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Thermal characteristics of the self-healing response in poly(ethylene-*co*-methacrylic acid) copolymers

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A class of poly(ethylene-*co*-methacrylic acid) (EMAA) copolymers and ionomers has shown the unique ability to instantaneously self-heal following ballistic puncture. It is noteworthy that the thermomechanical healing process active in these materials appears to be significantly different in capability and mechanism than any of the other self-repairing systems studied. To better understand this phenomenon, the thermal response during EMAA self-healing was examined. Tests of various damage types, including sawing, cutting and puncture, revealed high-energy transfer damage modes to produce heat and store energy favourable to healing. DSC probed healed specimens revealing they had reached the viscoelastic melt believed requisite to healing response. Low-temperature ballistic experiments demonstrated films continue healing even when punctured at −30°C; analysis showed healing efficacy comparable to room temperature, holding significant pressures of approximately 3 MPa. At the lowest temperature, brittle fracture occurred in one material indicating insufficient heat transfer to store recoverable energy. In total, the results supported the defined healing model and provided additional information on the healing process in both its thermal dependence and general mechanism. Finally, a new DSC method was developed for probing the thermal history of healed films which may lead to a more complete mechanistic model.

Keywords: self-healing; ballistic puncture reversal; self-repair; poly(ethylene-*co*-methacrylic acid); EMAA; ionomer

1. INTRODUCTION

The idea of a self-healing material has led to significant interest in the current literature. Many elegant techniques have focused on the ability to heal internal cracking and delamination in structural thermosets and thermosetting matrix composites (Dry & Sottos 1993; Dry 1996; Kessler & White 2001; White *et al.* 2001; Pang & Bond 2005*a*,*b*). However, numerous other forms of damage exist for materials and devices in service applications. Thermoplastic poly(ethylene-*co*-methacrylic acid) (EMAA) copolymers have shown the unique ability to heal damage of a different nature. Films of these EMAA materials repair the puncture created by ballistic impact (Fall 2001; Kalista 2003; Coughlin *et al.* 2004; Kalista *et al.* in press). Although the projectile passes completely through the film, this puncture reversal has been observed to occur almost instantaneously and automatically leaving only a small scar at the healed puncture site. Healed strength is also considerable, as even approximately 1 mm thick healed films have subsequently been observed to hold significant pressures in excess of 3 MPa (Kalista *et al.* in press). While not yet well understood, such a unique impact healing mechanism could prove beneficial in numerous previously inconceivable applications. These might include use as a healing layer in combat aircraft fuel tanks (Coughlin *et al.* 2004), for maintaining a pressurized atmosphere in aircraft or spacecraft, as a protective self-sealing barrier for chemical containment, or in medical applications whereby a self-healing thin membrane may prove beneficial. While EMAA is currently observed to heal only for certain damage types discussed in this paper, a magnetic induction technique has been proposed to heat the polymer and repair damage that does not automatically heal (Owen 2006). In order to apply the technology to a designed system, the mechanism and capabilities of the EMAA healing process must be well understood. Further, by developing a greater understanding of the mechanism responsible, novel polymeric materials possessing this ability may ultimately be produced.

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While it was initially thought that healing was the result of ionic attractions between the polymer chains only in EMAA ionomers, it was shown that ionic content was unnecessary to the healing response as both ionomers and the non-ionic copolymers of these materials were observed to heal (Kalista *et al.* in press). Hence, continued study here and beyond is necessary to uncover the healing mechanism. Rather than relying on the chemical healing means of other systems, the EMAA healing phenomenon is believed to occur through a thermomechanical process (Kalista *et al.* in press). It also differs from others because the healing process is already self-contained rather than engineered into the material. The goal in examining EMAA healing is to understand how the phenomenon occurs. In a study by Fall, thermal IR imaging showed these films to heat to the viscoelastic melt state locally during the puncture–healing event (Fall 2001). Specifically, they were observed to reach temperatures of approximately 3°C above T_m in the immediate vicinity of the puncture site. Previous research has proposed a model for the ballistic self-healing of these EMAA copolymers and ionomers (Kalista *et al.* in press). Here, it was proposed that self-healing occurs through at least a two-stage process. Upon impact, energy is transferred to the polymer film from the projectile, heating it locally to the melt state. In the first stage, the polymer elastically rebounds under melt conditions to close the hole following release of the projectile. In the second stage, the film is then sealed through autohesion and interdiffusion of the EMAA polymer chains. This model prescribes melt heating as necessary to eliciting the healing process following projectile puncture. The present study will help verify the theory of the two-stage model and act to clarify the healing process in both its thermal dependence and general mechanism.

