Smart Rubbers

Mechanical and Dynamic Mechanical Performance

Uniqueness of Rubber

Thermal Conductivity, Gas Permeability, Electrical Conductivity, Sensors Application, Semiconducting application, Actuators, Optical properties, etc.

Classical Properties
Problem to apply the findings and reports

- Laboratory based sample preparation
- Small scale
- Complicated processing or fabrication
- High cost
- Synthesized by own laboratory
- May not be reproducible
- Ageing effect
- Robust
- Mechanical performance
Commercially Available Rubber Additives and Ingredients with High Mechanical Performance
Montmorillonite clay


Layered Double Hydroxides (LDH)


Carbon Black


Ionic Liquids

Layered Double Hydroxides
Layered Double Hydroxides (LDH)

**Chemical Formula of LDH**

LDH: \([M^{II}_x M^{III}_{1-x}(OH)_2]^{x+} A^{n-}_{x/n} \cdot yH_2O\)

\([Mg_xAl_{1-x}(OH)_2]^{x+} A^{n-}_{x/n} \cdot yH_2O\)

Preparation of zinc oxide free, transparent rubber nanocomposites using a layered double hydroxide filler

A Das, DY Wang, A Leuteritz, K Subramaniam, HC Greenwell, *Journal of Materials Chemistry*, 21 (20), 7194-7200
Layered Double Hydroxides (LDH)

The curing package is comprised with 1 phr TMTD and 0.5 phr sulfur, the control compounds contain 1 phr TMTD, 0.5 phr sulfur, 5 phr zinc oxide and 2 phr stearic acid.
Layered Double Hydroxides

- From opaque to transparent (reversible) with a temperature change
- The effect more powerful at high loading of LDH
- Independent with matrix polymer and type of LDH
Carbon based Nano-Particles-MWCNTs and Graphene Nano-platelets
Graphene in rubber: Enhanced Gas Barrier Functionality

3D-TEM visualisation of GnP composites

3D-TEM visualisation*

of a nanocomposite from SSBR, filled with 5 phr Graphene nano-Platelets (GnP) and 35 phr Carbon Black (CB)

Schematic depiction of a elastomer composite, filled by 5 phr GnP and 35 phr CB

Movie from a series of TEM micrographs from -68° to +68° with an increment of 2° at a magnification of 39.000x Horizontal width 0.7791 μm

3D tomographic reconstruction of the composite: yellow and green regions represent CB and GnP respectively

* in cooperation with Dr. Daniel Wolf, TU Dresden, Speziallabor für Höchstaufloesende Elektronenmikroskopie und Elektronenholographie Triebenberg

Graphene in rubber: Enhanced Gas Barrier Functionality

**GnP-Composites with Gas Barrier Properties**

**Gas Barrier Properties for Tire Inner Liner**

Graphene nano-Platelets (GnP), together with Ionic Liquids (IL) as dispersion agents show a drastic reduction in the gas transmission rate of Bromobutyl Rubber (BIIR).

Gas Transmission Rate (GTR) of pure butyl rubber (BIIR) and composites of BIIR with Graphene nano Platelets (GnP) and Ionic Liquid (IL). One sample was pre-dispersed in Ethanol.

Schematic illustration of the tortoise gas permeation path in GnP filled Elastomers.


Conducting Carbon Particles and Development of Sensor Materials

Sensor Materials > CNT / Conducting Blacks

Elastomers filled with Conductive Nanofillers

Imidazolium based Ionic Liquids can act as dispersion and coupling agents for carbon based fillers in elastomeric nanocomposites.

Conducting Carbon Particles and Development of Sensor Materials

Sensor Materials (Carbon Nanotubes in NR)

DMA – equipped with electrical resistivity measurement
Top: Dynamic mechanical measurement (force / strain)
Bottom: Dynamic resistivity / conductivity measurement

> Stress, strain and relative resistance responses of in 5 sec window
> In accordance to the strain, there is a proportionate response for stress and resistance
Sensor Materials  (Carbon Nanotubes in NR)

Possible application:

> Piezoresistive sensors in tires for information on running conditions, oscillation frequencies of the tire, acceleration signals, temperature, deflation, rolling resistance, roughness of the road surface, tire wear, or fatigue of the tire

> Structural health monitoring of elastomer materials, as sealing gaskets, bearings …

Response of electrical resistance on dynamic mechanical stress/strain
→ Carbon Black
Flexible conductors

Construction of an Interconnected Nanostructured Carbon Black Network: Development of Highly Stretchable and Robust Elastomeric Conductors using S-SBR

Conducting Carbon Particles and Development of Sensor Materials or Flexible Conductors

Hybrid fillers: large silica and ultrafine carbon black

Incorporated in S-SBR together

Synergistic effect!!

