

# The effect of cluster plasticisation on the self healing behaviour of ionomers

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## ABSTRACT

This paper explores the effect of cluster plasticisation on the autonomous damage initiated self healing behaviour of a partially neutralised poly(ethylene-co-methacrylic acid) ionomer copolymer, Surllyn 8940<sup>®</sup> (DuPont). Aliphatic di- and tri-carboxylic acid based modifiers and their analogues were blended with the ionomer at 10 wt% concentration using twin screw extrusion methods to study their effect upon self healing. In-situ mechanical evaluation of the healing process showed that carboxylic acid modifiers reduced the elastic properties of the blend, increased elastomeric behaviour and enhanced elastic healing. The sodium neutralised carboxylic acids analogues and succinamide modifiers displayed the opposite behaviour, increasing elastic properties, decreasing elastomeric behaviour and reducing elastic healing. A proposed relationship which accounted for both the elastic and elastomeric behaviour during impact was found to correlate well with independent measurements of elastic healing or hole closure. Thermal analysis suggested that the carboxylic acid modifiers plasticised the ionic clusters, reducing their strength and increasing their rate of recovery. The sodium neutralised analogues and succinamide modifiers, again conversely, produced negligible plasticisation but reduced the rate of reformation of the ionic clusters after annealing. Examination of the impact zone using scanning electron microscopy complemented the mechanical and thermal results revealing increased elastomeric and viscous behaviour for the carboxylic acid modified samples but increased brittle failure for the sodium neutralised analogues and succinamide modifiers. Systematic modification of the ionomer therefore has clearly illustrated the importance of the ionic clusters in determining static and dynamic properties. In addition to this, controlling their strength and mobility is shown to have a profound effect upon the efficiency of the damage initiated healing event.

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## 1. Introduction

The creation of self healing materials provides an attractive alternative strategy to the endless pursuit of increasing the damage tolerance of a structure. They create a new paradigm whereby materials manage, rather than prevent damage, providing new solutions for materials and design engineers in demanding environments [1–5]. Despite the variety of materials and applications under investigation, all self healing materials have similar mechanisms which must operate synergistically for healing to occur. These mechanisms include the ability to sense damage, and ‘deliver’ some healing agent to a damage zone efficiently in a manner appropriate to the application. Equally as important however, is the fact that the healing agent and transport

mechanism must not significantly interfere with the primary function of the material.

This work focuses upon a special class of self healing polymers; ionomers which are known to more or less completely close or heal a cavity formed by the impact by a pointed high speed projectile, leaving only a scar on the original surface. This unique feature creates interesting opportunities for these polymers in environments prone to impact related damage because the actual impact itself can initiate healing. Ionomers consist of up to 15 mol% of ionic [6,7] species incorporated into the polymer structure which create interactions or aggregates not present in non-ionic polymers. The resulting reversible physical crosslinks combined with a complex microstructure have a profound effect upon the mechanical and physical properties of the polymer and underpins the self healing behaviour. One important consequence of this structure is the creation of an order to disorder transition ( $T_{ord}$ ) which effectively creates a network polymer consisting of reversible crosslinks and is analogous to a glass transition temperature in a thermoset.

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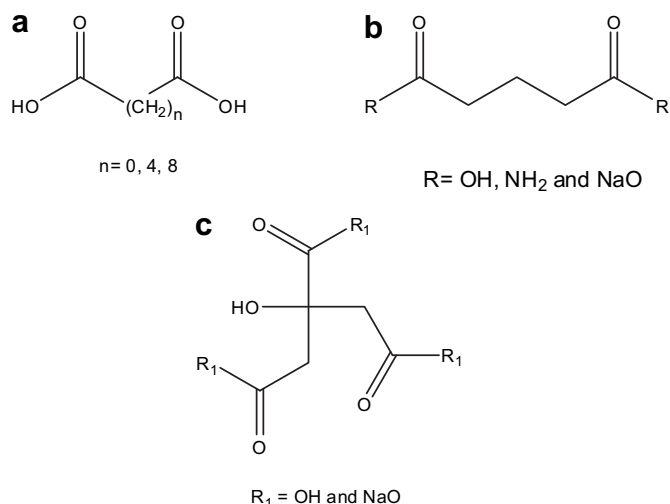
The model developed by Tadano et al. [8] succinctly describes the possible transitions and properties of an ionomer and how the ionomer transforms between a (physically) crosslinked network polymer, an elastomer and a molten/viscous polymer depending upon the temperature. These thermo-reversible transitions provide a mechanism by which an ionomer can transform instantaneously during a rapid temperature increase into a viscous yet high strength elastomeric material. As the temperature decreases, there is a two stage recovery process by which the ionomer can re-crystallise rapidly while taking much longer for the ionic clusters to re-order themselves. The micro- and nano- structures of an ionomer, however, are complex and it is important to recognise that they are only partially neutralised and that un-neutralised carboxylic acid functional groups remain in the polymer. In fact, Kalista et al. [9] and Fall [10], have both reported that the presence of ionic clusters is not necessarily a pre-requisite for healing and have shown that ethylene-co-methacrylic acid copolymers (the un-neutralised versions of self healing ionomers) can also heal in a similar manner. In addition to this, healing has also been shown to decrease with increasing ionic strength further complicating the role of ionic aggregates and un-neutralised carboxylic acid in facilitating the healing process. Walters et al. [11], studied blends of neutralised and un-neutralised ionomers, using FTIR analysis and found that no free di-carboxylic acids existed because they either formed dimers or associated with the other neutralised aggregates. The degree, to which this occurred however, depended upon the level of neutralisation of the other ionomer in the blend. Vanhoorne and Register [12] observed the decrease in zero shear viscosity when adding un-neutralised acid groups to an ionomer and proposed that the acid groups effectively plasticized (or reduce the charge in) the associations in sodium ionomers. It was suggested that the un-neutralised acid groups effectively accelerate the ion hopping process, (critical to self healing) as it facilitates the phase transitions during thermal energy transfers. They also noted that sodium clusters were affected by an un-neutralised acid, while zinc ionomers were not. Previous studies therefore, have clearly shown that interactions between carboxylic acids and ionomers have substantial impact on the microstructure and viscoelastic properties and thus it is important to fully explore the implications for self healing ionomers.