Since thermal response has proved so critical, this analysis will focus on the thermal character of these polymers. EMAA ionomers and copolymers have shown unique thermal characteristics due to their morphology. One important characteristic is the presence of a sub-T_m 'quasi-crystalline' peak during differential scanning calorimetry (DSC; Tadano *et al.* 1989). This peak has been observed to grow and shift with ageing time and temperature. While its precise origin is not completely understood, its presence provides a useful record for understanding the healing process as discussed in detail below.

This investigation will examine the thermal response of the EMAA copolymers during the puncture–healing process. Well-designed experimentation is necessary for uncovering the mechanism behind EMAA self-healing. Using various non-puncture damage methods, the correlation of heating to healing ability will be examined. These methods along with puncture testing will qualitatively examine the speed and energy transfer critical to the healing process. Next, testing of films at room and sub-ambient temperatures will examine both the capability and the thermomechanical mechanism of the puncture–reversal process. Given the importance of heating, low-temperature puncture testing will also examine the range of temperatures over which healing can occur. Finally, DSC is used to probe the effect of the puncture–healing event on the thermal history of the polymers, providing a record of thermal experience of EMAA materials.

2. EXPERIMENTAL

2.1. Materials

Four poly(ethylene-*co*-methacrylic acid) (EMAA) polymers were examined. These random copolymers contained methacrylic acid (MA) groups of 5.4 mol%. Specifically, these were DuPont Surlyn 8920 with 60% of the MA groups neutralized by sodium, referred to as EMAA-0.6Na, and DuPont Surlyn 8940 with 30% of the MA groups neutralized by sodium, referred to as EMAA-0.3Na. These ionomers had melt transition temperatures at $T_m = 93$ and 92°C, respectively, measured as peak values in DSC. Two non-ionic copolymers were also examined including DuPont Nucrel 925 and DuPont Nucrel 960 referred to as EMAA-925 and EMAA-960 ($T_m = 93$ and 91°C, respectively). All were donated by DuPont. Additionally, React-a-Seal, a proprietary ionomer material based on the Surlyn 8940 formulation was also examined (denoted EMAA-RS). React-a-Seal is produced by Reactive Target Systems, Inc., but owing to its unknown composition, it was not examined in-depth during the course of this study. React-a-Seal was obtained as a 6.35 mm (0.25 in.) thick sheet ($T_m \sim 95$°C; Fall 2001) while the four EMAA materials above were in pelletized resin form.

2.2. Sample preparation

Pelletized resin was compression moulded to produce thin films using a stainless steel mould with DuPont Kapton as a release film. The mould was placed in a pre-heated hot press at 150°C and allowed to heat for 4 min. Samples were then pressed with a ram force of approximately 178 kN (40 000 lbs) for 30 s before being removed to air cool under ambient laboratory conditions. This identical process was used for all materials and yielded clear, smooth films. No preparation was necessary for the already pressed React-a-Seal sheet. Films were stored in a desiccator until testing.

