

IONOMERS AS SELF-HEALING AGENTS FOR ELASTOMERIC PRODUCTS

Andreas C. Schüssele¹, Rolf Mülhaupt¹

¹Albert-Ludwigs-Universität Freiburg, Freiburger Materialforschungszentrum
Stefan-Meierstr. 21, 79106 Freiburg. Germany.
Email: andreas.schuessele@makro.uni-freiburg.de

Keywords: self-healing, elastomer, ionomer, reversible network

ABSTRACT

In spite of decades of continual improvement elastomeric materials often fail due to the formation of microcracks. Within the scope of the cooperative project BIONA supported by the German Federal Ministry of Education and Research (BMBF) we are developing a self-healing elastomer for sealant application. As sealants are often used in sandwich-like bonded systems replacement or repair at an early stage of crack formation is impossible. The challenge of the project is to develop a self-healing material as an additive to commonly used elastomer compositions.

To improve the resistance against crack formation and crack propagation we used the co-network concept. Such networks consist of covalent elastomeric bonds together with reversible links (Figure 1). Upon exposure to mechanical stress these reversible crosslinks break and enable network reorganisation. After the microcracks have occurred the incorporated polymer metal complexes [1] – in contrast to the covalent bonds – are capable of rebuilding the network.



Figure 1: Concept of the elastomeric network enhanced by reversible connections. Shear - or temperature induced rearrangement.

Ionomeric structures [2, 3] were obtained by reacting a difunctional acid-terminated oligomer with zinc complexes. The Oligomer functionality was increased from two to four to six acid groups per molecule by grafting further acid molecules. Because of the use of unsaturated oligomers the ionomer [4] is anchored within the elastomeric matrix during the process of vulcanization. These functional additives were integrated in an NBR elastomer during the typical processing using an internal mixer, rolling mills for homogenising and a panel press for vulcanisation. The amount of self-healing additive was increased from 5 to 12.5 to 20 phr. We determined the shore-A hardness as well as the stress-strain parameters of the produced vulcanisates.

Instead of adopting a dynamical long-term experiment we employed an accelerated test. At first the self-healing ability was verified optically. After a controlled deformation of about 1 mm, with a crack initiated by means of a razor blade, we brought the crack areas of the specimen into smooth contact with each other by using a sample holder. Hence a constant pressing force was applied. We varied the temperature of the pure NBR elastomer from 25 to 100 °C to evaluate possible temperature dependence; there was none. After a healing period of 12 hours at 100 °C the samples were relaxed for 12 hours. To examine the stability of the healed crack we introduced stress in a third step by putting the samples on a curved base with a radius of 25 mm. We compared the crack healing efficiency of the unmodified NBR elastomer with the neutralised oligomers.

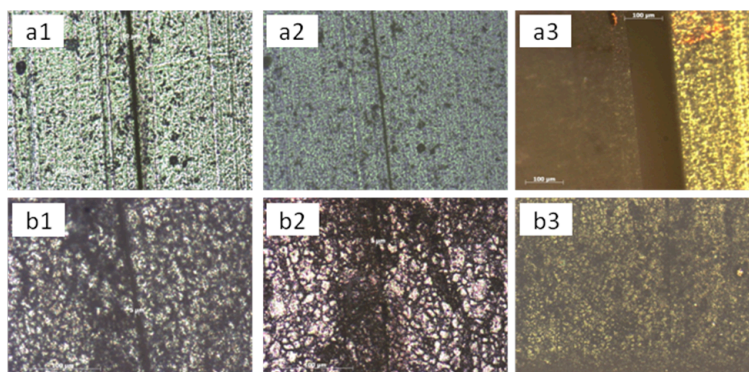


Figure 2: Light microscope pictures with a 20-fold magnification displaying damaged samples before (a1 and b1) and after annealing.

In the absence of the additive the NBR elastomer (Figure 2, a series) was irreversibly damaged and incapable of self-repair. By introducing 20 phr of the additive consisting of the difunctional zinc-ionomer the crack healing is achieved and the crack was stopped (Figure 2, b2), and did not propagate further upon straining (Figure 2, b3). The former crack has not been widened by the introduced tension (b3).

In order to quantify the healing ability we cut test samples with a cross section surface of 12.5 mm^2 into two pieces and used the above mentioned method for healing. After relaxation time we measured stress and strain with a tensile speed of 50 mm/min. By blending the NBR elastomer with 20 phr of the neutralised system with an ionic amount of 4.8% the mechanical stability was increased by 73%.

REFERENCES

- [1] A. Eisenberg, B. Hird, R.B. Moore. *Macromolecules*, **23**, 1990, pp. 4098-4107.
- [2] S.J. Kalista, T.C. Ward, Z. Oyetunji, *Mech. Adv. Mater. Struct.*, **14**, 2007, pp. 391-397.
- [3] R.J. Varley, S. Shen, S. van der Zwaag, *Polymer*, **51**, 2010, pp. 679-686.
- [4] G. Broze, R. Jérôme, P. Teyssiè, C. Marco, *Macromolecules*, **18**, 1985, pp. 1376-1382.