The work presented here explores the modification of the ionomer Surlyn 8940<sup>®</sup>, a partially neutralised poly(ethylene-co-methacrylic acid) random copolymer, with a variety of additives which attempt to systematically alter the microstructure and hence properties of the blends. The chemical structures of the modifiers, shown in Fig. 1, are a combination of organic di- and tri-carboxylic acids, an organic amide and two already neutralised organic carboxylic acid salts. Through these modifiers, the importance of the role of clusters, their mobility and strength has been explored, providing new insights into the healing mechanism. This work has been carried out using thermal analysis methods such as dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). The penetrative impact healing behaviour was characterised using a similar method to that developed by Varley and Van der Zwaag [13]. The healing mechanism has been further elucidated using scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials (preparation of blends)

The polymer used here was the commercially available Surlyn 8940<sup>®</sup> ( $T_{ord} = 47\text{ }^{\circ}\text{C}$ ;  $T_m = 93\text{ }^{\circ}\text{C}$ ) obtained from DuPont (Australia), a partially neutralised random poly(ethylene-co-methacrylic acid) ionomer (EMAA). The polymer contains 5.4 mol% of methacrylic



**Fig. 1.** Chemical structures of the polymer and modifiers used in this work. a)  $n = 0$ , oxalic acid,  $n = 4$  adipic acid,  $n = 8$  sebacic acid; b)  $R = \text{OH}$ , succinic acid,  $R = \text{NH}_2$  succinamide,  $R = \text{NaO}$ , sodium succinate; c)  $R_1 = \text{OH}$ , citric acid,  $R_1 = \text{NaO}$ , sodium citrate.

acid groups, of which 30% have been neutralised with the sodium cation. All of the modifiers used in this work, namely, oxalic acid, succinic acid, adipic acid, citric acid, sebacic acid, succinamide, sodium succinate and sodium citrate were obtained from Sigma-Aldrich Australia. They were all dried overnight at  $80\text{ }^{\circ}\text{C}$  and then used without further purification. Blends containing 10 wt% of each of the modifiers with Surlyn 8940<sup>®</sup> were prepared using a DSM mini-extruder using a twin screw configuration at  $150\text{ }^{\circ}\text{C}$ . Circular samples, 2 mm thick and about 30 mm in diameter were then produced using a DSM mini-injection moulder. Unmodified samples were also prepared for comparison purposes. Samples were stored at room temperature in a dessicator until required.

### 2.2. Mechanical/thermal properties

The method used to determine the mechanical response of the polymers during impact was performed according to the method previously reported by Varley and Van der Zwaag [13]. To perform this test, two intersecting incisions, each of 2 mm in length, into the centre of a sample approximately  $27\text{ mm} \times 27\text{ mm}$  were made using a modified razor blade. The blunt end of a spindle was carefully pushed through the sample so that a 9 mm diameter disk (made of copper) at the base of the spindle was approximately 30 mm from the ionomer sample. The unit was placed into an 810MTS universal testing machine fitted with a 10 kN load cell and then pulled through and out of the sample at a rate of  $150\text{ mm}^{-1}$ . For each sample, 4 coupons were tested and the results were appropriately averaged.

To promote the healing process, additional thermal energy was applied locally to the sample by placing a 10 mm diameter copper heated disk underneath the basal disk at a controlled temperature for 60 s. This was done using a modified commercially available soldering gun. The temperature applied was set to  $130\text{ }^{\circ}\text{C}$  which was adjusted downwards to  $127\text{ }^{\circ}\text{C}$  based upon a calibration curve constructed by comparing the set temperatures on the controller with the actual temperatures measured on the topside of the basal disk after 60 s of application.

The penetration test performed here, subjects a sample to consecutive mixed modes of deformation, namely flexural followed by tensile deformation. This complicates the interpretation of the

results since the contact area of impact changes continuously as the disk is pulled through the sample. However, the circumference of the basal disk remains in continuous contact with the material during impact and does not change. Therefore the following linear stress,  $\sigma_{\text{linear}}$  relationship has been developed [14] to quantify the observed deformations:

$$\sigma_{\text{linear}} = \frac{F}{2\pi r} \quad (1)$$

where  $F$  is the load exerted on the polymer, and  $r$  is the radius of the impacting disk. Two strains have been defined and determined here, namely the onset of failure strain,  $\varepsilon_f$  and the puncture strain,  $\varepsilon_p$  of the polymer which reflects the strain as the penetrant exits the polymer. The failure strain was calculated as follows:

$$\varepsilon_f = \left( \frac{d_f - d_0}{r} \right) - 1 \quad (2)$$

where  $d_f$  is the displacement at maximum load,  $d_0$  is the initial displacement of the disk, immediately prior to contact with the polymer sample and  $r$  is the radius of the impacting disk. Similarly, the puncture strain,  $\varepsilon_p$ , representing the strain at complete exit of the penetrant is calculated as follows:

$$\varepsilon_p = \left( \frac{d_p - d_0}{r} \right) - 1 \quad (3)$$

where  $d_p$  is the displacement at full puncture. A positive value of  $\varepsilon_p$  represents some additional tensile deformation (or stretching) as the null condition occurs when the cavity is opened and penetrated totally by bending forces only. The impact stiffness,  $E_{\text{impact}}$ , is then calculated as follows:

$$E_{\text{impact}} = \frac{\sigma_{\text{linear}-2} - \sigma_{\text{linear}-1}}{\varepsilon_2 - \varepsilon_1} \quad (4)$$

where the values of  $\sigma_{\text{linear}-n}$  and  $\varepsilon_n$  are chosen from the linear viscoelastic region of the stress versus strain curve during the early stages of impact. The raw load versus displacement data was exported into a spreadsheet for further data analysis.

Differential scanning calorimetry (DSC) was performed using a Pyris Diamond Perkin–Elmer instrument by placing a sample of approximately 5 mg (known accurately to 2 decimal places) in a sealed aluminium crucible. Samples were ramped from 30 °C to 120 °C at rate of 10 °C/min. After the initial ramp, the temperature was reduced at a rate of 10 °C/min followed by another identical ramp at 10 °C/min. Subsequent to this, separate samples were re-run after 1 day storage at room temperature as well as 7 days storage at room temperature. The order to disorder transition ( $T_{\text{ord}}$ ) and the melting point ( $T_m$ ) were determined from the observed peaks at about 45 °C and 90 °C respectively. Dynamic mechanical analysis (DMTA) was performed using a Perkin Elmer/Seiko II Pyris Diamond DMA in the 3 point flexural deformation mode. Samples were ramped from 0 to 120 °C at a rate of 2 °C/min and deformed at 1 Hz. The  $T_{\text{ord}}$  was determined from the peak in the  $\tan \delta$  spectra.