2.3. Projectile testing

Polymer films were punctured under controlled laboratory conditions using the projectile test station described previously (Kalista *et al.* in press). Added to this testing device has been the ability to perform testing below room temperature. Polymer films were clamped into the sample holder and placed in the oven. For sub-ambient temperatures, cooled air via heat exchange in a liquid nitrogen containing dewar was pumped into the chamber with the oven closed. The heat controls on the oven compensated to heat the oven and hold at the desired temperature. Samples were allowed to equilibrate for 20 min before the small window in the oven door was opened and the sample shot. For room temperature tests, samples were shot immediately without the above heating/cooling

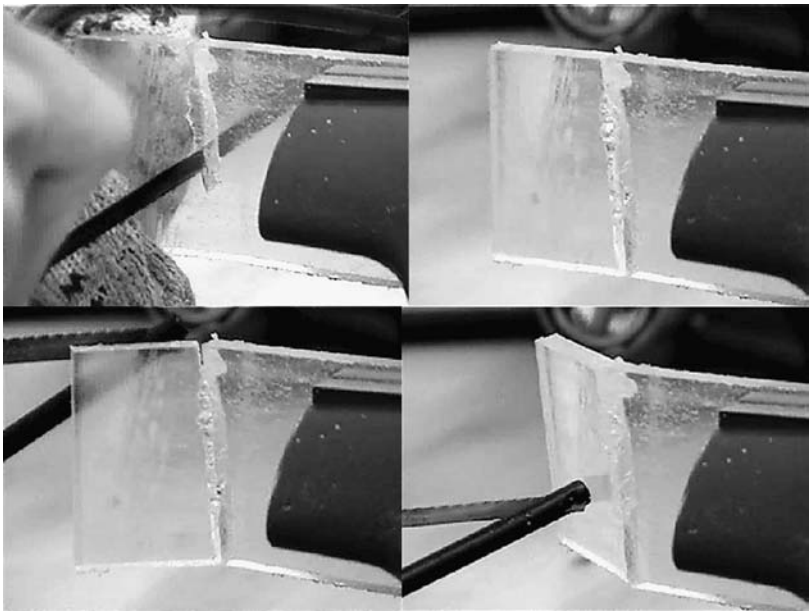

Figure 1. Time-lapse images of the self-healing of sawed React-a-Seal. Images progress clockwise starting with the upper left (R. Fall 2001, unpublished work).

method. For elevated tests, cooled air was not used and films were allowed to equilibrate for 5 min before shooting through the window in the oven door.

Films were shot using a Crosman Model 664GT, 0.177 calibre air rifle loaded with Crossman Copperhead 0.177 calibre (diameter 4.5 mm) pointed pellets. For all tests, the rifle was pumped to the maximum pressure of 10 MPa obtained at 10 pumps (1500 psi according to the manufacturer) yielding a projectile speed of approximately 197 m s^{-1} and a momentum of approximately 0.10 kg m s^{-1}. Films of all materials (except EMAA-RS) were tested at room temperature; sub-ambient temperatures of 10, −10 and −30°C; and elevated temperatures of 60, 70, 80 and 90°C. Film thickness was approximately 0.9 mm.

2.4. Healing assessment

As described previously, the pressurized burst test (PBT) was used to examine films and quantify their healing following puncture (Kalista *et al.* in press). Films were first examined using a magnifying lens. Any film that appeared to be potentially healed was examined further. In this test, the potentially healed film was placed into a testing fixture. The healed site was then loaded from the impacted side with pressurized nitrogen gas at a rate of approximately 690 kPa min^{-1} (100 psi min^{-1}). For healed films, the subsequent pressure at failure was recorded, providing a measure of the 'strength' of the healed puncture site. This allowed a quantitative comparison of healing quality between the different materials. If a film was unable to hold measurable pressure, then it was determined to be non-healed.

2.5. Differential scanning calorimeter (DSC)

The TA Instruments DSC 2920 was used to examine the thermal characteristics of the polymer samples. This DSC was equipped with an RCS cooling system and used nitrogen as a purge gas.

