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

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Abstract
Recently, elastomers that possess a self-healing capability gathered more and more attention in scientific research. Different principals were applied to trigger the restoration of mechanical properties and various characterization methods were applied to prove the concept.
Based on biological self-repairing mechanisms, we have developed and realised several self-healing strategies for elastomers. Biological role models were analysed concerning their healing behaviour by the Plant Biomechanics Group Freiburg. Ionomeric modification has proven to be most advantageous, especially for elastomers. Based on pure materials, we applied different polymer-analogous side-group modifications followed by ionisation of incorporated side-groups, the so called neutralisation step.
Modified polymers are EPDM (ethylene propylene diene-terpolymer type M), NBR (nitrile butadiene rubber) and SEBS (styrene ethylene butylene stryrene).
Most positive self-healing results were observed for modified NBR-grades. After a macroscopic cut, reassembling, storage at 55 °C for 24 h and subsequent tensile testing, samples made from unvulcanised material showed a recovery of 100 % (elongation at break) and 80 % (breaking stress). Vulcanised samples, after the same treatment, showed an elongation at break of 18 %, breaking stress of 15 %. This implicates that healing effectiveness strongly depends on degree of vulcanisation, neutralisation degree and healing temperature.

1. Introduction

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. Non-covalent ionic bindings play an important role

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in nature's self-healing procedures. One example is the role of cations in the coagulation of natural latex. These cations are needed to dimerize two protein molecules and in this way enabling the proteins to attach to latex particles, initiating the coagulation-based wound repair process (Figure 1) [1, 2].

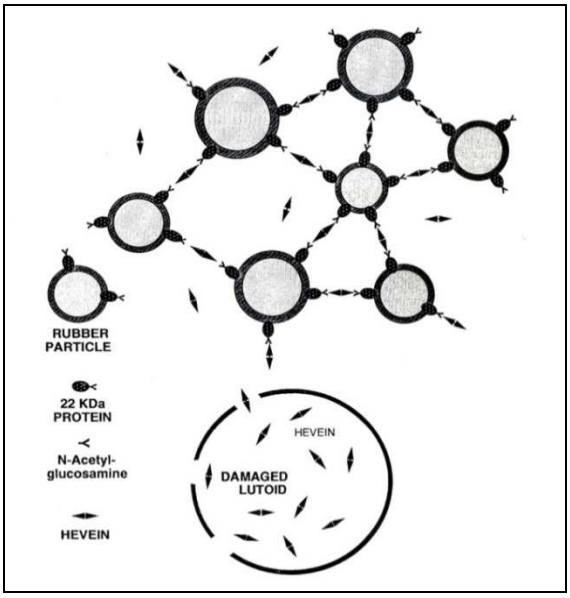

Figure 1. Coagulation of caoutchouc from *Hevea brasiliensis.* Reprinted with permission from [1]. Copyright 1995, Elsevier.

A possibility to transfer this concept to synthetic polymers is to equip polymer chains with ionic groups and to add an adequate counter ion to the polymer matrix.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 2).

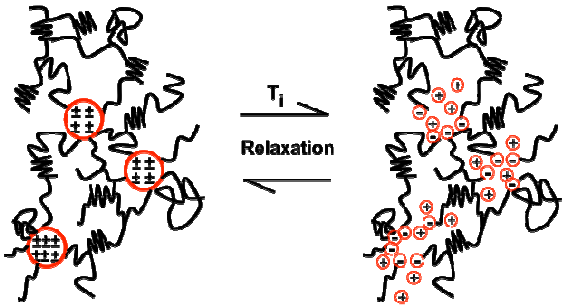

Figure 2. Molecular model, illustrating the proposed healing mechanism, T_i describes the transition temperature for ionic domains [3]

2. Materials and Methods

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.
The modified matrix polymers are EPDM (ethylene propylene diene-terpolymer type M), NBR (nitrile butadiene rubber) and SEBS (styrene ethylene butylene stryrene) in which EPDM and NBR are cross-linked by vulcanisation whereas SEBS is a thermoplastic elastomer.

