Synthesis of Self-Healing Inorganic-Organic Nanocomposites by the Incorporation of Iron Oxide Nanoparticles in Organic Polymers

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Introduction

Self-healing mechanisms represent a potential solution to enhance the life-times of materials. The chemical design of intrinsic self-healing materials allows the optimization of healing rates whilst retaining the desired material properties.[1-4] While this concept is well-known for polymeric systems, pure inorganic materials lack potential healing mechanisms, or require high energy input to work due to the bonding situation in inorganic solids. In polymeric systems the reversible bond formation via Diels-Alder chemistry (DA) and supramolecular interactions, such as hydrogen bonding and electrostatic interactions, are regularly used healing mechanisms. However, many of the polymeric materials lack mechanical stability due to the necessary high backbone flexibility realized by low T_g materials. The incorporation of inorganic nanoparticles and rigid molecular structures and thus the formation of hybrid materials or nanocomposites allows to overcome the disadvantages of pure organic polymers and can induce better mechanical properties into the polymeric structures, higher thermal stability and additional properties, such as inductive heating or optical properties. To realize the formation of self-healing nanocomposites the particles have to be part of the self-healing systems. Hence, the particle surface as well as the matrix polymer have to be tailored in such a way that the functions fit to each other.[5] Here we present the surface-functionalization of superparamagnetic iron oxide nanoparticles and organic polymers for the formation of self-healing nanocomposites in which the self-healing mechanism can be triggered by external alternating magnetic fields.

Types of Self-Healing Mechanisms

Autonomous Systems | **Non-autonomous Systems**

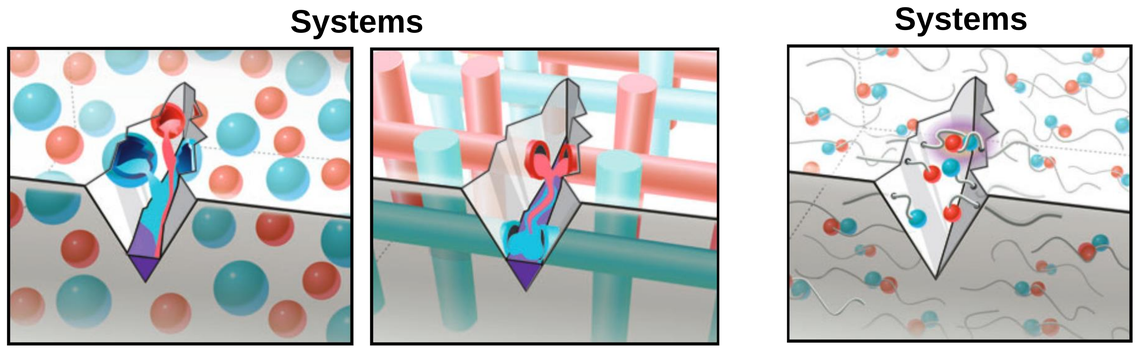
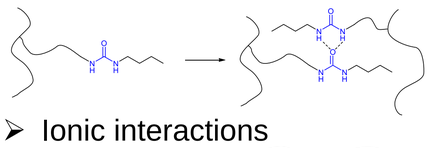
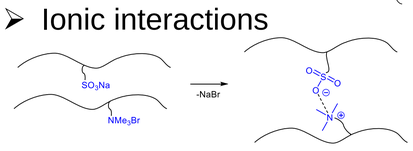


Fig. 1: Approaches to self-healing systems.[6]

- **Capsule based/Vascular Systems**
- **Supramolecular Systems:**
  - Hydrogen bonds

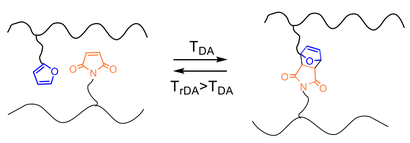


  - Ionic interactions



Healing induced by:

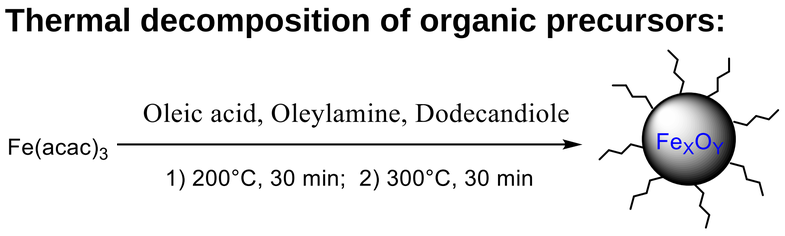
- Heat



- Light
- Mechanical stress
- Adding healing agens

Particle Synthesis and Functionalisation

Thermal decomposition of organic precursors:



