Self-Healing Inorganic-Organic Nanocomposites based on Iron Oxide Nanofillers in Organic Polymers

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Introduction

Self-Healing properties can be implemented into materials by autonomous and non-autonomous mechanisms. Especially in polymer chemistry, hydrogen bonds and electrostatic interactions as well as the thermoreversible Diels-Alder reaction between a diene and an dieneophile are commonly used, giving the possibility to heal micro cracks and fractures thus increasing the life-times of such materials greatly[1-5]. However, many of the polymeric materials lack mechanical stability due to the necessary high backbone flexibility realized by low T_g materials. On the other side, pure inorganic materials lack potential healing mechanisms, or require high energy input to work due to the bonding situation in inorganic solids. Inorganic-organic hybrid materials or nanocomposites are a new class of materials that combine the low T_g required for self-healing of the polymer systems with the mechanical strength of the inorganic nanoparticles. To establish self-healing nanocomposites the particle surface has to be tailored to achieve a strong interaction between organic and inorganic material and a homogeneous distribution within the material.[5] Here we present the synthesis of ionically functionalized superparamagnetic iron oxide nanoparticles as well as organic polymers for the formation of self-healing nanocomposites in which the self-healing mechanism can be triggered by external alternating magnetic fields.

Autonomous Self-Healing

- **Capsule Based / Vascular Systems**

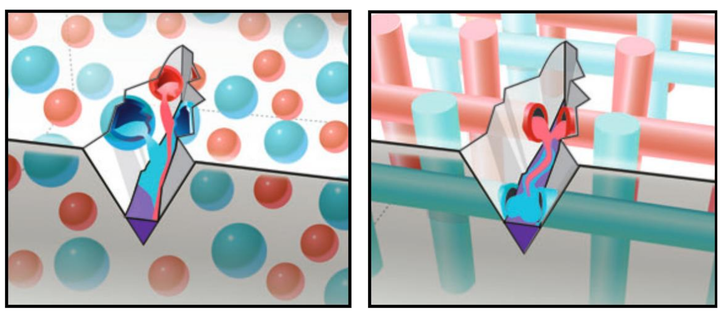
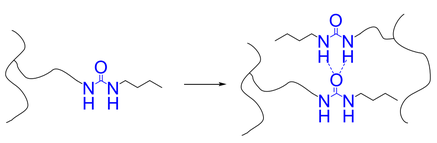


Fig. 1: Capsule based / vascular self-healing.[7]

- Healing based on the release of an healing agent as a response to external damage.
- Systems are restricted to one time cure

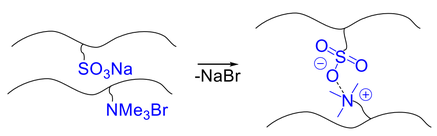
- **Supramolecular Systems:**

➢ Hydrogen bonds



- Highly dynamic supra-molecular systems
- Reversible

➢ Ionic interactions



Non-Autonomous Self-Healing

Non-autonomous self-healing-materials require external stimuli that are not generated from corrosion events to repair their bulk integrity or functional properties.

- **Shape Memory Based Systems**

recover original shapes from a temporarily fixed deformation by applying external stimuli such as heat or light

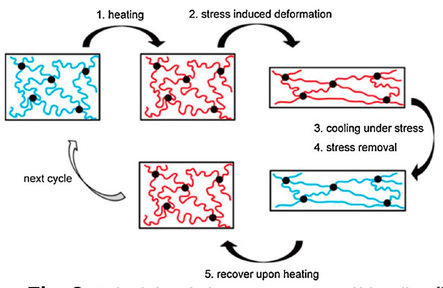
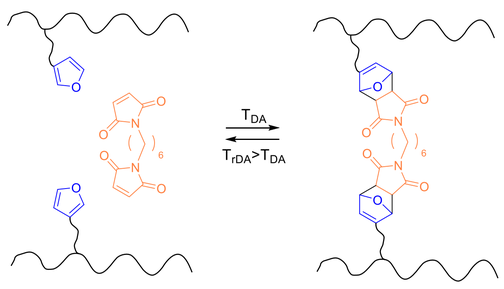


