New attitude in polymers – self-healing

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Abstract

Elastomeric polymers are nowadays used in a broad variety of highly demanding applications. Due to alternating loads, microsized cracks may occur in the material, even before its loading- and lifetime-limit. The consequences can be drastic – failure of components often leads to the loss of production, delays, raising costs or facilities and – in rarely cases – personal injuries. Our endeavour is the equipment of such technically relevant elastomers with a self-healing agent. If microcracks occur in the material, this system should be able to prevent further growing and seal parts of the crack or even the complete crack to restore the mechanical properties.

The idea to equip an elastomeric matrix with a self-healing agent is bio-inspired: In case of breaks, a variety of plants segregate latex particles and proteins that crosslink in an addition reaction and close the fissure.

The matrix elastomers investigated within the presented project are EPDM (ethylene propylene diene-terpolymer type M), NBR (nitrile butadiene rubber) and SEBS (styrene ethylene butadiene styrene), a thermoplastic elastomer. After a centrical splitting of died-cut elastomer strips, SEBS exhibits minor autonomous, intrinsic self-healing effects which are probably caused by molecular inter-diffusion processes as postulated by Wool and O'Connor. EPDM and NBR show no such intrinsic self-healing which can be ascribed to their rather stiff und cross-linked structure. Injured specimens from EPDM and NBR do not exhibit subsequent vulcanisation that might initiate intrinsic self-repairing. It was also found that blending the elastomeric matrix with middle or high molecular polymers till a limit of 30% leads to distinctive self-healing results for EPDM and SEBS. Another presented strategy is the partial microencapsulation of two-component adhesives. In case of a crack, the

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encapsulated component is released and initiates a polymeric reaction with the second component which is directly embedded into the elastomeric matrix.
Keywords: self-healing, self-repairing, polymer, elastomer, microcapsules.

1 Introduction

Nature provides a broad variety of problem-solving approaches for technically relevant topics. In particular, the ability of several latex containing plants to

Table 1: Current research activities in the field of self-healing materials.

Workgroup/ Curative Material	Procedure
Chung et al., Korea/ PMMA (thermoplastic) [4]	Repairing-system for PMMA based on a reversible [2+2] cycloaddition; SH is initiated by UV irradiation and temperature
Wool, R.P., O'Connor, K.M., USA/ Thermoplastics [5]	Intermolecular diffusion model for thermoplastics; Description of reorganization of polymer chains & recovery of mechanical properties
Fall, R. et al., USA/ Ionomers (thermo-plastic) [6]	Thermoplastic ionomers neutralized with adequate counterions; After being detached oppositely charged ions restructure to restore mechanical properties
Leibler, L., Cordier, P., France/ Elastomers [7]	New elastomer based on fatty acids, amino acids and urea; high number of hydrogen bonds that reorganize and reassemble after cut
van der Zwaag, S. et al., Netherlands/ Metal alloys, polymers, ceramics, concrete [8]	SH Al & Fe based alloys; Ionomers and quantification of healing ability; encapsulated healing liquids in polymers; SH thermoplasts, HT ceramics & TBC coatings; novel fiber architectures for SH
Bond, I.P., United Kingdom/ Thermosets, composites [9]	Hollow glass fibers and vascular networks in fiber reinforced polymer composites. SH via two-components (epoxy & hardener)
Sottos, N.R., White, S.R., USA/ Thermosets, composites [10]	Microencapsulated dicylclopentadiene (DCPD) & Grubb's catalyst in an epoxy polymer: damage releases DCPD initiating a ROMP, solvent microencapsulation, microvascular networks
Wack, H. et al./ Germany; Elastomeric composites [11]	Hydrogel-elastomer composites; SH for sealings occurs only in contact with water; swelling of hydrogel phases seals cracks
Wudl, F. et al., USA/ Thermosets, composites [12]	Reversible Diels-Alder reaction (furan derivative & e.g. bismalein-imidophenyl-methane); crack energy causes retro-Diels-Alder; healing occurs reversely
Ghosh, B., Urban, M., USA/ Thermosets, composites [13]	Two-component polyurethane matrix; Healing occurs by oxetane-substituted chitosan with reactive chain-ends crosslinking under UV-exposure

