A QUANTITATIVE DESCRIPTION OF THE SURFACE HEALING OF IONOMERS

Santiago J. García[1], Russell J.Varley[2], and Sybrand van der Zwaag[1]

[1] Novel Aerospace Materials, Faculty of Aerospace Engineering, Delft University of Technology. Kluyverweg 1, 2629 HS Delft. The Netherlands.
Email: S.J.GarciaEspallargas@tudelft.nl; S.vanderZwaag@tudelft.nl

[2] CSIRO Materials science and Engineering,
Private Bag 33, Clayton South VIC 3169, Australia
Email: Russell.Varley@csiro.au

Keywords: Ionomers, Surface healing, Scratch

ABSTRACT

Ionomers are a well-known and potentially important example of self-healing polymers [1]. These systems have demonstrated autonomous healing capabilities upon high speed impact (e.g. such as bullet penetration) due to the localized temperature rise produced by the kinetic energy of the object and the role of ions in the network. The non-covalent (physical) bonds instantly acquire mobility during high energy impact providing the impetus for the thermo-responsive self healing behaviour. However, the self healing capabilties of this class of polymers under conditions other than ballistic have received little attention in the literature.

In this work we evaluate the surface healing mechanics of several ionomers used in previous works [2-4], and compare their behaviour with that of recently released commercial organic coatings that claim to have a self healing response to surface scratches.

In order to quantify the surface scratch healing mechanics of both types of systems, a new experimental procedure combining an instrumented micro scratch testing machine and a confocal microscope has been developed. The procedure consists of the following steps:
- Controlled scratching with a micro-scratch tester. The equipment offers important information about the after-scratch elastic recovery and penetration depth obtained during scratching.
- The sample is then evaluated under a confocal microscope obtaining the empty volume the scratch has created. In order to normalize the data, the volume values were corrected by the area (V/A_{BH}). Each sample was evaluated at different spots of the scratch four times.
- The sample is then introduced in an oven at a controlled temperature and time, after which, it is left to cool down at room temperature.
- Finally, the sample is taken again to the confocal microscope and the value V/A_{AH} is obtained (after healing removed volume).
- The obtained values with the confocal microscope are then used to calculate the healing efficiency in percentage as seen in equation 1.

$$Healing(\%) = 100 - \left(\frac{V/A_{A.H.}}{V/A_{B.H.}} \right) 100 \tag{1}$$

The tests were realized to several ionomers [2-4] under different loads and healing temperatures and times.

Figure 1a shows an example of Surlyn 8940 before and after healing at 80C for 4h where it is possible to observe the initial scratch damage as well as the mark left by the scratch after healing, indicating an incomplete healing under these conditions.

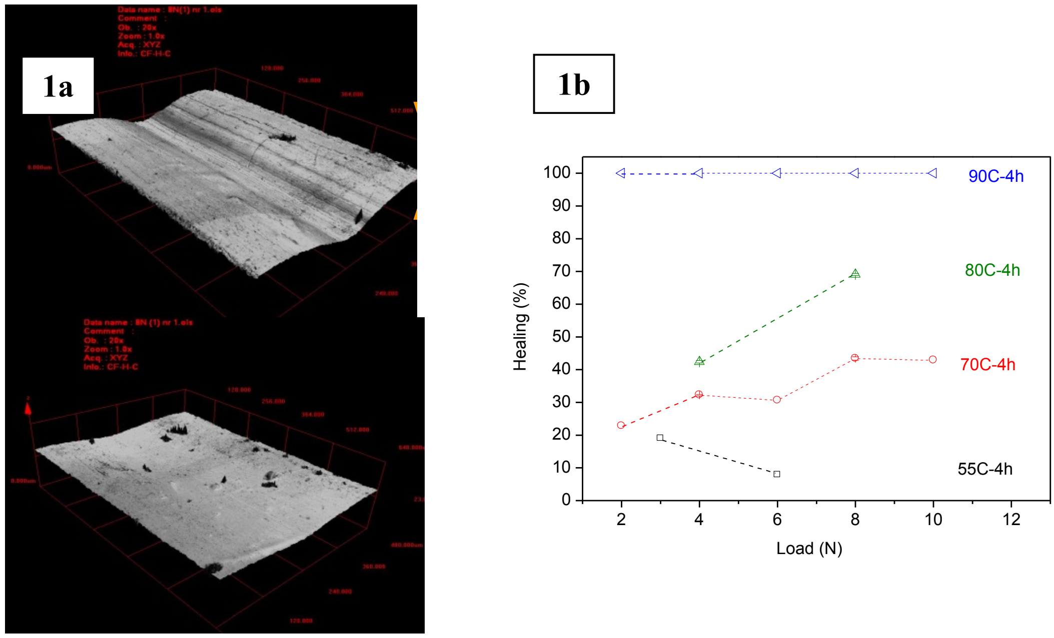

Figure 1: a) 8N Scratch on Surlyn 8940 surface before and after heat treatment (80C-4h); b) Surface healing of Surlyn 8940 upon different heat treatments and scratch loads.

As can be seen in Figure 1b, the increase of the healing temperature gradually lead to higher healing of the samples, independently of the applied load. Temperatures slightly above the T_{ord} of Surlyn8940, which is estimated to be 47°C [3], do not lead to significant healing (55°C-4h), while only temperatures close to T_m of Surlyn lead to complete healing of the system (90°C-4h) independently of the applied load and penetration damage. Furthermore, it was also observed for all healing conditions that, the higher the applied load the higher the healing, suggesting an effect of the relaxation of the deformed polymer (i.e. elastic spring back).

The obtained results suggest that a complete healing can not be obtained unless the healing temperature is close to the T_m. Nevertheless, for small damages (small loads), despite the healing is not very high, the after healing scratch mark may not be easily visually detectable, thus being enough healing for practical applications.

In this research we present a methodology to evaluate surface healing based on the combination of a microscratch tester and a confocal microscope. In this work we evaluate the degree of surface healing for various ionomer grades and link it to their ballistic healing capability.

REFERENCES

[1] K. Tadano, E. Hirasawa, H. Yamamoto, and S. Yano, Order-Disorder Transition of Ionic Clusters in Ionomers, *Macromolecules,* **22**, 1989, pp. 226-233.

[2] R. Varley, and S. van der Zwaag, Towards an understanding of thermally activated self-healing of an ionomer system during ballistic penetration, *Acta Materialia,* **56**, 2008, pp. 5737-5750.

[3] R.J. Varley, and S. van der Zwaag, The effect of cluster plasticisation on the self healing behaviour of eionomrs, *Polymer*, **51**, 2010, pp. 679-686.

[4] R.J. Varley, and S. van der Zwaag, Development of a quasi-static test method to investigate the origin of self-healing in ionomers under ballistic conditions, *Polymer Testing* **27**, 2008, pp. 11-19.