Fig. 2: Principle of shape memory self-healing.[8]

- **Systems Containing Dynamic Covalent Bonds**



- Thermoreversible formation of C-C single bonds
- Diels-Alder (DA) / Retro Diels-Alder (rDA) reaction lead to cross-linking / separation of the network, giving the advantages of a thermoset and a thermoplast

Double Self-Healing Hybrid Materials

The combination of covalent self-healing based on DA-chemistry and hydrogen bonds in one material is already well-known.[6] Here we extend the range of reversible bonding to ionic interactions. Di(ethylene glycol) methyl ether methacrylate constitutes an amphiphilic polymer backbone required for systems consisting of monomers of such different polarity.

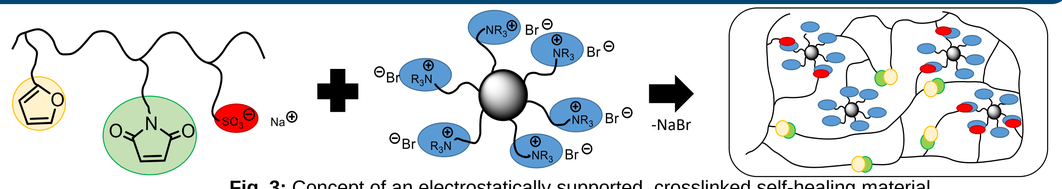
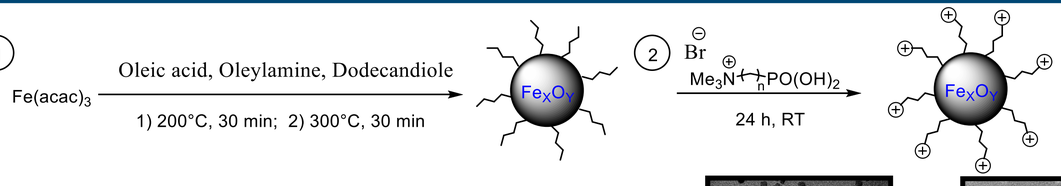


Fig. 3: Concept of an electrostatically supported, crosslinked self-healing material.

Particle Synthesis



① Thermal Decomposition of Organic Precursors:

➢ Accurate size control (~10 nm): Fe_XO_Y particles show superparamagnetic behaviour

➢ Alternating magnetic fields induce heat for DA

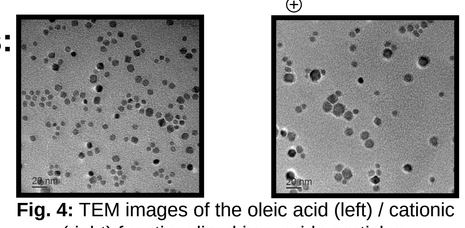
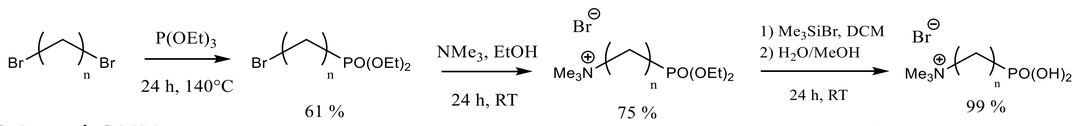


Fig. 4: TEM images of the oleic acid (left) / cationic (right) functionalized iron oxide particles.