repair fissures in an autonomous manner presents an imitable approach for synthetic structures like polymers. Many plants seal fissures by the coagulation of lattices as healing agents. In the case of the Para rubber tree (*Hevea brasiliensis*) and *Ficus benjamina*, latex particles as well as hevein containing spherical organelles (lutoids) are stored in branched micropipe systems which exhibit an internal pressure of about 8 bar. After being injured, the enclosed lutoids burst due to pressure differences in planta and ex planta. Segregation of the protein hevein initiates a cross-linking reaction which results in the formation of chemical covalent bondings [1, 3]. Experiments under defined outer pressures revealed the pressure dependence of the coagulation. Pressures of at least 2 bar strongly inhibited the coagulation by preventing lutoids from burst [3].

These findings serve as role models for the development of self-healing elastomeric materials. The aim is to equip technical relevant elastomeric components like sealings or vibration dampers with a healing functionality. Here, healing means stabilization or closures of occurring microcracks. The healing system should work autonomously and without the influence of outer stimuli like heat, humidity or exposure to light. Cracking energy presents the only available stimulus e.g. to initiate a chemical reaction.

Over the last ten years, different approaches to embed a self-healing functionality into polymeric materials have been presented. These systems have been so far described either on a conceptual level, within relatively constrained application areas or they refer to specially synthesized polymers whose properties strongly differ from those of technical relevant materials. Table 1 gives an overview of important and current researches in the field of self-healing materials. It becomes evident that only few activities focus on self-healing elastomeric materials.

2 Materials and methods

The polymeric matrix materials investigated in the project are three elastomers of different chemical composition, EPDM (ethylene propylene diene-terpolymer type M), NBR (nitrile butadiene rubber) and SEBS (styrene ethylene butadiene styrene). During processing and moulding, EPDM and NBR are vulcanized and cross-linked via covalent oxygen or sulphur bonds. SEBS instead is a thermoplastic elastomer (TPE), which does not undergo cross-linking during processing, and exhibits thermoplastic properties.

Self-healing systems presented in this paper are based on different chemical and physical principles:

- Reversible semi-covalent bonds
- Systematic use of Van der Waals forces
- Polymerisation, cure and formation of covalent bonds

In this paper, results of the addition of middle- and high molecular hydrophobic polymers, middle-molecular polymers with reversible semi-covalent bonds building a three-dimensional molecular network as well as two-component adhesives will be presented. All self-healing components have to

exhibit a viscous flow behaviour enabling them to penetrate upcoming microcracks.

Synthesized self-healing components are embedded into the polymeric matrix either in pure or in encapsulated form. Two component adhesives are processed by adding one component in pure form and the second component encapsulated to the corresponding matrix.

Healing components, in pure as well as in encapsulated fashion, are compounded with elastomers using a laboratory kneader (Brabender Lab-Station 350 E, PlastiCorder), a two-roll mill (Labtech LRM-S-110) and a laboratory press. Hydrophilic or hydrophobic silicon dioxide particles with diameters of about 30 μm are applied as carrier particles. Their sponge-like scaffold is loaded with healing material until saturation eventuates. After elimination of the solvent, the loaded carriers are dispersed in an aqueous phase and encapsulated by in situ polymerisation or polycondensation (e.g. melamine-formaldehyde). Additional encapsulation experiments are carried out using matrix material as capsule wall. Loaded carrier particles are coated with solvated elastomer and dried in a rotation process. Depending on the desired wall thickness, coating has to be repeated several times.

Particle size distribution of the received capsules is measured by a laser diffractometer (Mastersizer 2000, Malvern Instruments) Blue laser light is conducted through a transparent cell and inflected at the particle surface. The detected inflection is converted to a particle size distribution. Measurements are carried out in solution and under the application of ultrasound.

