SELF-HEALING ELASTOMERS – HEALING FUNCTIONALISATION BY POLYMER ANALOGOUS SIDE-GROUP MODIFICATION

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ABSTRACT

The spectrum of applications, in which elastomeric materials and components are applied, is broad and still expanding. Technical standard materials are more and more substituted by tailor-made materials due to special needs in applications. Elastomeric components nowadays have to combine a portfolio of mechanical requirements, resistance against solvents, UV radiation and ozone exposure, pleasant haptics and optics and preferably entire recyclability. The implementation of an intrinsic self-healing capability within these materials has not been realised yet. The consequences can be fatal – failure of components often leads to the loss of production, delays, raising costs and – in rarely cases – personal injuries.

Based on biological self-repairing mechanisms, we have developed, realised and proved different self-healing strategies for elastomeric materials starting with microencapsulation, vascular systems, high molecular blend systems and ionomeric polymers. Biological role models were analyzed in detail concerning their healing methodology and their healing capacity by the Plant Biomechanics Group Freiburg. Thereby, ionomeric modification has proven to be the most advantageous of the so far investigated strategies, especially for elastomers (Figure 1). Based on the pure materials, we applied different kinds of polymer-analogous side-group modifications followed by the ionisation of the incorporated side-groups, the so called neutralisation step.

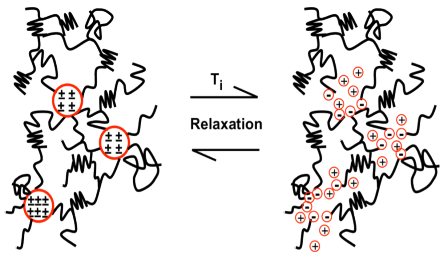

Figure 1: Molecular model, illustrating the proposed healing mechanism, T_i describes the transition temperature for ionic domains [1]

The modified matrix polymers are EPDM (ethylene propylene diene-terpolymer type M), NBR (nitrile butadiene rubber) and SEBS (styrene ethylene butylene stryrene) whereby EPDM and NBR are cross-linked by vulcanisation and SEBS is a thermoplastic elastomer.
EPDM was sulfonated at the exo-cyclic double bond of the norbornene co-monomer and neutralised with Zn^{2+} as counterion. SEBS was carboxylated at the styrene units and neutralised with Na^{+}-ions. Similarly, hydrogenated as well as unsaturated NBR were also modified by carboxylation, but in contrast to SEBS, neutralised with Zn^{2+}-ions (Figure 2). Modifications were verified by IR-, ^{1}H- and

^{13}C-NMR spectroscopy and thermal analyses by DSC and DMTA. Post processing was performed similar to technical compounding and processing.

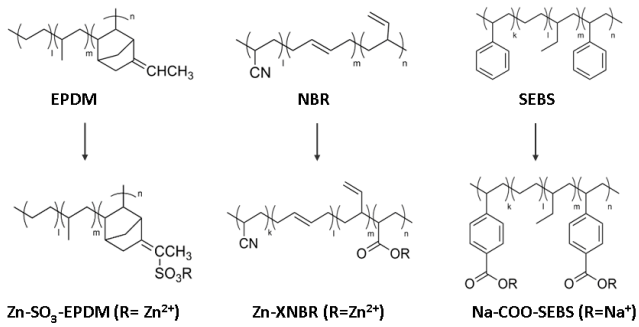

Figure 2: Synthesis/Modification routes for self-healing polymers

The most positive self-healing results were observed for the carboxylated, zinc-neutralised and hydrogenated NBR-grades. After a macroscopic cut, reassembling, storage at room temperature for 24 h and subsequent tensile testing, samples made from unvulcanised material showed an elongation at break recovery of 80 % and 30 % recovery of breaking stress compared to the undamaged reference sample. After tempering at 55 °C for 24 h, a recovery of even 100 % (elongation at break) and 50 % (breaking stress) were measured (Figure 3).

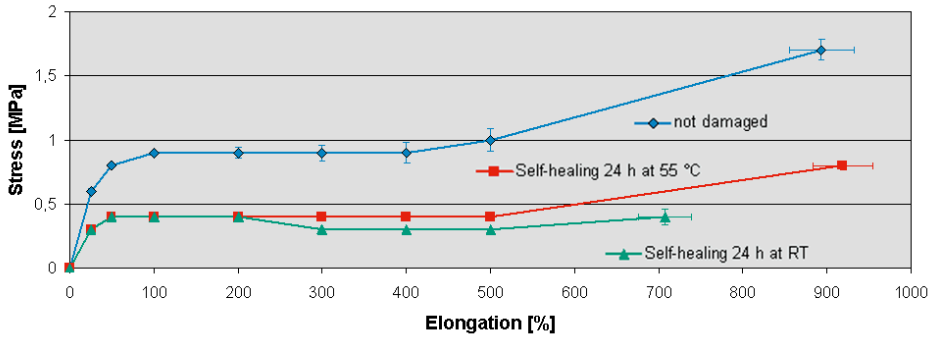

Figure 3: Stress-strain curve for unvulcanised NBR-based self-healing polymers

In case of the vulcanised samples, after tempering at 55 °C, elongation at break was restored to 18 %, breaking stress to 15 %. Unmodified and vulcanised NBR materials do not exhibit distinctive self-repairing properties.
These findings implicate that healing effectiveness strongly depends on the molecular structure, more precisely on degree and kind of vulcanisation, intrinsic mobility of polymer chains, neutralisation degree and additionally on processing parameters for the matrix materials as well as the healing temperature.
Additional fields of work will be: further enlightenment of structure-property relationships in self-healing elastomers, advancing polymer analogous modifications and different methods of post-processing as well as the scale-up.

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REFERENCES

[1] Modified from: K. Tadano et al., Order-Disorder Transition of Ionic Clusters in Ionomers, *Macromolecules*, **22**, 1989, pp. 226-233