The specific DSC procedure was as follows:

(i) equilibrate at 20°C,
(ii) first heat to 120°C at 5°C min^{-1},
(iii) first cool to 20°C at −10°C min^{-1}, and
(iv) second heat to 120°C at 5°C min^{-1}.

More specific details of the DSC test procedure are provided below with necessary discussion of their method and purpose.

3. RESULTS AND DISCUSSION

As discussed above, self-healing occurs automatically and instantaneously upon projectile puncture. However, other damage mechanisms are first examined to better understand the healing process.

3.1. Sawing

In a previously unreported study (R. Fall 2001, unpublished work), a 6.35 mm thick sheet of EMAA-RS roughly 10×25 cm was mounted in a vice and sawed through its width with a hacksaw. Though it had been completely sliced, following the cut, the two halves had self-bonded to each other, leaving a healed elastic hinge. Some key mechanics of the process were revealed during the experiment. Four time-lapse images from a video of the process are shown in figure 1. They progress clockwise starting with the upper-left image. During the very rapid sawing, a great deal of heat was generated due to the friction in sawing. The material responded by 'gumming up' in a molten state and bonded together filling the void behind the saw. Not only did this autohesion quickly reattach the two pieces, but its rapidity made sawing very difficult. This correlation of heat with healing behaviour is consistent

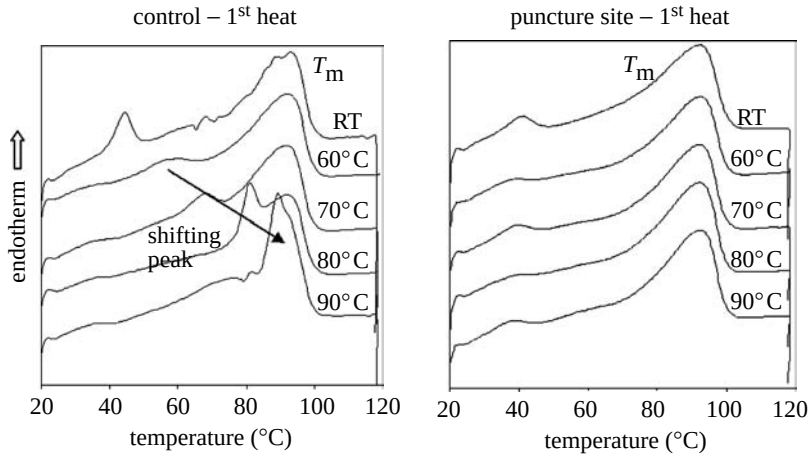

Figure 2. DSC thermograms for samples at and away from the puncture site. The curve temperatures provided are the temperatures of the oven during testing. RT denotes room temperature. Results provided are representative of all the four EMAA materials tested.

with the results from the thermal IR camera data discussed above (Fall 2001) and elsewhere (Kalista *et al.* in press), and it emphasizes the importance of heat energy in eliciting the healing response.

3.2. Cutting

The next experiment studied the healing response during simple cutting. Here, EMAA films of varying thickness (0.8–1.6 mm) were cut by razor blade and/or scissors. Afterwards, there was no observable healing in any of the films. While heat was generated via friction in the sawing process, this was absent in cutting by scissors or razor. Though a similar type of damage to sawing, the cutting experiment produced very different results and suggests that the damage mechanism must be a high-energy transfer process which generates heat in the material. With this result, one expects yielding-type deformations and high-friction mechanical impacts to be required for healing.

3.3. Nail puncture

A film of EMAA-0.3Na (approx. 1.6 mm thickness) was punctured by driving a nail through the sample. Upon removal of the nail several seconds later, no healing was observed. The model proposed for puncture healing suggested that melt elastic retraction is the first step in healing (Kalista *et al.* in press). Given the high speed of healing observable during projectile tests, it is expected that the continued presence of the nail blocked hole closure. This delay in removing the nail produced an observable permanent deformation (plastic drawing) rather than the necessary retraction for healing. Additionally, it is hypothesized that the nail served as a heat sink for any generated frictional heat energy as time passed following puncture. This test provides support for the proposed first stage of healing as an elastic response to the projectile puncture. The nail puncture test shows not only that puncture reversal demands an energetic damage process producing heat, but also that the puncture occurs as an immediate momentary event.