For optical analyses, a digital optical light microscope (Keyence VHX 100) with a maximum resolution of 18 million pixel and enlargements of five hundred times to a thousand times, is used.

Healing efficiencies are measured by a modified tensile test. The functionalized elastomers are pressed and stamped out to elastomeric stripes (width x height x depth, 100 mm x 15 mm x 2 mm). The stripes are centrically split and reassembled under defined pressure. Tensile tests are performed using a tensile test machine (Zwick 1474, 2,5 kN load cell, Software testXpert, Version 11.02).

3 Results and discussion

3.1 Microencapsulation

The idea to incorporate encapsulated components is bio-inspired by the favourable composition of latex containing plants. Encapsulation leads to the isolation of healing component in the elastomeric matrix and avoids unintentional interactions between matrix and healing component. When micro-cracks occur, the enclosing capsule shell bursts and releases the capsule content. This ensures the selective disposal of healing component to restore mechanical properties and avoid further crack growth.

During compounding, the healing additive has to resist high mechanical and thermal stresses such as shear load and temperatures up to 200 °C. The

development of filled microcapsules that are able to withstand compounding processes has not been reported up to now. To enhance the mechanical stability of the capsules used here, hard, porous, inorganic silica particles have been used to build a stable capsule core. These capsules were found to withstand typical thermoplastic and elastomeric compounding processes.

Due to high shear loads, microcapsules without a stabilising silica core do not withstand compounding. REM observations of compounded elastomeric polymer with unstabilised microcapsules do not exhibit any intact microcapsule (figure 1, left). Stabilised microcapsules reveal their stability against high shear loads during compounding. After cryogenic fractures, REM observations show the elastomeric matrix loaded with well dispersed capsules (figure 1, right).

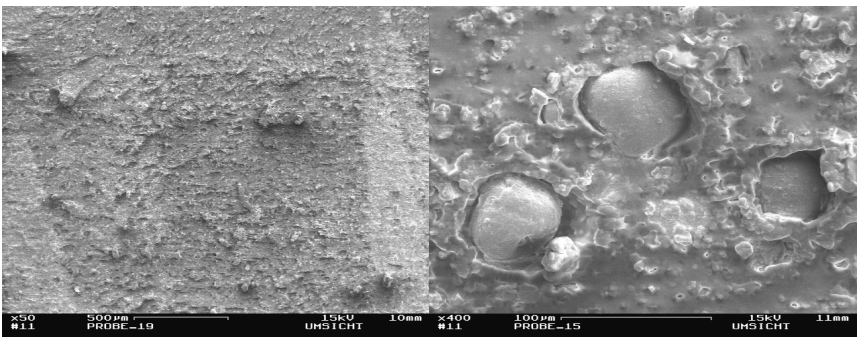

Figure 1: REM observation after compounding with elastomers. Left: Unstabilised microcapsules do not withstand compounding. Right: Microcapsules with carrier core after compounding.

The particle size of unstabilised microcapsules typically varies in a range from 6 µm to about 70 µm with a wall amount of 20 wt-% (figure 2, left). Particle size depends on the stirring rate during microencapsulation, the amount of deployed dispersant, the temperature and the use of an emulsifier. Compared to this broad size distribution, microcapsules with silica core reveal a uniform particle size with diameters of about 30 µm representing the size of employed silicon dioxide particles (figure 2, right). Furthermore, unstabilised microcapsules are susceptible to agglomeration because of the present fine fraction.

Agglomeration is considered especially problematic for compounding and may result in the formation of nests in the elastomeric material. Microencapsulation with traditional wall material is regarded as specifically problematic due to inhomogeneity and decomposition effects between wall material and elastomeric matrix. A certain space between capsule and surrounding elastomer is visible (figure 1, right). In order to circumvent this, loaded SiO_2 cores were loaded with healing agent and encapsulated with solved matrix material.

