

SELF HEALING OF BLENDS BASED ON SODIUM SALT OF POLY(ETHYLENE-CO-METHACRYLIC ACID)/ POLY(ETHYLENE-CO-VINYL ALCOHOL) AND EPOXIDIZED NATURAL RUBBER FOLLOWING HIGH ENERGY IMPACT

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ABSTRACT

This research work deals with the investigation of autonomous healing behaviour of blends composed of an ethylene-methacrylic acid sodium salt ionomer (EMNa) with epoxidized natural rubber (ENR) or with poly(vinyl alcohol-coethylene) (EVA). Several important researches investigated the instantaneous and autonomous self-healing of ionomers in response to high energy impact such as projectile puncturing. Ionomers are thermoplastic ionic polymers, in which the maximum ion group content is approximately 15 mol% [1]. The presence of ionic clusters [2] and the order-to-disorder transition phenomenon [3] of the clusters have been related to healing effects in ionomeric materials. Initial studies by Fall [4] and Kalista *et al.* [5,6] reported a two stage healing mechanism for ionomers under projectile puncture tests. In a first stage, elastic/viscoelastic recovery is supposed to close the damage, while in a second stage, welding by some local melting/solidification process allows full closure of the puncture. This self-healing mechanism was also supported by Varley and Van der Zwaag, who also showed that the ultimate healing level depends on the elastic response during the impact and post-failure viscous flow [7, 8]. The occurrence of consecutive healing events during high impact penetration of ionomers was also reported. The physical-crosslinking between acid functional groups and salt ions is thought to have influence on the healing mechanism and efficiency. However, Kalista *et al.* [5] and Fall [4] reported that the presence of ionic clusters seems to have limited significant influence on the self-healing of ionomers. This behaviour is however usually presented within a limited range of ambient conditions, where the mechanical characteristics are subjected to little variations. On the other hand, the availability of materials with controlled properties can greatly extend possible applications.

Polymer blending is a common route to obtain mechanical performances spanning over wide limits. In this work, the effect of blending of an ethylene methacrylic acid copolymer ionomer with different polymers on the self-healing behaviour was investigated. In particular binary blends of different compositions based on EMNa/EVA and ENR, were studied by ballistic puncture tests and characterized with thermal and mechanical tests. The healing of each blend composition after ballistic puncture tests was checked applying a pressure gradient and was observed at optical and electron microscope. In the composition range explored (15-50% weight of EVA and ENR), the self-healing response decreases with the increasing amount of EVA but is maintained in all range for ENR/EMNa blends.

Projectile puncture tests were performed in a ballistic laboratory by shooting 4.65x19.2 mm bullets through 100x100x2 mm square plates at 23 °C at a speed range of 703/730 m/s. To check for the healing efficiency, a pressure difference of 0.8 bar was applied in the puncture zone by a vacuum pump. All specimens were observed by optical stereo-microscope both in the bullet entrance and exit sides at 10 to 100x magnifications. Scanning electron microscopic (SEM) analyses were performed on the damaged surfaces of the specimens. Complete self-repairing behaviour was evident for all the blend compositions of ENR/EMNa blends. Also EVA/EMNa blends up to 30% EVA show that self-

healing behaviour is well maintained and only in blends containing 50% EVA full repair was not observed. Figure 1 shows SEM micrographs of bullet impact zones of pure EMNa (a) and 50 wt% ENR/EMNa blend (b), respectively. Tensile tests were carried out to determine the mechanical property of the blends. These tests showed that the blending process gives the opportunity to develop interesting combinations of mechanical properties without significant loss in the self-healing behaviour, particularly in ENR/EMNa blends. It should be noted that the addition of the two polymeric components to ionomer introduces different mechanical effects, i.e. with increasing stiffness, in case of EVA, and reducing it in case of ENR. Moreover, the presence of ethylene units in EVA is expected to promote a good degree of compatibility between the two components while vinyl alcohol units can interact with functional acid groups by modifying the ionic clusters. On the other hand, amorphous ENR introduces more rubbery domains with highly mobile macromolecular segments.