3.4. DSC of ambient and elevated temperature punctures

With the emphasis on heat generation as key to self-healing in the above experiments and the previously observed thermal infrared heating during projectile puncture (Fall 2001), more must be understood about the EMAA thermal response during the puncture–healing event. To do this, DSC was used to examine the effects of puncture/healing on the thermal characteristics of the materials. Such a study is also critical to analysing the theorized two-stage model for self-healing, which prescribes elevated thermal character (melt) for both stages.

In the current experiment, materials from two different locations of the same film were compared using DSC following projectile testing at room and elevated temperatures. Here, the first location tested material from an undamaged location several centimetres (more than 3 cm) *away from the puncture site*. The second tested material *at the puncture site*. For healed samples, this was the healed material itself. For non-healed samples, it consisted of the damaged material which was a plug of material typically ejected from the film with the pellet or still attached at the non-healed hole. Since each of the paired locations was from the same film, both had an identical thermal history prior to the puncture/healing event. By comparing the first (initial) DSC heating curves from the two locations, the effect of the puncture/healing process on the thermal character of the polymer was determined. Of particular interest is the effect on the quasi-crystalline annealing peak mentioned above. This test was performed on films of EMAA-925, EMAA-960, EMAA-0.3Na and EMAA-0.6Na for projectile tests of samples at room temperature and elevated temperatures of 60, 70, 80 and 90°C.

DSC results for each location were consistent for all the four EMAA materials and representative data are provided in figure 2. The DSC first heat of all samples away from the puncture site (control) showed that the polymer had undergone an annealing process indicated by an endothermic peak. This ageing peak was present

at room temperature and was observed to shift to progressively higher temperatures with increased annealing temperature while in the oven of the projectile test station prior to damage. As described above, this peak has been attributed as a 'quasi-crystalline' peak characteristic of EMAA ionomers and forms with ageing and annealing (Tadano *et al.* 1989). Conveniently, its presence here serves as an artefact for comparing the two locations and hence the effect of the puncture/healing process.

While the annealing peak was present in the control location first heat, it was *not present* in the first heat of any of the EMAA polymers *at the puncture site* (figure 2). Such a disappearance is consistent with what would be observed during any DSC second heat (following first heat above T_m) in customary DSC practice. In other words, the first heat at the puncture site resembles the second heat of the control site such that the annealing peaks have been erased. This indicates that the puncture/healing event has provided the heating necessary to erase the thermal history of the polymer. The results were consistent for all the four materials with representative DSC thermograms provided in figure 2. Hence, the disappearance of the annealing peak confirms that samples heated at least above the annealing peak temperature locally for lower temperature tests and likely above the melt temperature during puncture testing (as no remaining sub-T_m features are found).

Further, this heating/erasure can be attributed to one of the two events (puncture or healing). From the previous research, it was observed that films of all the four EMAA materials healed at room temperature, while those punctured at elevated temperatures did not (Kalista *et al.* in press). Since the annealing peak was erased in both samples that healed (at room temperature) and those that did not (at elevated temperatures), it is concluded that it is the puncture (and the temperatures it produced) rather than the healing process responsible for erasing the thermal history.