② Particle Functionalization with Ionic Phosphonic Acids:

➢ Homogeneous incorporation in anionic polymer is achieved by cationic functionalization



- **IR**, **TGA** and **CHN** analysis confirm ionic surface functionalization
- Reaction occurs within 24 h at room temperature

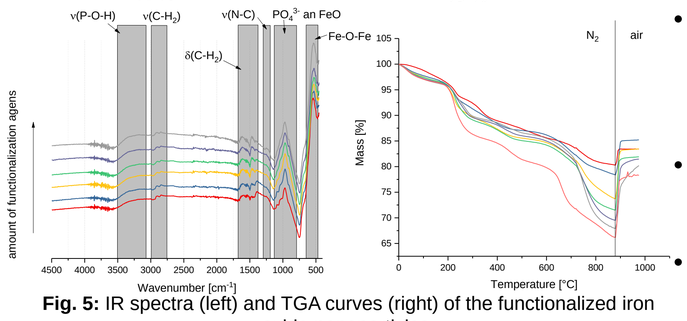
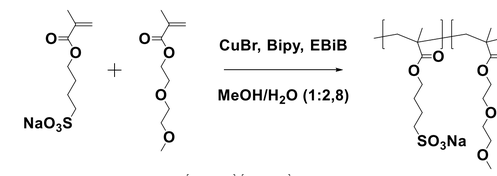


Fig. 5: IR spectra (left) and TGA curves (right) of the functionalized iron oxide nanoparticles.

- Particles are readily dispersible in common solvents
- Range of organic content: 20 – 35 %
- Surface coverage: up to 2 molecules/nm²

Polymer Synthesis and Tailoring of T_g

- ATRP allows tailoring of molecular weight
- Monomer ratios match polymer composition
- Proportion of ionic species: 0 – 25 %
- Range of T_g: -23 - 50°C



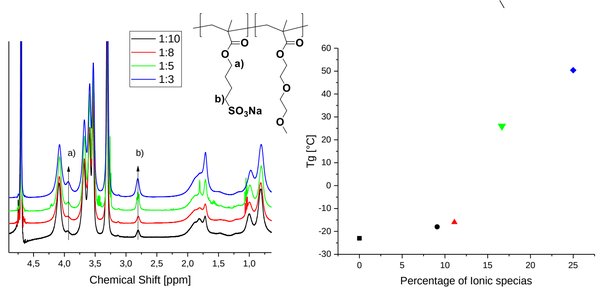


Fig. 6: ^{1}H NMR spectra (left) and T_g values (right) of the two component ionic copolymers.

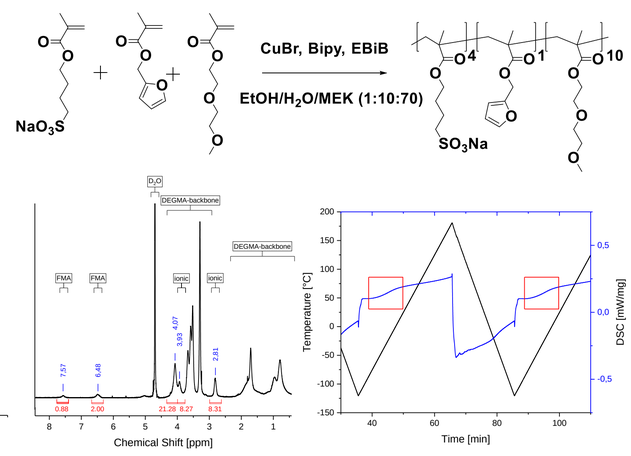


Fig. 7: ^{1}H NMR spectrum (left) and DSC curve (right) of the three component ionic copolymers.

Synthesis of the Hybrid Material

- Polymer and particles are readily soluble / dispersible in a H_2O / THF mixture and show a good miscibility
- Particle contents of up to 20 % are possible

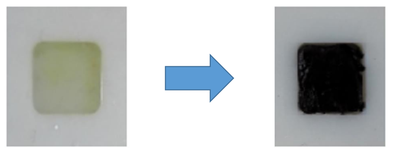


Fig. 8: Ionic copolymer (left) and hybrid material (right), particle content 20 wt.%.

Conclusion

➢ Building blocks for self-healing polymer matrices were synthesized, containing furan- and ionic functionalities

➢ Iron oxide nanoparticles were synthesized and functionalized with cationic phosphonic acid derivatives

➢ Diethylenglycol methacrylate based polymers were synthesized via ATRP and FRP polymerization techniques

➢ Polymer matrix and inorganic filler showed excellent miscibility, yielding self-healing nanocomposites

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