Self-healing flexible laminates for resealing of puncture damage

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Abstract

A flexible self-healing system capable of healing puncture damage has been manufactured. Our material consists of three layers: a poly(dimethyl siloxane) (PDMS) composite, embedded with a self-healing microcapsule system, sandwiched between two layers of poly(urethane) coated nylon. The total structure thickness ranges between 0.84 and 1.5 mm. A protocol is established in which samples are damaged using a hypodermic needle or a razor blade, and a successful heal is defined as the ability to reseal the damage to withstand a pressure differential across the laminate of 103 kPa (∼1 atm). Trends in healing success are analyzed as a function of microcapsule size, self-healing layer thickness, and puncture diameter. Healing varied significantly with microcapsule size, with the maximum healing success rate (100% successfully healed) occurring in samples with 220 μm microcapsules and a puncture diameter of 0.49 mm. For this puncture size, an increase in microcapsule diameter corresponds to a decrease in healing efficiency. However, samples with larger microcapsules (up to 500 μm avg.) demonstrate more effective healing for larger puncture diameters, up to 1.61 mm. Additionally, healing increased with composite layer thickness, and decreased with increasing puncture hole size.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Self-healing polymers are an emerging technology based on embedded microcapsules that provide an autonomic repair mechanism. In brittle, thermosetting polymer systems, healing has been demonstrated for quasi-static fracture [1–5] and for fatigue damage [6, 7]. Recently, a flexible, elastomeric PDMS self-healing system has been developed that is capable of recovering significant amounts of the virgin tear strength [8, 9]. In both brittle and elastomeric systems, microcapsules containing chemically active healing agents are embedded in the polymer matrix. A propagating crack or tear triggers the healing response by microcapsule rupture and release of microcapsule contents onto the damage surfaces. The released healing agent comes into contact with a catalyst

material, either liquid or solid, and polymerization is initiated. The resulting polymer then bonds the crack faces together, regaining much of the original mechanical strength of the material.

Previous research on incorporating self-healing functionality into structural materials has focused on reinforced fiber composites [1, 2, 6, 7, 10–13]. The development of an elastomeric healing system allows for application to non-traditional engineering systems such as inflatable structures. An example of such a structure is NASA's lightweight inflatable habitat (TransHab). This structure consists primarily of a large flexible membrane that is inflated by a breathable atmosphere to define the internal habitation space and the overall shape [14]. Inflatable habitats provide several advantages when compared to conventional rigid structures, including high strength-to-weight ratio, increased damage resistance, and low manufacturing costs [14]. However, small damage such as

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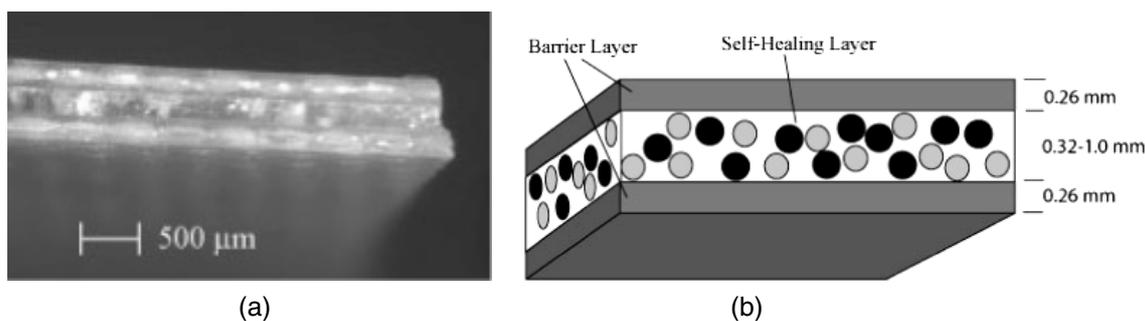
Figure 1. (a) Optical image of the laminated self-healing PDMS structure, and (b) schematic diagram representing the two-part microcapsule system within the laminated structure.

punctures or tears in the flexible outer skin can produce sub-optimal performance through loss of the enclosed atmosphere. To address this issue, a model flexible, laminated, self-healing bladder material is investigated to mediate the impact of small tears and punctures.