### 2.3. Characterisation of healing: pressurized water flow

The extent of autonomous post impact hole closure was determined using a pressurised water flow device which consists of two Aluminium blocks able to securely fit an impacted sample between two black rubber gaskets. At either side of the gaskets there are conduits, the inlet side fitted with a pressure gauge, which allow water to flow from the mains outlet and through the sample at constant pressure. The flow of water passing through the cavity was

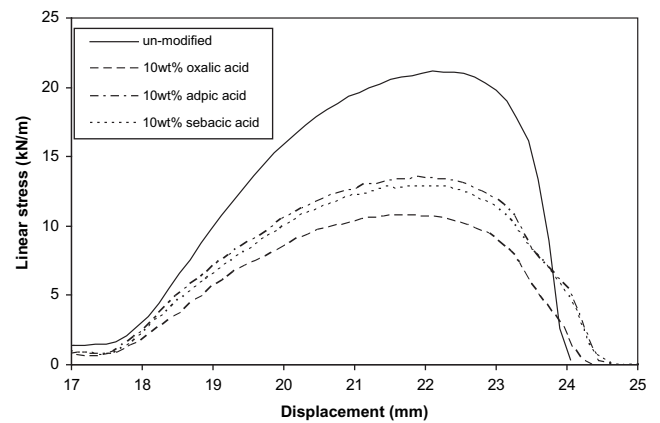


Fig. 2. Linear stress,  $\sigma_{\text{linear}}$  versus displacement plots showing the effect of di-carboxylic acid modifier upon the properties of the unmodified Surlyn 8940®.

determined gravimetrically and enabled the diameter of the cavity to be calculated using Bernoulli's laminar flow equations [15]. The time between the impact and the hydrodynamics test was typically of the order of 1 week or more.

### 2.4. Microscopy

Scanning electron microscopy was performed using a Philips XL30 field emission instrument. The images were observed using an accelerating voltage of 5 keV and the samples were coated with approximately 200 Å of iridium.

## 3. Results

### 3.1. Characterisation of healing

Fig. 2 shows a selection of linear stress,  $\sigma_{\text{linear}}$  versus displacement curves for the di-carboxylic acid modified samples compared to the unmodified Surlyn 8940®. These traces compare well with similar results reported elsewhere [14], exhibiting an initial (flexural) elastic response, an anelastic response as the deformation transforms into tensile elongation, followed by a pseudo brittle failure in the case of the unmodified ionomer. The di-carboxylic acid additives are clearly seen to plasticise the unmodified ionomer decreasing the impact stiffness,  $E_{\text{impact}}$ , and linear strength,  $\sigma_{\text{linear}}$ , while increasing the extent of post failure elongation. The mechanical properties determined from these curves for all samples tested are shown in Table 1 which present the post failure

Table 1

Mechanical properties determined *in-situ* during high energy impact at 130 °C for the 10 wt% modified and unmodified Surlyn 8940® samples prepared.

Modifier	Post failure strain (%) ( $\varepsilon_p - \varepsilon_f$ )/ $\varepsilon_p$	$\sigma_{\text{linear}}$ (kN/m)	$E_{\text{impact}}$ (kN/m)	Cavity diameter (mm)
unmodified	0.90	19.1 (0.3)	29.0 (0.5)	1.14
oxalic acid	1.03	10.0 (0.5)	15.4 (0.7)	0.93
succinic acid	0.95	11.1 (1.3)	17.5 (2.4)	0.96
adipic acid	0.99	12.5 (0.6)	20.4 (0.6)	1.10
sebacic acid	1.00	12.3 (0.8)	19.8 (0.7)	1.04
succinamide	0.86	19.9 (0.6)	32.1 (1.1)	1.22
NaSuccinate	0.88	21.1 (0.6)	33.9 (1.2)	1.28
citric acid	0.99	11.5 (0.5)	17.5 (0.8)	1.14
NaCitrate	0.73	23.1 (0.6)	35.6 (1.2)	0.94

Values in parenthesis are the standard error.

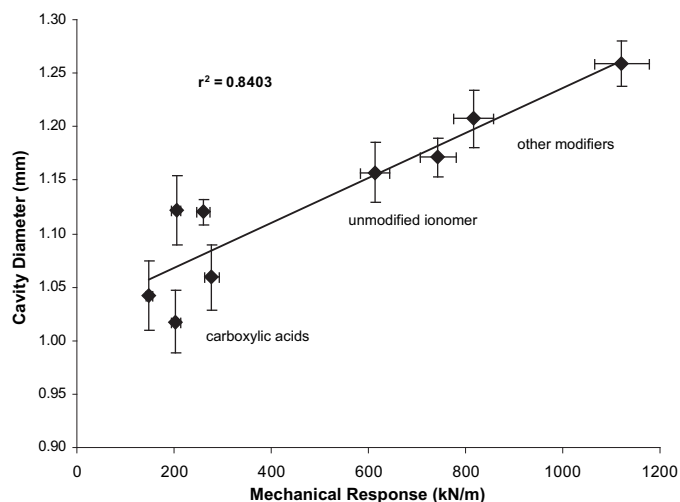


Fig. 3. Plot of cavity diameter versus mechanical response for all samples, demonstrating the close relationship between in-situ and post impact behaviour.

strain, linear strength and impact stiffness. Overall these results show that the addition of the carboxylic acid modifiers reduces the elastic properties, the impact stiffness  $E_{\text{impact}}$ , and linear failure strength,  $\sigma_{\text{linear}}$ , in order of increasing concentration of carboxylic acid functional groups. For example, the oxalic acid produces the largest level of plasticisation while the longer chain adipic and sebacic acid produce the least. The level of post failure strain  $[(\epsilon_p - \epsilon_f)/\epsilon_p]$  however, increases with carboxylic acid addition indicative increasing elastomeric behaviour. Conversely the succinamide and sodium salt based modifiers are found to have an opposite effect upon the properties. The impact stiffness  $E_{\text{impact}}$ , and linear failure strength,  $\sigma_{\text{linear}}$ , all increase while the post failure strain  $[(\epsilon_p - \epsilon_f)/\epsilon_p]$  was either unaffected or decreased.

