AN INVESTIGATION OF THE SELF HEALING MECHANISM OF IONOMER BASED SYSTEM

Russell J. Varley* and Sybrand van der Zwaag†

* CSIRO Molecular and Health Technologies, Bag 10 Clayton South, 3169 Australia
† Faculty of Aerospace Engineering, Technical University of Delft, Kluyverweg 1, 2629 HS Delft, The Netherlands
e-mail: russell.varley@csiro.au

Ionomers are a class of polymers which have up to 20mol% of ionic species incorporated into the structure of the organic polymer. These ionic species create interactions or aggregates [1, 2], not present in comparable non-ionic polymers, have a profound effect upon the mechanical and physical properties of the polymer. As a result there has been much research in both academia and industry over the last 30 years [3, 4] aimed at increasing the understanding of structure-property relationships in polymers while also exploring new commercial applications. The observed self healing capability that ionomers can exhibit is one of these applications arising from the unique chemical structure and is the subject of this paper.

1 Introduction

Despite the long standing commercial availability of ionomers and the comprehensive structural characterisation of ionomers, however, there has been comparatively little research carried out (at least in the open literature) on their self healing characteristics [5-7]. Self healing in ionomeric systems has been observed during high impact ballistic projectile puncture where the cavity created by a bullet is immediately sealed over when the bullet exits the polymer. This paper presents the results of a two part investigation into the self healing mechanism of ionomers. In the first instance, the self healing mechanism of ionomers was investigated by examining the morphology of the impact zone and the surrounding regions after ballistic penetration. Secondly a rapid screening method was developed that produces self healing in a laboratory scale environment and facilitates further examination of the mechanism.

2 Background

The self healing mechanism of ionomers is unlike other self healing mechanisms in that it is controlled by the inherent chemical structure and morphology of the polymer. The benefit of this, in contrast to other self healing processes where a “healing agent” is added, is that the process is potentially repeatable many times, being dependent only upon subsequent polymer degradation. In addition, this mechanism is not an autonomic process but must be “activated” through the sufficient transfer of high thermal energy forces. During impact, the transfer of energy from the bullet first rapidly heats up the impacted polymer through frictional forces.
The local temperature is increased rapidly and melts the impacted polymer while having little effect upon the temperature of the surrounding polymer. The elastic nature of the molten polymer, allows high levels of elongation, but when failure occurs the polymer rebounds to its original position and closes the original cavity created. Full healing occurs more slowly as the chemical species are able to diffuse across the discontinuities and create sufficient entanglements so that healing is completed. However, it is the presence of important chemical and morphological structures and transformations introduced through the ionic species that promote this alternative self healing mechanism. Some of the key parameters, such as the physical crosslinking, the order to disorder transition and ion hopping that facilitate this mechanism concepts such as will be briefly discussed. An important aspect of self healing is that ionomers can behave as both thermoplastics and thermosets. The presence of ionic species creates ionic domains or “aggregates” [8, 9], which have generally interpreted as consisting of several ion pairs known as multiplets [10, 11]. The size and number of ion pairs in any given multiplet will be governed by steric factors, flexibility of the polymer chain, the size of the ion pairs and the dielectric constant of the polymer backbone. These multiplets also create regions of restricted mobility which effectively form a “physical crosslink”. A schematic representation of a multiplet and the region of restriction of mobility are shown in Figure 1.

![Figure 1: A multiplet and region of restricted mobility. [Eisenberg et al (1990)]](image)

As the ion content or strength increases separate phase transition behaviour can be observed with new morphologies and structures which can begin to dominate the structure and hence properties of the ionomer. The potential reversible nature of these physical crosslinks is a critical factor in the ability to self heal. The order to disorder transition phase diagram (Tadano et al (1989) [12]) discusses in more detail the effect on the physical state of the polymer during difference transformations of the physical crosslinks. Figure 2, the model consists of three different phases that are controlled by temperature. The first phase or the ordered state, consists of ordered ionic domains or clusters, polyethylene crystallites and an amorphous region.
When the temperature is increased to above the order to disorder transition temperature \((T_{\text{dis}})\), the order within the ionic aggregates is lost along with the strength of the physical crosslinks. As the temperature is further increased, the polymer crystallites melt at \((T_m)\) despite the continued presence of the disordered aggregates in the molten state.

So in relation to the ionomeric self healing mechanism, as the temperature cools down (as it does immediately after ballistic impact) from above the melting point, re-crystallisation takes place rapidly while the re-ordering of the ionic clusters occurs more slowly through a relaxational process.

The behaviour of the polymer in the melt is also critical to the self healing process. Even though the polymer is heated above its melting point, the ionic domains although disordered do in fact persist up to 300\(^\circ\)C [13, 14]. This has the effect of ensuring that the molten polymer still has elastomeric properties thus giving it the ability to rebound elastically after penetration. The ion hopping mechanism, which is a result of ionic species constantly moving from one cluster to another, allows the macromolecule to relax and is a critical factor in providing the molten polymer with elastomeric properties.

![Figure 2: Model for the order to disorder transition of ionic clusters. [Tadano et al (1989)]](image)

### 3 Experimental

#### 3.1 Materials

The ionomer used in this work was the commercially available ionomer Surlyn 8940™ (Dupont, USA) well known to have the structural requirements suitable for high impact self healing. The polymer was dried overnight at 80\(^\circ\)C prior to use and was then processed using a platen press at 180\(^\circ\)C. Samples of 2mm x 10 cm x 10 cm were prepared for further analysis and characterisation. The samples were taken to a firing range where bullets with diameters of 5 and 9mm were shot at the polymer by experienced shooters. The samples were characterised according to scanning electron microscopy. Other polymers used in this work were polypropylene and linear low density.
3.2 Self healing mimicry

A rapid screening method was developed to imitate the self healing process. In this method a spindle with a shaft of diameter 1mm and a disc at the base of varying diameters was placed carefully through the polymer as shown in Figure 3. The sample was then securely fixed into a Universal Testing Machine (MTS) and pulled through the sample at a rate of 1000mm/min. In an attempt to mimic the thermal transfer during impact, the spindle was heated locally using a heated metal block and the temperature monitored prior to impact. The method was then utilised to investigate the effect of local temperature, spindle size and comparison with other non-ionic parent polymers.