These results show that the addition of a second component to a ionomer base can deeply change the mechanical properties, thus providing materials with selectable performances over a wide property range, preserving self-healing behaviour and extending the potential application areas of such materials.

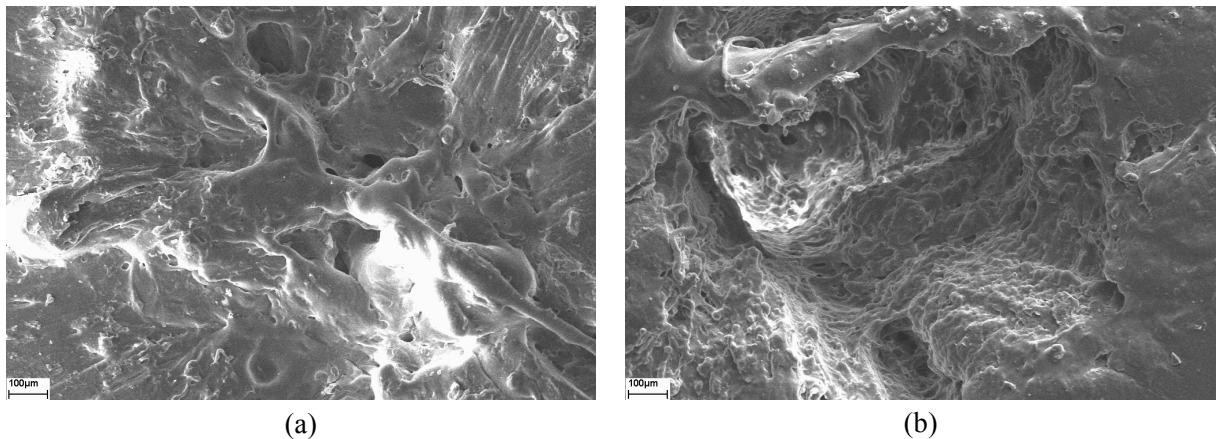


Figure 1: SEM micrographs of pure EMNa (a) and 50% ENR/EMNa blend (b).

REFERENCES

- [1] M. R. Tant, and G. L. Wilkes, Viscoelastic behavior of ionomers in bulk and solution, in *Structure and Properties of Ionomers* (eds M. Pineri and A. Eisenberg), D. Reidel Publishing, Dordrecht, 1987.
- [2] A. Eisenberg, B. Hird, R. B. Moore, A new multiplet-cluster model for the morphology of random ionomers, *Macromolecules*, **23**, 1990, pp. 4098-4107.
- [3] K. Tadano, E. Hirasawa, H. Yamamoto, S. Yano, Order-disorder transition of ionic clusters in ionomers, *Macromolecules*, **22**, 1989, pp. 226-233.
- [4] R.A. Fall, *Puncture reversal of ethylene ionomers - Mechanistic studies*, Master's thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, 2001.
- [5] S. J. Kalista and T. C. Ward, Thermal characteristics of self-healing response in poly(ethylene-co-methacrylic acid) copolymers, *Journal of the Royal Society Interface*, **4**, 2007, pp. 405-411.
- [6] S. J. Kalista, T. C. Ward and Z. Oyetunji, Self-healing of poly(ethylene-co-methacrylic acid) copolymer following projectile puncture, *Mechanics of Advanced Materials and Structures*, **14**, 2007, pp. 391-397.
- [7] R. J. Varley and S. Van Der Zwaag, Development of a quasi-static method to investigate the origin of self-healing in ionomers under ballistic conditions, *Polymer Testing*, **27**, 2008, pp. 11-19.
- [8] R. J. Varley and S. Van Der Zwaag, Autonomous damage initiated healing in a thermo-responsive ionomer, *Polymer International*, **59**, 2010, pp. 1031-38.