Special Carbon Black
DBP number: 350 - 410 ml/100g
Surface Area: 1002 m²/g
Primary particle size: 35nm

Special silica (Sidistar)
Surface Area: 20 m²/g
Primary particle size: 150 nm

Special Rubber Composites

- Very high structure carbon black with very large surface area
- Non reinforcing microsize silica particles (Sidistar) with very low surface area
Conducting Carbon Particles and Development of Sensor Materials

**Highly electrical conducting filler network**

- Addition of Sidistar the electrical conductivity can be increased by ~ 100 times
- More conducting pathways
- A strong filler-filler network (Payne effect)
Conducting Carbon Particles and Development of Sensor Materials

Carbon black and Graphene like Morphology

TEM images of silica (micro) and conducting carbon black filled SSBR, Parsekha et al (manuscript in preparation)

Highly reinforcing carbon black (XE2, BET surface area 1002 m²/gm) also exhibits graphene like carbon layers

Reason of conducting character

Dielectric Actuators
General Purpose Rubber
Dielectric elastomer actuator (DEA) can have more promising future in the application of artificial muscles due to its physical nature like human muscle and various adjustable properties which can be tailored according to the demand.
Dielectric Actuators: General Purpose Rubber

Dielectric Elastomer Fabrication

General purpose rubber for actuator fabrication

Commercial vs. developed material

- 3M tape
- NBR

Electric field:

60 kV/mm

16 kV/mm

Flexible Solid Polymer Electrolyte
Elastomeric material for battery applications

- Completely amorphous
- A relatively thick membrane act as separator to avoid short-circuit
- Elastomeric separator buffer the large volume expansion during cycling
- Flexible

**Eco (copolymer)**

**CO (homopolymer)**

**GECO (terpolymer)**

Epichlorohydrin
- Polarity
- Heat + Chemical
- Gas Barrier

**Ethylene oxide**
- Low Temperature Flex
- Electrical – Dissipation
- Rebound

**Allyl glycidal ether**
- Unsaturation
- Sulfur and Peroxide Cure
- O₂ Attack
- Anti-thermal degradation
- Low Temperature Flex

**Lithium ion transport**

- Sulfur containing solvent
- TP ion – oxygen containing network

- Oxygen, Carbon, Oxygen-containing points, Lithium ion
Battery fabrication and Cyclic Voltammetry

Carbon / Sulfur → Ball Mill → homogeneous C/S → Battery fabrication

6h, 155°C
PVdF, NMP
C/S/C-black
/binder/slurry

- Characteristic CV peaks of Li-S batteries
- GPE membrane act as separator as well as electrolyte store

A Highly Stretchable Gel-Polymer Electrolyte for Lithium-Sulphur Batteries, T. Saha, S. Choudhury, K. Naskar, M. Stamm, G. Heinrich, A. Das (communicated to Polymer)
Self Healing Rubber Materials
Butyl and bromobutyl rubber application

- Very low gas permeability
- Chemically inert
- High tensile strength
- Heat and weathering resistant
- High damping

Bromine modified Poly-isobutylene-isoprene co-polymer (BIIR)
Modification of the bromobutyl rubber by imidazole (polyisobutylene-isoprene copolymer)

![Chemical structure diagram]

**Network formation by ionic association**

- **BIIR**
- **Ionic Modification**
- **Phase Separation**
- **Network Structure**

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Rheometric curves of the imidazole modified BIIR. The sulfur based mix contains MgO 0.5 phr, stearic Acid 1 phr, sulfur 0.5 phr, ZnO 3 phr and 2-mercaptobenzothiazole 1.5 phr (organic accelerator).

- Optimum rheometric torque or elastic modulus is highest at 100 °C
- Higher temperature decreases the ionic crosslinking (association)
- Indication of a reversible nature of the ionic network
Self Healing Rubber Materials

Stress-strain behavior

- Stress-strain plots of modified and sulfur cured BIIR
- The modified rubber behaves like crosslinked rubber
- Typical Mullins effect can be found from both the samples
- The hysteresis loop is narrow in modified rubber
- The permanent set is ~ 40% for both the samples
Self-healing nature of modified BIIR

Modified rubber strip was cut into two pieces and allowed to mend for 24 hrs and finally tested!
Healing was carried out at room temperature after keeping the damaged samples for 1h to 192 h (black); some samples were kept at 100 °C for the first 10 min of the total healing time (red).
Self Healing Rubber Materials

Tear-fatigue Analysis

Sulfur crosslinked

Imidazole modified

Lake and Lindley

Similar effect is common when rubber is filled with reinforcing fillers

Pure-shear specimen

A fine dispersion of the tubes can be observed from Transmission Electron Microscopy (TEM).

- Application Voltage ~12 only
- Fluctuation of the electric current
- Resistance of the samples changes during heating

Thank you!

Acknowledgement:

My colleagues in IPF Dresden, Germany and Tampere University of Technology Finland