3.5. Low-temperature puncture

As observed above, local heat generation during puncture has been shown to be phenomenologically critical to the puncture–healing process. Given this result, the persistence of the healing behaviour over a range of temperatures must be explored. It is already known that elevated temperatures (60°C or above) hinder healing by dispersing energy viscously throughout a larger region of the polymer (Kalista *et al.* in press). Additionally, thermal infrared analysis showed that films shot at room temperature only heated to a few degrees above the melt temperature (approx. 98°C) regardless of impact speed (Fall 2001). Since thermal response is so critical to healing mechanics, one question that must be answered is will impact events *below* room temperature produce the sufficient local temperature rise into the viscoelastic melt region necessary for healing? Or, instead, will the low temperatures shift the material response into the rubbery domain (sub-melt) producing brittle fracture rather than healing? Additionally, if the films heal, will they have heated to the viscoelastic melt state or somewhere below?

As a thermal camera can neither be placed easily nor accurately to record film temperature inside the projectile test station, other methods must be used to provide a record of the thermal response. Using the low-temperature procedure described above, projectile tests of films of the four EMAA materials were performed at 10, −10 and −30°C. The purpose of testing was to determine whether healing was possible for each of the low temperatures rather than provide a definitive measure of healed strength at each temperature. If burst testing of a film indicated that pressure was indeed held, it was said that healing was possible for that temperature. If it did not, additional samples were tested to verify that healing would not occur. Future studies will expand on this more qualitative approach to provide detailed analysis of the measured healed strengths.

Surprisingly, an examination of films punctured at low temperatures revealed that the healing behaviour persisted into the low-temperature range. For this to be possible, the local temperature rise (ΔT) had to be much greater than that for samples shot at room temperature. In fact, samples shot at −30°C heat approximately 55°C greater than those starting at room temperature ($\Delta T \approx 125$°C for samples tested at −30 versus 70°C for samples tested at room temperature).

Two observations verify this significant temperature rise into the viscoelastic melt state. The first considers the particulars of the proposed two-stage model of healing. In stage I, the polymer is believed to elastically retract to close the hole under molten conditions. It is theorized to then weld together (stage II) to produce sealing as verified previously (Kalista *et al.* in press). For the current low-temperature experiments, the films are closed and sealed as shown by the PBT. In fact, neither of these stages would have been possible if the polymer had not heated into the melt. Secondly, melt heating is verified by DSC analysis. In this case, the same DSC technique used above for room and elevated temperatures was employed. By examining the endothermic peak left as an artefact of ageing in EMAA films, the effect of the puncture process was examined for films shot at the lowest temperature. To verify the expected temperature rise, a film of EMAA-0.3Na that had healed following a shot at −30°C was tested. As shown in figure 3, a DSC sweep of this sample revealed a significant reduction in the size of this peak as produced by puncture (approx. 40%). Though the peak was not completely erased, its size reduction *indicated a heat to the melt state* of a portion of the polymer fragment analysed by DSC. Part of the peak remained because the other portion of the analysed fragment had not reached melt during puncture. A sample of material larger than the melted region alone was chosen because it was desired to include both the entire melt area and the surrounding non-melt region. The concept is depicted in figure 4 and will serve as a technique for determining the size of the melt puncture region in future testing. As shown in the figure, a central region around the puncture site melted, erasing its thermal history. However, the remaining portion surrounding

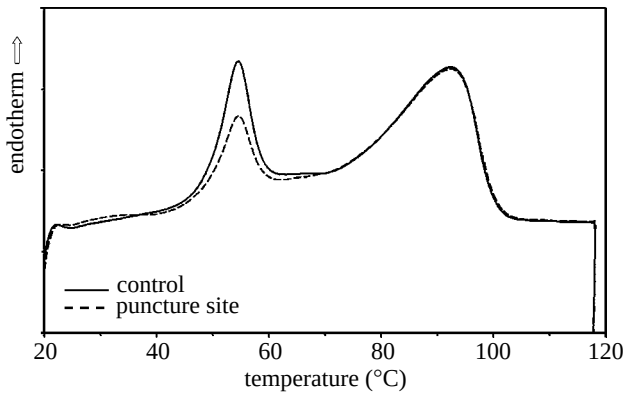

Figure 3. DSC thermogram for EMAA-0.3Na following puncture at −30°C.