These coated carrier particles exhibit a particle size of 30 µm to 90 µm. Depending on the stirring rate, up to four loaded carriers can be found in one

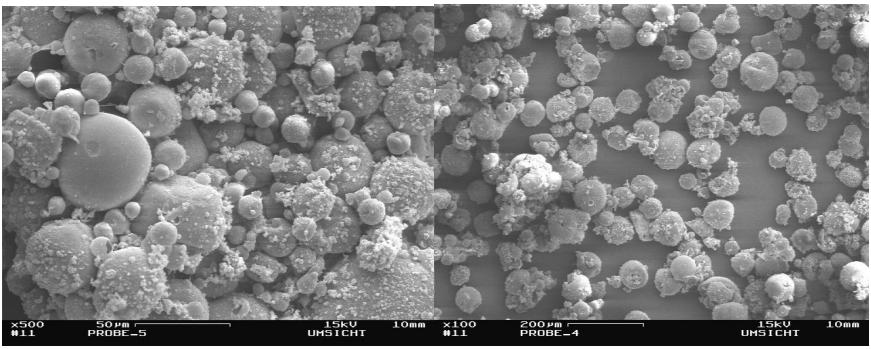

Figure 2: Microcapsules containing healing agent. Left: Unstabilised microcapsules. Right: Microcapsules with SiO_2-carrier.

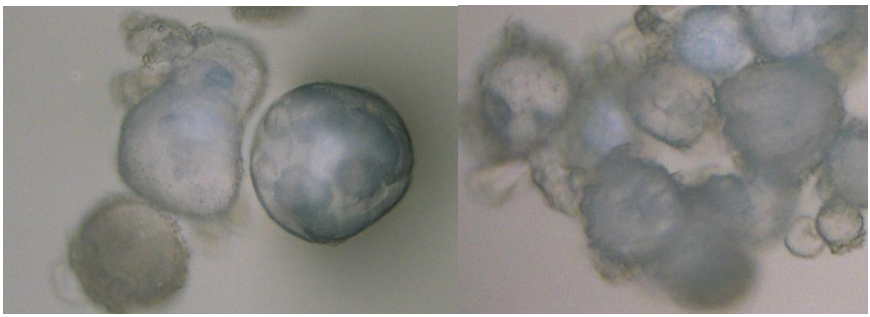

Figure 3: Silica particles loaded with healing agent, encapsulated with elastomer.

microcapsule (figure 3). First compounding trials show great potential for further experiments. Compounds of the received capsules with the corresponding elastomer may be specified as a "solid emulsion".

3.2 Direct compounding of self-healing agents

Besides encapsulation, pure healing agents may be directly embedded into the elastomeric matrix. These compounds have been analysed with regards to their self-healing ability.

For the characterisation of the self-healing effect, the elongation at break and the tensile strength were measured using the modified tensile test described above.

Figure 4 shows the elongation at break of a high molecular one-component adhesive polymer system that is directly embedded into the SEBS matrix. The addition of 30 wt-% additive leads to a recovered elongation at break of about 35% whereas only 2% recovered elongation of break could be found for the pure polymer after macroscopic cuts. Healing duration plays a minor role. Elongation at break is even higher after 24 h dwell time than after 72 h. Shorter healing durations (1 h) exhibit similar results.