In attempting to better understand a materials mechanical response to damage and its ability to self heal, the following relationship has been proposed [14] which takes into account the initial elastic properties and the materials behaviour during post failure strain.

$$\text{Mechanical Response} = (E_{\text{impact}}\sigma_{\text{linear}})/\left(\frac{\epsilon_p - \epsilon_f}{\epsilon_p}\right) \quad (5)$$

where  $E_{\text{impact}}$  is the impact stiffness,  $\sigma_{\text{linear}}$  is the linear strength,  $\epsilon_f$  is the failure strain and  $\epsilon_p$  is the puncture strain. This relationship is based on the recognition that elastic healing arises from a balance between the initial elastic response and the subsequent elastomeric response. Thus the mechanical response is a product of the impact stiffness and failure strength, representing the elastic response, while the second term represents the comparative level of elastomeric behaviour or post impact shape memory. The impact cavity diameters, (shown in Table 1) measured using the flow meter described previously are plotted as a function of the mechanical response and shown in Fig. 3. The correlation between the two measurements, (independently measured) provides strong support for the proposed relationship and highlights the importance of the interplay between the elastic and elastomeric in determining healing. This plot clearly shows the improved healing arising from the addition of the di- and tri- carboxylic acids compared to the unmodified ionomer as well as the deleterious impact upon healing for the neutralised salts and amide additives. Reducing elastic behaviour while enhancing elastomeric properties is therefore shown to aid damage induced healing, while equally the opposite effects are shown to reduce elastic healing.

### 3.2. Morphology of impact surfaces

To further understand the healing mechanism occurring during impact it is necessary to investigate the morphology of the damage

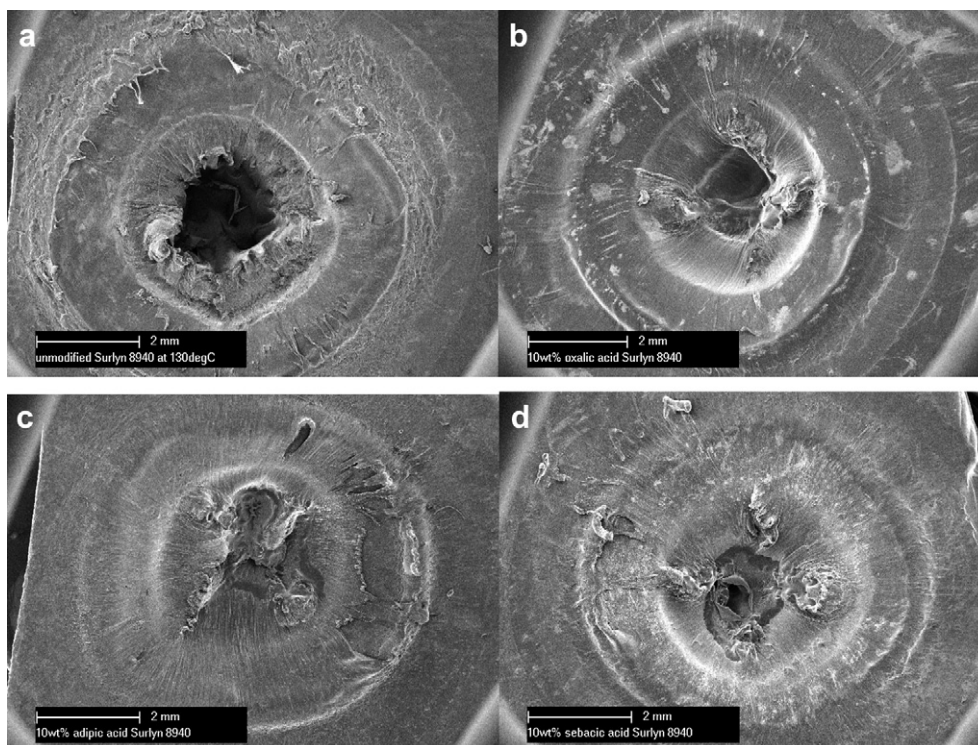
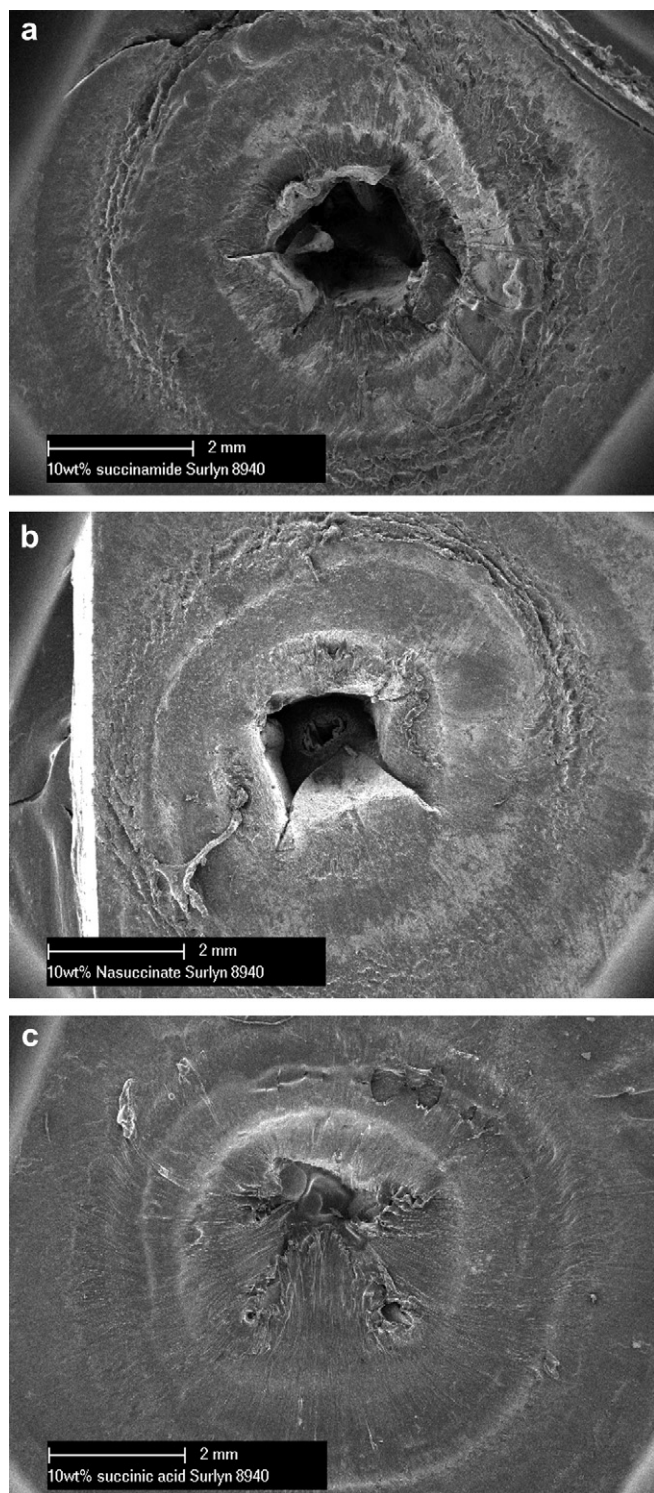