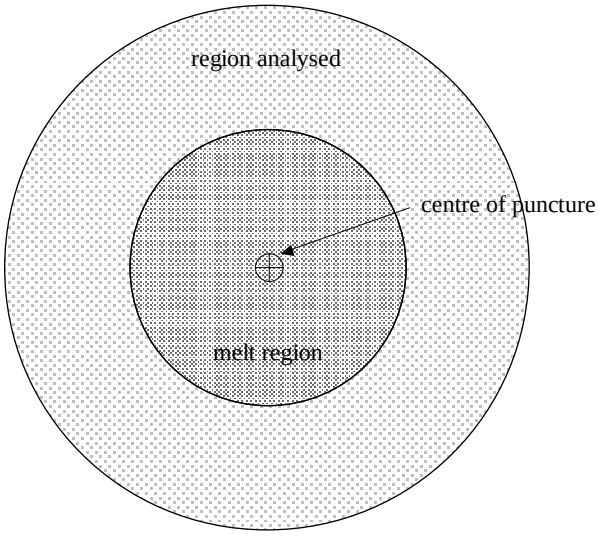

Figure 4. Schematic of region analysed by DSC (not to scale).

the melt region did not reach sufficient temperature to erase its thermal history leaving behind a portion of the ageing peak. Hence, rather than complete erasure of the ageing peak, only the portion which reached viscoelastic melt was erased. Interestingly, here the DSC thermogram provides an 'image' or record of the temperatures reached during puncture much like the thermal IR might. Future testing should use this artefact in an exhaustive analysis mapping the local melt region during puncture. However, as used here the technique has verified that localized melting persists in initially cold samples as required for healing. Finally, the inclusion and observation of the surrounding material in the DSC sample indicate that there is a non-molten region surrounding the melt portion which provides a rigid framework for elastic retraction and healing as expected by the self-healing model.

While low-temperature healing has been verified, it may be expected that the quality of the healing response is diminished versus that at room temperature. However, the healed strength has proved surprisingly high for the samples tested in the low-temperature range. In fact, pressurized burst testing (PBT) shows the healed strength in EMAA-960 and EMAA-0.3Na to be comparable to that obtained at room temperature previously (Kalista *et al.* in press). Healing in EMAA-960 was stronger than that for room temperature tests (2.5 MPa range versus 1.5–2.5 MPa, previously; Kalista *et al.* in press). EMAA-0.3Na also performed in a manner consistent with, if not better than, the previous tests having a healed strength up to and above 3.5 MPa for the lowest temperature tested (−30°C). EMAA-0.6Na continued to be inconsistent in its healing performance with low healed strength (below approx. 0.5 MPa) supporting the previous conclusion that high ionic content may inhibit the healing response (Kalista *et al.* in press). However, it also showed the ability to heal to −30°C. As a whole, low-temperature tests have shown that not only does healing persist into a significantly low temperature range, but it may also perform better in some cases, given the performance of EMAA-0.3Na and EMAA-960. Additional testing is necessary to provide a definitive comparison of their healed strengths; however, the results indicate healing strength to be comparable in magnitude to the previous results at room temperature (Kalista *et al.* in press).