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EPDM was sulfonated at the exo-cyclic double bond of the norbornene co-monomer and neutralised with counterions. SEBS was carboxylated at the styrene units and neutralised with the respective counterions. Similarly, different NBR-grades were also modified by carboxylation and neutralised (Figure 3). 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.

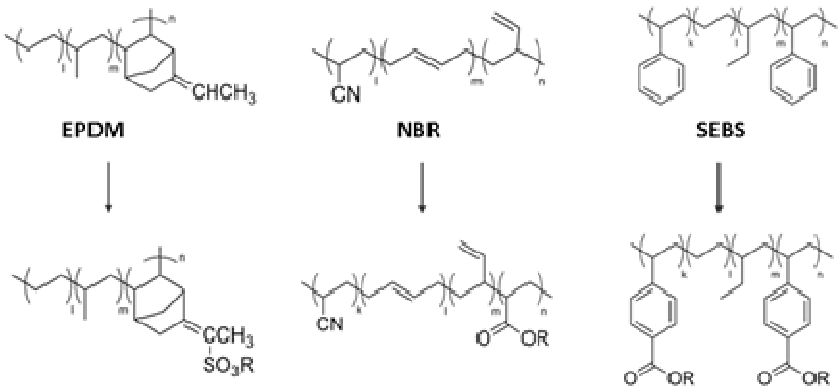

Figure 3. Modification routes for self-healing elastomers [4]

3. Results and Discussion

The most positive self-healing results were observed for the carboxylated 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 13 % and 36 % 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 96 % (breaking stress) were measured (Figure 4). It was also observed that caboxylated non-ionized NBR-grades show a self-healing behaviour.

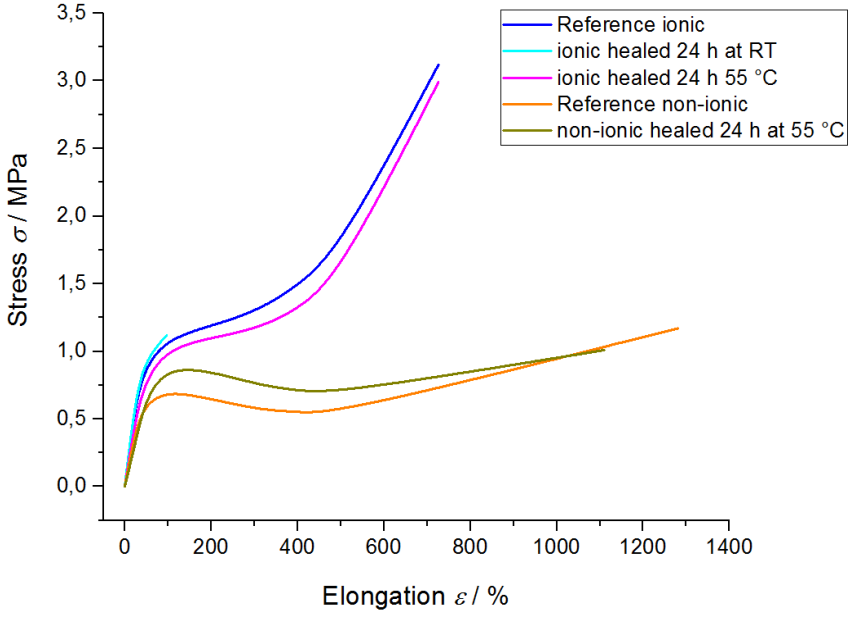

Figure 4. Stress-strain curve for unvulcanised NBR-based self-healing polymers

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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 [5].

4. Conclusion

The self-healing effect of different ionomeric systems aiming at the partial restoration of mechanical properties has been proven. Biological role models show various possibilities for an autonomous repair of damages. In caoutchouc tree, *Hevea brasiliensis*, it was found that firstly an expression of heveine (a proteine) takes place, which is than dimerized by Ca^{2+}-ions leading to the coagulation of latex.
Most promising results have been found for ionomeric elastomers: the shown unvulcanized material showed a complete recovery concerning elongation at break after a nmacroscopic cut. The aim is now to optimize the materials for their application in real life.

Acknowledgments

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