Figure 2: basis of method showing the spindle penetrating the a) polymer and b) the heated block

3.3 Characterisation

The samples that had been impacted with a real bullet at the firing range were characterised using scanning electron microscopy. The healing efficiency of the ionomers as determined using the laboratory method was performed using a gravimetric leak detection method as well as optical microscopy.

4 Results

4.1 Ballistic penetration

Figure 4 shows a range of images obtained from SEM of the impact zone after ballistic penetration. Figure 4a) shows the overall impact zone showing a central crater, with a seemingly smooth lip around the crater and sharp crazes radiating out from the centre. Note that the total diameter of this region is around 5mm, almost half that of the 9 mm diameter of the bullet. The remaining images probe the morphologies of the different regions of the impact zone at higher magnifications. The region consisting of the radial crazes (Figure 4b) exhibits a rough nodular morphology consistent with a pulling or tearing of a ductile polymer. Figure 4c) shows the crater lip which exhibits a smooth featureless surface. This seems to indicate that at this point substantial melting has taken place in a very localised region. The image from within the crater also appears smooth in places, but also exhibits many fibrils stretching across separated polymer. This highlights the level of elasticity and elastomeric behaviour that has occurred during penetration. Examination of the crater also reveals that the material has healed completely in that across the base of the crater solid polymer is present.
These images tend to support the proposed mechanism already discussed with respect to evidence for 1) localised heating and melting of the polymer, 2) elastomeric behaviour at the centre of the crater and 3) more solid ductile like behaviour around the edges “holding on to the impacted zone”.

Figure 3: SEM characterisation of the a) overview of impact zone, b) outer radial crazes, c) lip of crater and d) crater

4.2 Self healing mimicry

An alternative method to investigate the self healing process has been developed in this work as a tool to further understand the self healing process. An important aspect of the mechanism is to understand the role of localised heating (ie polymer melting) on the self healing capacity. Therefore, the self healing mimicry experiment was performed with the temperature of the spindle varied from room temperature to 142°C. A selection of the resulting optical micrographs is shown in Figure 5 and illustrates a systematic improvement in healing efficiency. As can be seen, the cavity size decreases with increasing spindle temperature and importantly the healing appears complete to the naked eye at when the spindle temperature is 105°C and above. The melting point of Surlyn 8940 was measured at 92°C and thus correlates well with the current understanding that the polymer needs to melt before healing can occur.
The healing efficiency was further quantified using gravimetric methods and optical analysis as shown in Figure 6 further reinforces the improvement in healing as a direct result of increasing the localised temperature of the ionomer. The level of plastic deformation also shown in Figure 6 also decreased with increasing local temperature. Again the higher levels of elastic rebound at higher spindle temperatures, reflect the more elastic behaviour in the melt. This is another critical aspect of the healing phenomenon and highlights the importance of the balance between elastic rebound and polymer flow (ie. molecular mobility) in achieving healing.

Figure 5: Effect of localised heating on the size of the cavity and the plastic deformation of Surlyn 8940

The size of the spindle was varied from a diameter of 9, 11 and 13 mm, at a spindle temperature of 105°C to investigate the effect of the “size of the bullet” on the capacity to heal. Using the same characterisation methods as discussed above, healing was found to be considerably reduced, increasing the size of the cavity while increasing the plastic deformation of the protruding polymer. Another important aspect of this work was to validate that self healing was in fact, dependent upon the unique structural features introduced by the ionic domains. To do this, two non-ionic aliphatic based hydrocarbon polymers, polypropylene and low density polyethylene were evaluated according to the same methodology as the Surlyn. Figure 7 shows optical micrographs illustrating the relative self healing capabilities for the three polymers. It is evident that the non-ionic polymers provided little evidence of healing compared to the Surlyn.
In addition to this, the plastic deformation of the polymer after impact was significantly higher for the non-ionic polymers highlighting the lack of elasticity of the non-ionic polymer compared to the Surlyn materials as shown in Figure 8. This highlights the lack of elasticity of the non-ionic polymers in the melt and reinforces the importance of the clustered ionic domains in conveying elastomeric properties in the melt and thus promoting self healing.

Figure 6: Comparative elasticity of ionomer with non-ionic polymer post impact

Figure 7: Overview of the healed impact zone for the Surlyn 8940 ionomer and non-ionic polymer LLDPE and PP

ACKNOWLEDGEMENTS

This work was performed by Dr. Varley while a visiting scientist from CSIRO at TUD. He gratefully acknowledges the support of CSIRO, Australia and TUD, The Netherlands for the opportunities provided to him to carry out this research.

SUMMARY

In conclusion, this work has presented new experimental evidence to support the current understanding of the self healing mechanism of an ionomeric polymer.
SEM studies have shown that the morphology of the impact zone clearly indicates the presence of 1) molten flow of the polymer and 2) elastic deformation and polymer relaxation within the crater.

In addition to this, the self healing mimicry studies also emphasise the requirement for the polymer to move into the molten state for optimum healing to occur. The unique ability of ionomers to self heal is comparison to non-ionic polymers was also demonstrated and the lack of elastic rebound was a clear determinant given the polymer flow would be expected to be similar or even higher for the non-ionic polymer.

REFERENCES