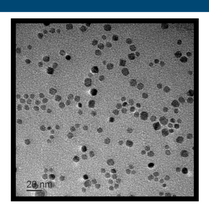
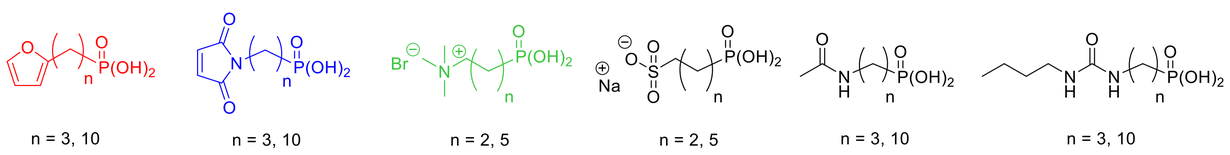


Fig. 2: TEM image of the iron oxide particles.

Possible coupling agents for the particle functionalization:



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

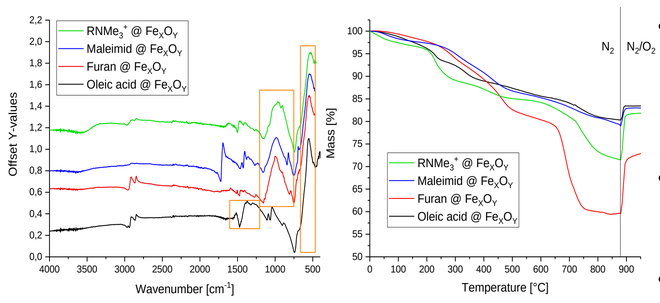
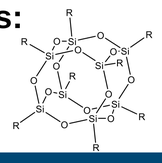


Fig. 3: IR spectra (left) and TGA curves (right) of the functionalized iron oxide nanoparticles.

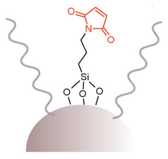
- Particles are readily dispersable in common solvents
- Range of organic content: 20 – 40 %
- Occupation density: up to 2 molecules/nm²

Alternative inorganic Systems:

- Spherosilicates/ silsesquioxanes

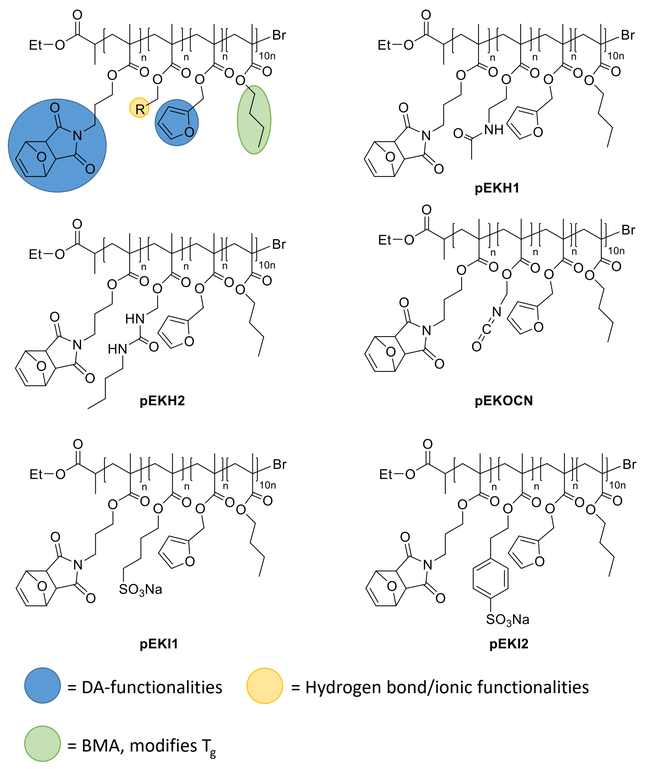


- Silica Nanoparticles



Polymer Synthesis

Synthesis of thermoplastic Copolymers via controlled/living free radical polymerization (ATRP/RAFT)



- ATRP/RAFT allow tailoring of molecular weight and polymer architecture under mild reaction condiions
- Polymerization yields flexible, linear polymer chains with narrow size distributions
- **^{1}H-NMR** and **IR** spectra show the formation of the desired copolymers
- Polymer functionalities affect T_g

Table 1: T_g temperatures of the polymers.