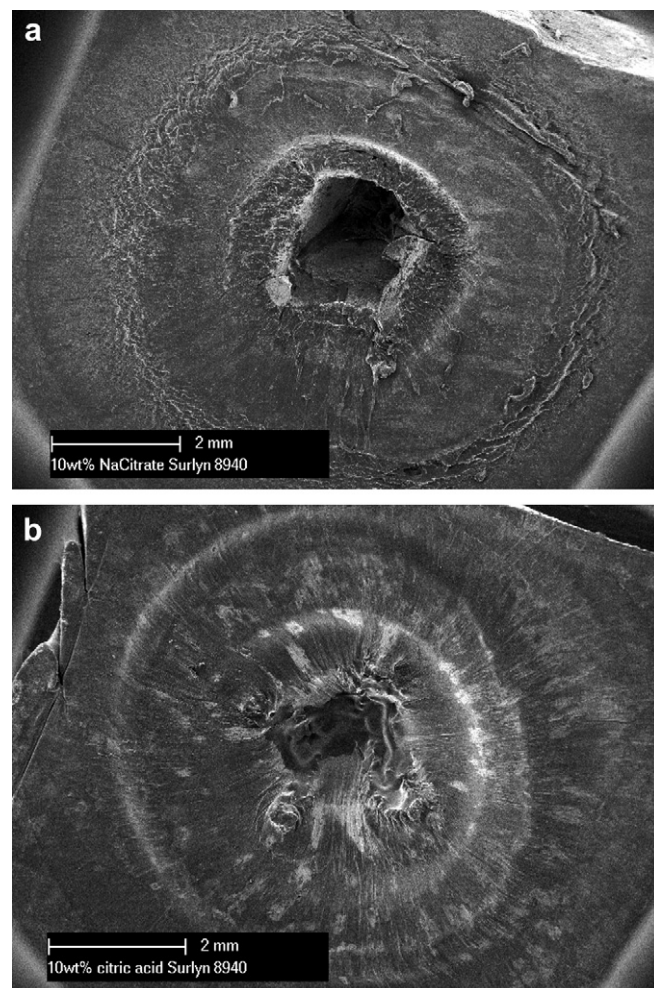
Fig. 4. Scanning electron micrographs comparing the impact site of a) unmodified Surlyn 8940® with b) oxalic acid, c) adipic acid and d) sebacic acid modified Surlyn 8940® at 130 °C.





**Fig. 5.** Scanning electron micrographs comparing the impact sites of Surlyn 8940® modified with a) succinamide, b) sodium succinate and c) succinic acid modified Surlyn 8940® at 130 °C.

site. Previous studies on actual ballistic impacts [16–18] have shown that the impact site consists of a combination of morphologies representing different viscoelastic responses. There is typically an outer region, where elastic ductile properties are evident, providing an anchoring point for the polymer during impact. Here, the gradient of properties from the less affected outer regions, are



**Fig. 6.** Scanning electron micrographs comparing the impact sites of Surlyn 8940® modified with a) sodium citrate and b) citric acid modified Surlyn 8940® at 130 °C.

critical in facilitating recovery post impact. At the centre of the impact site, there tends to be more elastomeric behaviour and viscous flow, evidenced by fibrillation or smooth undulating surfaces evident of molten behaviour. Fig. 4 shows the impact regions of the di-carboxylic acid modifiers compared to the unmodified ionomer which all display outer and inner regions, yet compared to the unmodified ionomer, the di-carboxylic acid modifiers clearly seem to improve hole closure. Similar impact sites in Figs. 5 and 6 shows the effect of varying the structure of a succinic and citric acid based modifiers respectively. Both sets of micrographs clearly emphasise the decrease in responsiveness of the sodium salt modified sample as well as the succinamide modifier compared to the di- or tri- carboxylic acid modifier. These blends result in poor shape memory post impact, presumably due to the increased elastic properties of the blend, but equally from the lack of elastomeric response evident (Note:  $(\epsilon_f - \epsilon_p)/\epsilon_f$ ; from Table 1). The micrographs indicate a distinct lack of viscous or molten polymer flow, despite the fact that the melting point is unaffected by the modification of the ionomer. These micrographs therefore, provide good support for the previous relationship between the mechanical response and actual healing.

Fig. 7 shows magnified micrographs of the lip of impact craters of various ionomer systems, further reinforcing the effect of carboxylic acid modifiers upon the healing mechanism. Fig. 7a shows the impact zone for the unmodified ionomer, which