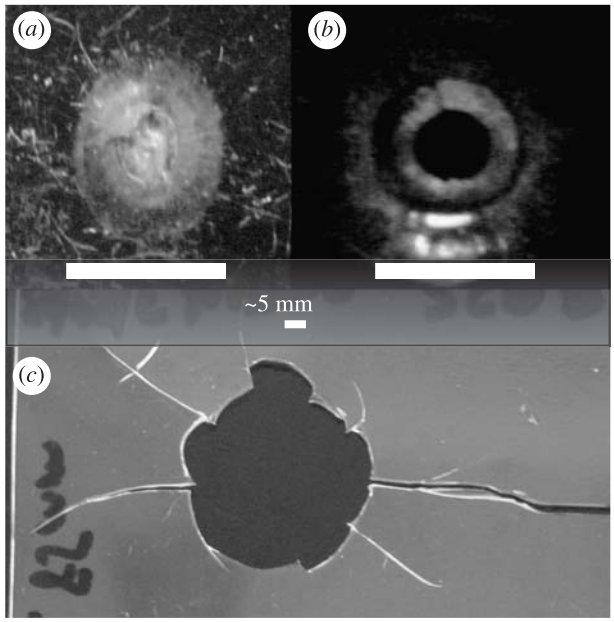

Figure 5. EMAA films following puncture. Shown are: (*a*) a healed film, (*b*) non-healed showing attempt and (*c*) the brittle fractured EMAA-925 film at −30°C (*a* and *b* adapted from the previous work; Kalista *et al.* accepted).

In previous work, EMAA-925 was shown to be the most consistently healing material at room temperature (with strength near 2.5 MPa; Kalista *et al.* in press). However, at −30°C, EMAA-925 showed a drastically different response. For all tests here and before, EMAA polymers have expressed similar behaviour upon puncture (uniformly showing the ability to heal, attempt to heal or not at all; Kalista *et al.* in press). In this instance, however, repeated tests showed that EMAA-925 experienced a clearly brittle fracture upon puncture quite different from the healing behaviour of the other materials. As shown in figure 5, this response is very different from that of a typical healed sample or a non-healed sample which expressed an 'attempt' at healing following brittle fracture by minimizing the energy forming a circular hole. Such a brittle response was the first departure from the

characteristic EMAA healing behaviour and may indicate −30°C to be near the lower temperature limit for healing in EMAA-925. In this case, energy transfer was insufficient to cause localized melting or to cause localized melting in a sufficiently large area to allow projectile passage. Instead of storing energy recoverably, the lack of chain mobility led to brittle film fracture. As the capability for sub-ambient testing is expanded below −30°C, the other materials will undoubtably reach a lower bound. Future testing will determine the lower bounds for healing in the other materials.

4. CONCLUSIONS

Key information was obtained about the thermomechanical nature of the healing process. In addition to puncture healing, EMAA films were able to heal upon sawing damage. This occurred through a heat-generating frictional process. By examining other damage modes (sawing, cutting and nail puncture), it was observed that healing of EMAA materials requires a high-energy transfer, unsustained damage event generating heat in the polymer which provided the ability to rebond and repair damage. Hence, high-friction impact methods such as ballistic puncture would be favourable.

Projectile tests were also successful and DSC analysis of the polymer thermal history revealed significant heating occuring during puncture. Here, puncture was observed to erase the thermal history of all films. By considering these results and the two-stage model, it was concluded that the puncture process heated films to the viscoelastic melt state. While low temperatures were expected to hinder the healing response, they surprisingly healed, experiencing an even greater temperature rise into the melt. In fact, the healing behaviour was effectively maintained down to −30°C with a significant healed strength showing a window for healing behaviour from at least −30 to 25°C and likely above. This was true for all materials except EMAA-925 at −30°C, which did not heat sufficiently to allow adequate energy storage for elastic retraction during stage I. As the capability for low-temperature testing is expanded, it is expected that other materials will show a lower bound.

Finally, a new DSC method was developed for the examination of the thermal profile of punctured films. Given its ability to record film heating during puncture, it will be used in future studies to explore the complex thermal response of the healing phenomenon and in calculation of the size of the melt region. This should provide necessary information leading to accurate mechanical modelling of the healing mechanism.

In summary, the importance of heating to the thermomechanical healing process of the EMAA copolymers is well established. The damage-induced heating stimulus has proved critical to healing in these materials. The above experiments provide support to the two-stage theory on healing. As a result of temperature rise, the melt condition provides the polymer with the mobility to both elastically close the hole in the first stage of healing and to bond together in the second stage.

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