Polymer	T_g (1/2 c_P) [°C]
pBMA	29
pBMAcoFMA	26
pBMAcoMiMA	30
pEKOCN	63
pEKH1	63
pEKH2	63

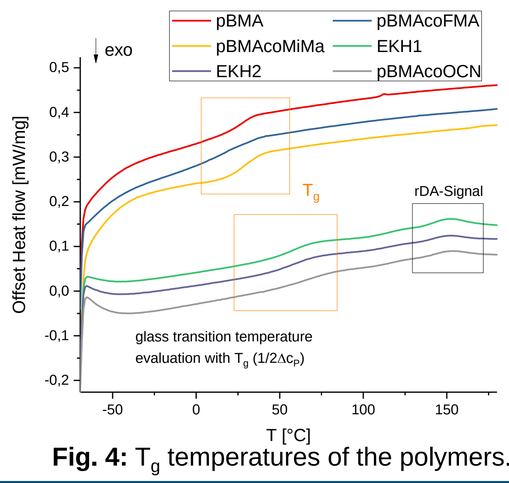


Fig. 4: T_g temperatures of the polymers.

Self-Healing Experiments

- Composite particle content: 5 - 20 wt%
- Sample is cut completely (d = 0,5 mm)
- Healing occurs within 15 min at elevated temperature

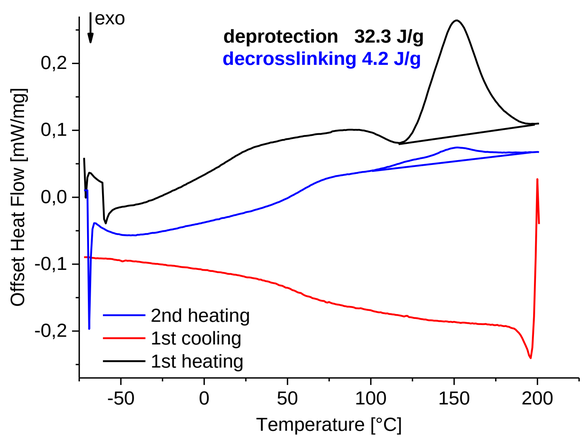
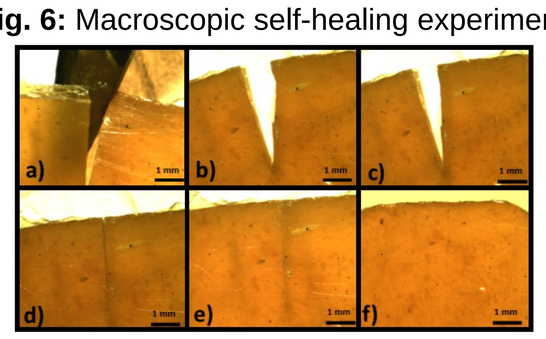


Fig. 5: DA/rDA cycles of EKH2.

Fig. 6: Macroscopic self-healing experiment.



DSC curve shows DA/rDA cycle:

- 1st heating: Maleimid deprotection at 150°C (32,3 J/g)
- 1st cooling: Crosslinking via DA-reaction
- 2nd heating: Decrosslinking at 150°C (4,2 J/g)

Conclusion

- Building blocks for self-healing polymer matrices were synthesized, containing furan-, maleimid-, ionic- and hydrogen donor/aceptor functionalities
- Iron oxide nanoparticles were synthesized and functionalized with phosphonic acid derivates
- Self-healing butyl methacrylate based polymers were synthesized via ATRP and RAFT polymerization techniques
- Polymer matrix and inorganic filler showed excellent miscibility, yielding self healing nanocomposites

[1] T. Engel, G. Kickelbick, *Polym. Int.*, **2014**, *63*, 915-923.

[2] T. Engel, G. Kickelbick, *Eur. J. Inorg. Chem.*, **2015**, 1226-1232.

[3] S. Schäfer, G. Kickelbick, *Polymer*, **2015**, 357-368.

[4] S. Schäfer, G. Kickelbick, *ACS Appl. Nano Mater.*, **2018**, *1*, 2640-2652.

[5] S. Schäfer, G. Kickelbick, *Macromolecules*, **2018**, *51*, 6099-6110.

[6] B. Blaiszki, S. Kramer, S Olugebefola, J. Moore, N. Sottos, S. White, *Annu. Rev. Mater. Res.*, **2010**, *40*, 179-211.