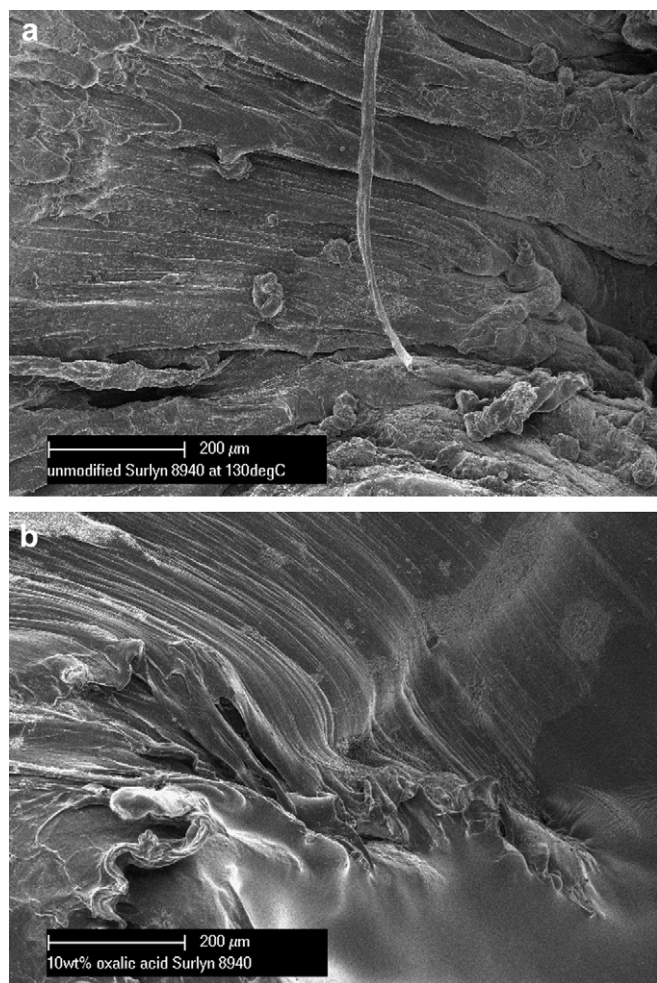


Fig. 7. Higher magnification scanning electron micrographs examining the crater lips for the a) unmodified Surlyn 8940® and b) oxalic acid modified Surlyn 8940®.

provides evidence for an elastomeric response evidenced by extensive stretching of polymer strands. Fig. 7b shows an enhanced level of elastomeric behaviour as well as some viscous flow shows the sample containing 10 wt% of the oxalic acid modifier as would be expected, given the higher level of hole closure.

### 3.3. Thermal analysis

The DSC thermograms of the unmodified ionomer are shown in Fig. 8 and are broadly representative of the behaviour found for all of the modified blends prepared. The traces reveal a two phase microstructure [8] typical of ionomers consisting of an order to disorder transition ( $T_{ord}$ ) at around 47 °C, reflecting the strength of the ionic clusters in the initial polymer, followed by the melting point transition ( $T_m$ ) at above 90 °C. A subsequent temperature ramp after a controlled cool to room temperature showed that ordering within the ionic cluster structures is erased by the melting process. After being left at room temperature for 1 and 7 days however, there is clear evidence of the re-appearance of microstructural re-ordering attributed to ionic cluster reformation. After 7 days at room temperature the magnitude of the  $T_{ord}$  peak was found to exceed that of the initial polymer. Tadano et al. [19] first reported this behaviour for the zinc salt of an ethylene-co-methacrylic acid copolymer and reported a return to equal strength of the virgin material after 38 days at room temperature. Despite the changes in the  $T_{ord}$  transition peak height and position, the  $T_m$  transition peaks were found to be extremely consistent regardless of prior thermal history.

The peak heights shown in Figs. 9 and 10 illustrate the effect of the addition of the aliphatic di-carboxylic acids and the alternative succinic and citric acid based modifiers respectively. Table 2 also describes the changes in  $T_{ord}$  in terms of temperature and peak area ( $\Delta H$ ) after the initial ramp and subsequent temperature scans after 1 and 7 days. As can be seen, all samples display a recovery in the  $T_{ord}$  transition after 7 days, although there are clear trends which differentiate between the different chemistries of the modifiers. The carboxylic acid modified samples all display a reduction in  $T_{ord}$  as a result of modification as measured by the peak area, peak height and  $T_{ord}$ . This is attributed to the ability of the carboxylic acid

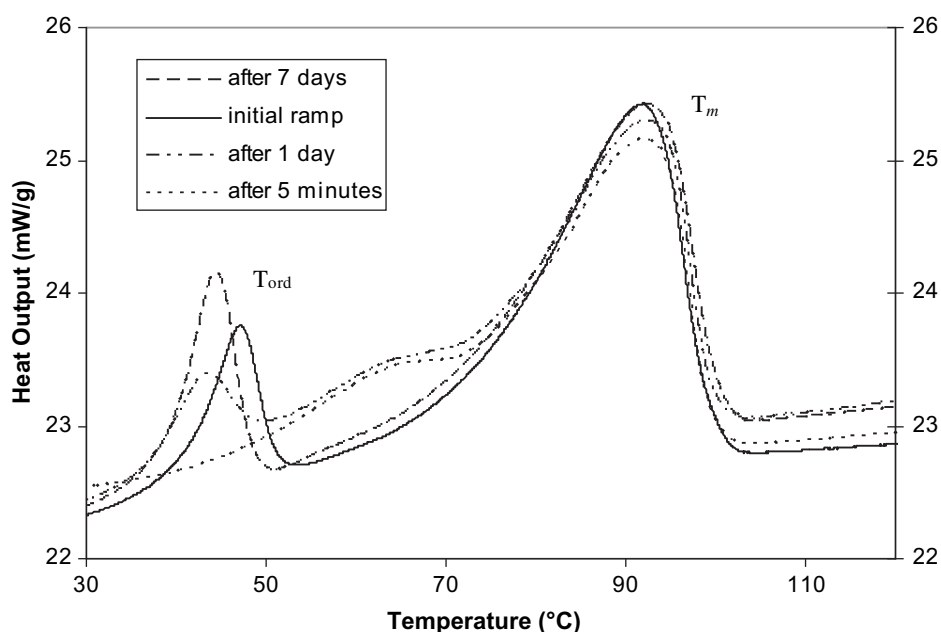
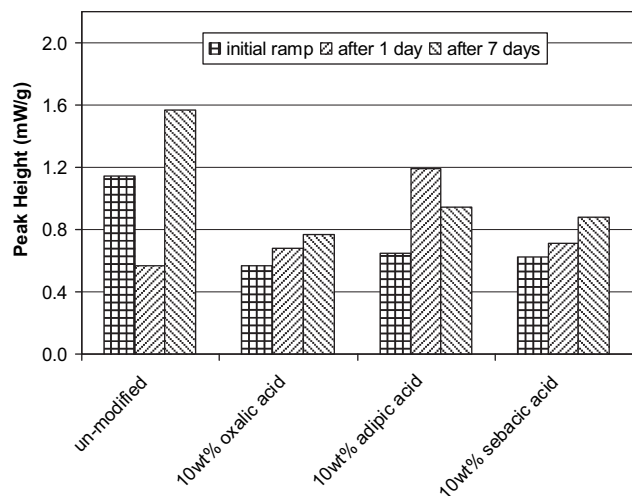