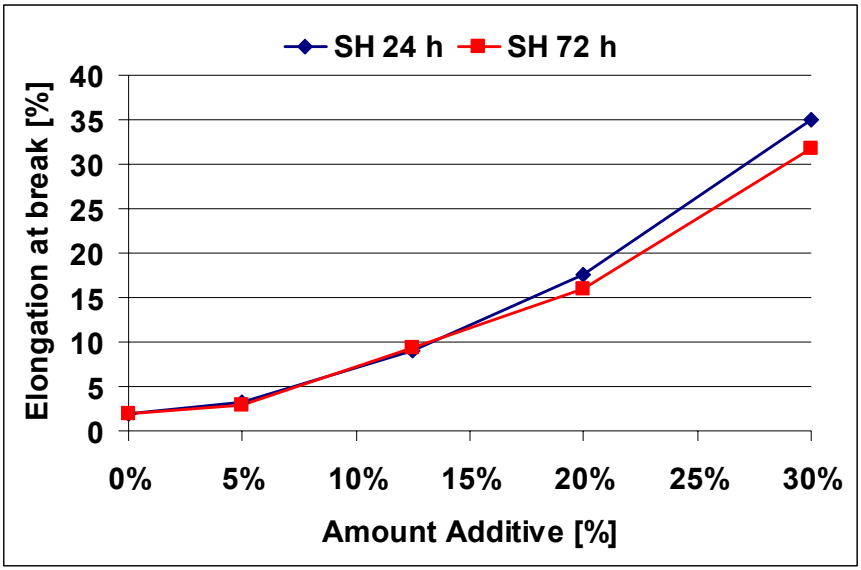

Figure 4: Elongation at break after direct compounding of high molecular one-component adhesives as healing components and different healing durations.

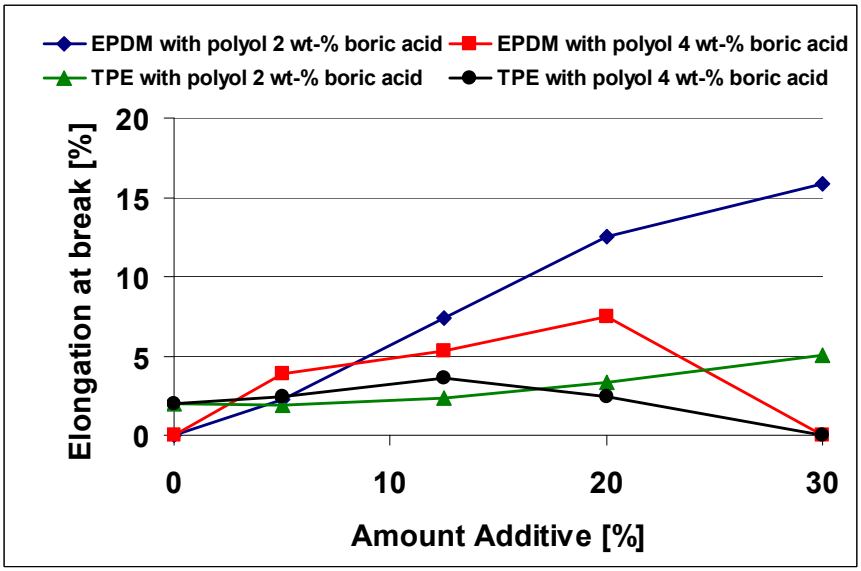

Figure 5: Elongation at break after direct compounding of semi-covalent cross-linked low molecular polyols, healing duration 72 h.

Figure 5 shows the values for the recovered elongation at break for semi-covalent cross-linked polyols in SEBS and EPDM. It is in particular interesting

that a higher amount of linking molecules leads to a worse self-healing effect. In case of 30% embedded amount of additive, polyols with 4 wt-% boric acid inhibit self-healing ability. In an EPDM matrix, elongations at break of 16% absolute for a compounded healing system of polyol/boric acid were measured.

4 Summary and outlook

The self-healing effect of different polymeric systems aiming at the partial restoration of mechanical properties has been presented. A distinction has been made between microencapsulation and direct compounding of pure healing agents. Microencapsulated self-healing systems show minor self-healing effects than direct compounded agents. This is due to not guaranteed capsule burst after polymer fracture. In case of SEBS, recovered elongations at break of 35% absolute can be found by embedding a high molecular one-component polymeric adhesive into the matrix. For EPDM, recovered elongations at break of up 16% absolute were found when using a polyol system with semi-covalent cross-linking points. These results show the great potential of these healing systems although the contact area of 30 mm^2 is rather small.

Ongoing activities aim at the improvement of polymeric self-healing systems as they have been presented. In addition, new healing agents will be synthesized and tested. To describe healing systems more realistically, macroscopic cuts will be replaced by a microcrack approach.

The unfavourable geometry of microcapsules will be replaced by microtubes or kind of a vascular system known from botanical role models.

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