The role of clusters on the healing efficiency of a modified Zn based ionomer

J.M. Vega 1,2, S. van der Zwaag 2 and S.J. Garcia 2

1 Materials innovation institute, Mekelweg 2, 2600 GA, Delft, The Netherlands. – e-mail: j.m.vegavega@tudelft.nl
2 Novel Aerospace Materials Group, Faculty of Aerospace Engineering, Delft University of Technology, Kluiverweg 1, 2629 HS Delft, The Netherlands – e-mail: s.vanderzwaag@tudelft.nl; s.j.garciaespallargas@tudelft.nl

Keywords: EMAA, ionomer, WAXS, scratch healing.

ABSTRACT

Poly(ethylene-co-methacrylic acid) (EMAA) ionomers have shown healing capabilities in both ballistic and static tests. In previous studies it was shown that the degree of crosslinking (clusters) affects (positively or negatively) the healing under impact tests. Moreover, it has also been reported that the modification of the ionomers by additives leads to different healing behaviours under static puncture tests. Despite the preliminary tests the effect of the additives on the ionomers was not clarified.

In this work we use scratch healing and WAXS to gain a major understanding of the effect of additives in ionomers. Several blends of a semi-crystalline ionomer partially neutralized with zinc (EMAA-Zn) with adipic acid were prepared.

Temperature assisted healing (well below the melting temperature) of artificial scratches in the surface of modified and unmodified EMAA-Zn ionomers was performed. A confocal microscope was employed for the healing quantification and measurements of Young modulus. Wide Angle X Ray diffraction (WAXS) was employed to track the effect of the additive in the polymer structure.

The results show a strong influence of the additive on the clusters leading to a clear increase of the healing efficiency when clusters disappear.

1. INTRODUCTION

Ionomers are partially neutralized polymers with their bulk properties governed by ionic interactions within discrete regions of the polymer structure [1]. The ionic interactions are obtained by the partial neutralization of the precursor polymer using monovalent and divalent cations. The presence of the cations leads to strong Coulombic interactions between the ion pairs yielding ionic aggregates, namely clusters, which act as multifunctional “electrostatic” crosslinks [2]. As a result, a supramolecular network of physical (reversible) crosslinks (clusters) is formed affecting the final properties (viscoelastic behaviour, absorption of solvents, etc.).

Earlier work has shown that the ionomers have a good self healing behaviour for ballistic impact [3], which could be tuned by addition of cluster modifiers [4]. The present work concerns a more detailed study into the role of adipic acid on cluster formation and low temperature scratch healing efficiency.
2. MATERIALS

A commercial Zn based semi-crystalline poly(ethylene-co-methacrylic acid) ionomer (EMAA-Zn) was used for this study as a precursor. The EMAA-Zn contains 3.5 mol% methacrylic acid, out of which 71 % have been neutralized with Zn$^{2+}$ ions. This polymer has two characteristic transition temperatures, the first one around 44 °C, linked with the clusters and semicrystals, and the second one at 97 °C linked to the melt of the main crystalline structure. Adipic acid (AA) was used as chemical modifier of the ionomer system. The blends were prepared in a DSM mini-extruder with twin screw configuration at 150 °C. The ionomer was dried overnight at 80 °C before blending with the adipic acid. Five EMAA-Zn / adipic acid blends were prepared containing 1, 3, 6, 10 and 20 wt% of adipic acid.

Two types of specimens were prepared by compression moulding using a hot press: (i) coated galvanized steel plates for scratch healing tests and (ii) free standing films for general characterization. During the compression moulding, the polymer blends were located between two fresh Kapton® sheets (or one Kapton sheet and the galvanized steel substrate). Compression was performed at 0.67MPa and 130 °C during 5 minutes. The hot press and, thus the samples, were water-cooled to room temperature before releasing the pressure. The thickness of both coatings and free-standing films was around 160 ± 10 μm as measured by a PosiTector® 6000 thickness meter.

3. METHODS

A microscratch tester (MST) from CSM Instruments was used to perform controlled scratches at 2N constant load on the polymer surface of the coated galvanized specimens. This same instrument was used to obtain the Young modulus (E) by indentation mode (load of 0.5N).

For the quantification of the subsequent scratch healing (i.e. viscoelastic recovery) upon exposure to 70 °C, a laser scanning confocal microscope Olympus OLS 3100 (software LEXT OLS 6.0.11) using a 20x objective was employed. After the initial scratch, the specimens were placed in a pre-heated circulating hot air furnace operating at 70 °C for 30 min.

The analysis consisted in following the evolution of the scratch profiles (healing) by taking 3D images before and after the heat treatment. In order to analyse the viscoelastic recovery (healing efficiency), the empty volume ($V$) of the scratch was measured before and after heating and corrected by the surface area of the measured region. The healing efficiency was quantified using equation 1:

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

Equation 1

where $V/A$ is the volume/area ratio after healing ($A.H.$) and before healing ($B.H.$). The $V/A$ values were averaged amongst 4 different sections along the scratch.

WAXS measurements were carried out using a Bruker D8 Discover X-ray diffractometer equipped with the 2-dimensional Hi-Star Area Detector and Cross Coupled Göbel Mirrors. The measurements were performed in transmission mode at room temperature using monochromatic Cu Kα1 radiation and a sample to detector face of 30 cm.
4. RESULTS

Figure 1 shows the healing efficiency and E as a function of the adipic acid content. From the plot it can clearly be seen that there is a strong influence of both parameters with the adipic acid content, especially in terms of healing efficiency. Healing efficiency increases dramatically with the adipic acid content until around 7% after which the healing remains constant independently of the adipic acid content. At the same time small additions of adipic acid (<5%) do not lead to an increase in healing. Nevertheless an addition of about 6% shows a dramatic increase of up to 55%. At the same time the elastic modulus shows a continuous decrease with adipic acid levels which saturates from about 10%. These results show a clear link between the decrease in Young modulus and the increase in healing efficiency for this system.

![Graph showing healing efficiency and Young modulus vs adipic acid content](image)

Figure 1: Variation of the healing efficiency (%) and Young modulus of the polymer blends with varying amounts of adipic acid content in the blend.

In order to understand the effect of the additive in the polymer structure, WAXS measurements were performed at room temperature (Figure 2). The EMAA-Zn ionomer shows a reflection at 5 (2θ) related to the clusters. The reflections at higher values are related with the main crystalline structure. The addition of 1% of adipic acid decreases the intensity related with cluster reflection although the cluster signal is still visible. This trend is kept for all the blends until 6% of adipic is added and the peak related to the cluster is not visible anymore. It results evident that the disappearance of the clusters occur at the same concentration of adipic acid at which the healing efficiency is boosted up to its maximum constant value.
5. CONCLUSIONS

In this work it was demonstrated that the addition of adipic acid leads to a suppression of the clusters formation in EMAA-Zn ionomers. Rather surprisingly the scratch healing efficiency increased with the disappearance of detectable clusters by WAXS. The suppression of clusters leads to a modest reduction of the Young modulus.

ACKNOWLEDGEMENTS

This research was carried out under projects M41.6.10400 and M41.6.12456 in the framework of the Research Program of the Materials Innovation Institute M2i (www.m2i.nl).

REFERENCES