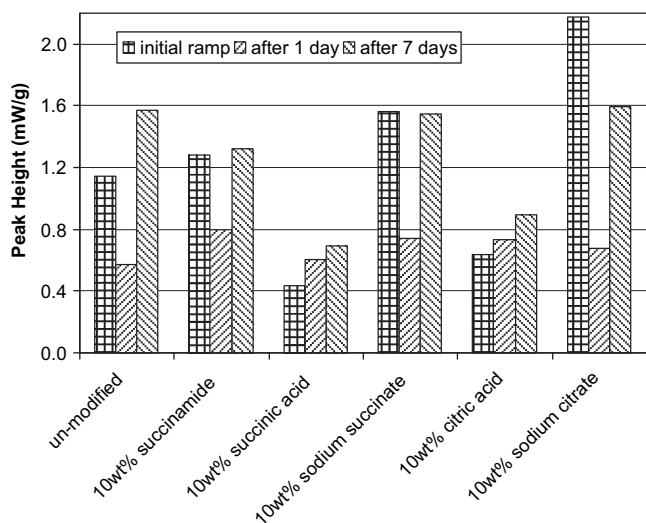
Fig. 8. DSC thermograms illustrating the variation in  $T_{ord}$  with time and temperature, and the comparative stability of  $T_m$ .





**Fig. 9.** Effect of unmodified and di-carboxylic acid modifiers on the peak height of  $T_{ord}$  of Surlyn 8940<sup>®</sup> after 1 and 7 days after erasing previous microstructure.

groups to plasticise the ionic cluster [12,20]. This plasticisation however, also appears to accelerate the recovery of the order to disorder transition ( $T_{ord}$ ), as evidenced by the larger comparative peak heights even after 1 day at room temperature compared to the unmodified ionomer. After 7 days the peak heights had increased further, above that of the initial peak and now quite similar to that of the unmodified ionomer. These results are in contrast to the succinamide, sodium succinate and sodium citrate samples which exhibited comparatively slower re-ordering of the ionic clusters, particularly after 1 day (Fig. 10). Even after 7 days, the height of the peaks were generally lower than or equal to the initial peak height. In addition to this, the initial peak heights of succinamide and sodium salt modified polymers all increased compared to the unmodified ionomer suggesting a strengthening of the order to disorder transition ( $T_{ord}$ ) and a distinct lack of plasticisation of the ionomer. DSC thermal analysis therefore can be seen to correlate well with the healing results described above. The addition of carboxylic acid groups appear to plasticise the ionic clusters and reduce their strength (as measured by the temperature and the peak height) while also increasing the rate of the ionic cluster



**Fig. 10.** Effect of unmodified and succinic and citric acid based modifiers on the peak height of  $T_{ord}$  of Surlyn 8940<sup>®</sup> after 1 and 7 days after erasing previous microstructure.

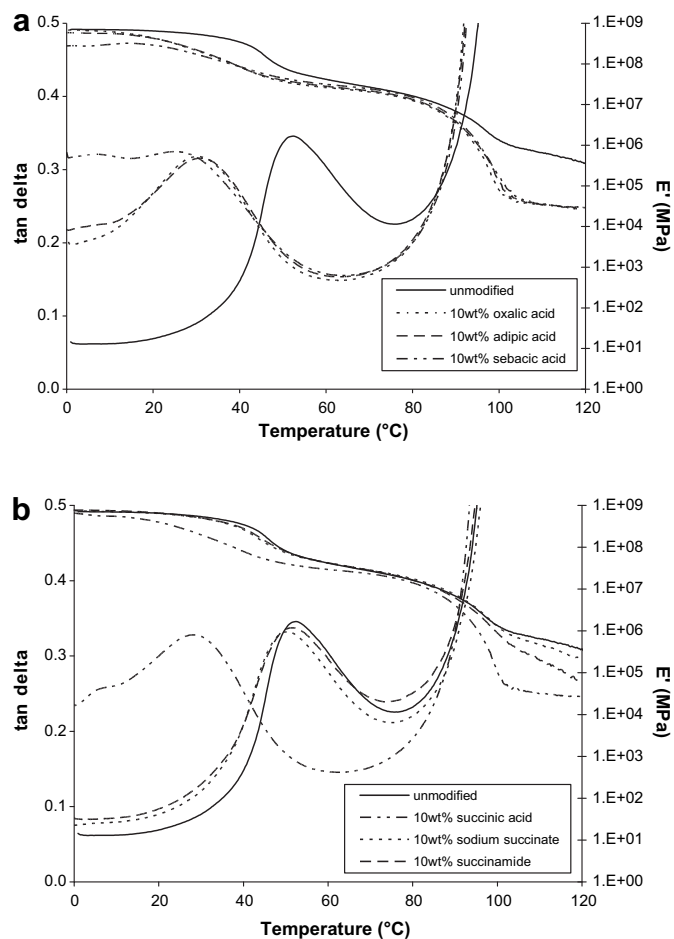
**Table 2**

Summary of all the key DSC parameters measured here for all 10 wt% modified Surlyn 8940<sup>®</sup> samples.

Modifier	Initial ramp/cool down			After 1 day		After 7 days	
	$T_{ord}$ (°C)	$\Delta H_1$ (J/g)	$T_{cryst}$ (°C)	$T_{ord}$ (°C)	$\Delta H_1$ (J/g)	$T_{ord}$ (°C)	$\Delta H_1$ (J/g)
unmodified	47.1	6.42	60.9	43.0	3.27	44.4	8.21
oxalic acid	43.9	3.86	70.9	36.5	3.77	38.0	4.53
succinic acid	41.9	2.45	70.4	36.5	3.30	39.7	3.61
adipic acid	41.5	3.86	74.9	38.6	6.27	38.5	4.87
sebacic acid	42.6	4.91	73.9	36.8	3.35	38.5	4.27
succinamide	41.9	2.45	69.7	36.5	3.30	39.6	3.61
succinamide	45.6	5.87	70.4	37.1	4.21	42.7	6.82
NaSuccinate	47.9	7.35	59.5	43.3	3.62	44.5	7.24
citric acid	41.0	3.37	74.0	36.9	3.37	37.9	4.07
NaCitrate	48.1	9.94	61.9	44.9	3.55	44.8	7.40

re-ordering and hence reduce healing. In contrast, the other modifiers increase the strength of the cluster, and reduce the thermo-mechanical responsiveness and hence reduce healing.

