = 9,4 \times 10^{-2} \) [S/cm]
- Percolation threshold  \( \phi^* \) at \(~0.9\) wt% CNT
Summary

- Carbon fillers – CB, CNTs, fullerenes, graphenes
- CNT: Low surface energy, high aspect ratio and high specific surface of CNTs - reason of advantage for mechanical and electric properties of composites
- Effective incorporation and dispersion of CNTs in NBR, FKM and EPDM- rubber (TEM, RPA) by melt mixing technology
- High increase in viscosity of uncured compounds by CNT
- Swelling: Filler /polymer interaction: FKM/CNT >> NBR/CNT > EPDM/CNT > NBR/CB N550)
- High reinforcing factors for CNT in comparison to CB, appr. factor 6 to 10 for all systems
- Electrical percolation for CNTs around 1-2 phr range (factor < 5 lower than CB) for melt mixing
- Mixing of low viscous silicone for electrode applications: Special mixing methodology
- Perculation threshold at appr. 0.9 wt.-%, conductivity at 5 wt.-%: 0.1 S/cm
Acknowledgement:
Funded by EU- Eurostar and DLR, !E!7836 NanoGummi

Partners:
• KKT, Osterode
• Nanocyl, Sambreville

Federeal Ministry of Education and Reasearch (BMBF), KMU innovativ - FlowTrode 13GW0050C

Thank you for your attention