The dynamic mechanical spectra were determined for all the modified ionomer systems and a selection of traces showing the varying effects of modifiers are shown in Fig. 11. The  $T_{ord}$  transitions based upon the peak in the  $\tan \delta$  traces and values of the elastic moduli at 10 °C, 60 °C and 110 °C for the full set of modified blends are also shown in Table 3. Fig. 11a shows that the addition of di-carboxylic acids create a consistent decrease in the elastic



**Fig. 11.** DMTA spectra illustrating the effect of di-carboxylic acid addition on the storage modulus ( $E'$ ) and  $\tan \delta$  spectra of Surlyn 8940<sup>®</sup>.

**Table 3**

Summary of the DMTA results showing the order to disorder transition temperatures ( $T_{ord}$ ) and storage moduli at 10 °C, 60 °C and 110 °C for all 10 wt% modified Surlyn 8940® samples.

Modifier	$T_{ord}$ (°C)	$E'$ at 10 °C (MPa)	$E'$ at 60 °C (MPa)	$E'$ at 110 °C (kPa)
unmodified	52.0	697	41.6	650
oxalic acid	31.0	621	26.3	34.8
succinic acid	28.4	547	29.2	31.0
adipic acid	31.0	560	28.2	35.3
sebacic acid	25.3	303	31.6	34.7
succinic acid	28.4	547	29.2	31.0
succinamide	51.4	743	41.7	198.4
NaSuccinate	50.6	708	41.9	474.0
citric acid	32.9	746	26.0	33.3
NaCitrate	52.4	677	41.0	651.0

properties across a range of temperatures. In particular, a large reduction in the elastic moduli at 110 °C (above  $T_m$ ) for the di-carboxylic modified samples is observed, complementing the abovementioned DSC results and supporting the hypothesis of the plasticisation of the ionic clusters. The corresponding  $\tan \delta$  spectra manifests this plasticisation via consistent reductions in  $T_{ord}$ , reducing from 47 °C for the unmodified ionomer to around 30 °C and less for the di-carboxylic acid modified ionomer samples. In contrast Fig. 11b shows the corresponding DMTA traces for the succinic based modifiers. These traces illustrate sharply the difference between carboxylic acid modifiers with the succinamide or sodium neutralised succinate. The carboxylic acid modifiers exhibit plasticisation in the  $\tan \delta$  and storage modulus spectra particularly at temperatures above  $T_m$ . The amide and sodium neutralised species in contrast, display no plasticisation at all, exhibiting storage moduli similar to the unmodified ionomer. However, at temperatures above the melting point some plasticisation compared with the unmodified ionomer, is evident. Again, similarly to the DSC thermal analysis these results illustrate the delicate balance of factors which facilitate elastic healing.

#### 4. Conclusion

The partially neutralised poly(ethylene-co-methacrylic acid) is known to exhibit damage initiated healing during ballistic or high energy penetration due to a balance of elastic and elastomeric properties facilitated by thermal energy transfer. The addition of carboxylic acid modifiers and their amide or sodium neutralised analogues to the ionomer has provided new insights into the healing mechanism and highlighted the importance of the ionic clusters in controlling healing. In-situ mechanical evaluation has shown that carboxylic acid modifiers improve healing efficiency by

reducing elastic properties and enhancing elastomeric behaviour. Thermal analysis revealed that the ionic clusters were reduced in strength as a result of plasticisation yet were able to reform more rapidly below their melting point. The combination of these factors combined to create polymer blends with enhanced elastic healing behaviour compared to the unmodified ionomer. In contrast, the neutralised analogue additives and succinamide increased elastic properties, reduced elastomeric behaviour, increased ionic cluster strength while reducing the rate of reformation after annealing. The result of these additives was to ultimately reduce healing during penetrative impact. Systematic modification of the ionomer therefore has clearly illustrated the importance of the ionic clusters in determining the efficiency of damage initiated healing. Plasticising and increasing the dynamic behaviour of the ionic clusters is shown to improve healing while strengthening and reducing the mobility of the ionic clusters reduces healing.

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#### References

- [1] Wu DY, Meure S, Solomon D. Prog Polym Sci 2008;33(5):479–522.
- [2] van der Zwaag S. In: Sv Zwaag, editor. Self healing materials: an alternative approach to 20 centuries of materials science, vol. 1. Dordrecht: Springer; 2007. p. 388.
- [3] Ghosh SK. Self healing materials: fundamentals, design strategies, and applications. Wiley; 2009. pp. 306.
- [4] Dry CM. In: Proceedings of the first European conference on smart structures and materials. Glasgow, Scotland: IOP; 1992. p. 367.
- [5] Wool RP. Soft Matter 2008;4(3):400–18.
- [6] Eisenberg A, Navratil M. Macromolecules 1973;6(4):604–12.
- [7] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23(18):4098–107.
- [8] Tadano K, Hirasawa E, Yamamoto H, Yano S. Macromolecules 1989;22(1):226–33.
- [9] Kalista S. Self-healing of thermoplastic poly(ethylene-co-methacrylic acid) copolymers following projectile puncture. engineering, vol. Master of Science. Blacksburg: Virginia Polytechnic Institute and State University; 2003.
- [10] Fall R. Puncture reversal of ethylene ionomers – mechanistic studies. Engineering, vol. Master of Science. Blacksburg: Virginia Polytechnic Institute and State University; 2001.
- [11] Walters RM, Sohn KE, Winey KI, Composto RJ. J Polym Sci Part B Polym Phys 2002;40(24):2833–41.
- [12] Vanhoorne P, Register RA. Macromolecules 1996;29(2):598.
- [13] Varley RJ, van der Zwaag S. Polym Test 2008;27:11–9.
- [14] Varley R and Van der Zwaag S. Polym Int, in press.
- [15] <http://www.tasonline.co.za/toolbox/pipe/velorif.htm>.
- [16] Kalista S, Ward TC. J Roy Soc Int 2007;4:405–11.
- [17] Kalista S, Ward TC, Oyetunji Z. Mech Adv Mat Struct 2007;14:391–7.
- [18] Varley RJ, van der Zwaag S. Acta Mater 2008;56(19):5737–50.
- [19] Tadano K, Hirasawa E, Yamamoto Y, Yamamoto H, Jap Yano S. J Appl Phys Part 2 Lett 1987;26(9):1440–2.
- [20] Ghosh SK, Khastgir D, De SK, De PP, Albalak RJ, Cohen RE. Plast Rubb Comp Proc Appl 1998;27(7):310–6.