Previous attempts at healing puncture damage have focused on ionomers [15] and space-filling gels [16]. A self-healing response in ionomers initiates through the transfer of energy from a fast moving projectile, which is typically a few millimeters in diameter. Frictional heating of the material from the passage of the projectile leads to a reorientation of the polymer chains in the ionomer. This rearrangement can, under some conditions, seal the hole generated by the projectile. However, this healing occurs only when the damaged area is heated to near the melt temperature of the material [15]. A second self-healing system proposed by Nagaya *et al* utilizes a water-saturated expanding gel to automatically repair tires [16]. In this system, the polymeric gel is bonded between two layers of rubber on the inner surface of a tire and then saturated with water. Upon puncture, the saturated gel expands and fills the puncture, sealing the leak. A 4 mm thick polymer layer is able to effectively seal nail puncture damage for typical tire pressures of 0.25 MPa [16].

In this paper we present a thin, lightweight, and flexible microcapsule-based self-healing membrane. This membrane consists of a self-healing poly(dimethylsiloxane) (PDMS) matrix sandwiched between two layers of standard gas barrier (bladder) material (figure 1). Since the membranes primarily function as gas-retention bladders, a new test protocol is developed based on the ability of the membrane to seal small punctures and cuts.

2. Experimental procedure

2.1. Microencapsulation of healing components

The autonomic healing response in PDMS is provided through the incorporation of two types of microcapsules, with differing core materials, into the parent matrix. One microcapsule type contains liquid, silanol-terminated PDMS (Gelest, Inc.) resin and a liquid poly(diethoxysilane) (Gelest, Inc.) cross-linker. The second microcapsule contains a liquid tin catalyst.

Microcapsules containing the liquid PDMS resin and cross-linker were manufactured via an *in situ* urea-formald-

Table 1. Stir rate dependent microcapsule sizes.

| Core material	Stir rate (rpm)	Avg. diameter (μm)	Std. dev. (μm)
PDMS/PDES	650	500	80
PDMS/PDES	750	400	60
PDMS/PDES	900	290	50
PDMS/PDES	950	220	50
Tin catalyst/chlorobenzene	900	180	20

ehyde (UF) microencapsulation described by Brown *et al* [17]. In this procedure, a water-immiscible encapsulent was emulsified in a water bath via mechanical stirring. Urea and formaldehyde were added to the encapsulation bath, where polymerization took place in the aqueous phase. Newly formed polymer was deposited at the droplet–water interface, generating the shell wall of the microcapsules. Microcapsule diameter was controlled by the droplet size of the emulsion, which was related to the agitation rate. In this study, UF encapsulated PDMS resin ranged from 220 to 500 μm in diameter. Microcapsule sizes are described in table 1.

A second microencapsulation method, interfacial polymerization, was utilized to encapsulate the di-n-butyldilauryl tin (Gelest Inc.) catalyst within a poly(urethane) shell [18]. In this encapsulation procedure, the shell wall was formed at the droplet–water interface through the reaction between a monomer dispersed in the oil phase and a water soluble monomer in the aqueous suspension phase. In this study, the catalyst filled microcapsules had a constant average diameter of 180 μm.

2.2. Laminate manufacture

Self-healing PDMS was prepared by mixing PDMS resin microcapsules (25 wt%) and tin catalyst microcapsules (0–6 wt%) into liquid PDMS resin (18 000 cSt silanol-terminated PDMS). Three weight percent poly(diethoxysiloxane) was added as a cross-linker and 3 wt% di-n-butyldilauryl tin was added as a cure catalyst to the microcapsule-filled resin material. The mixture was degassed for 15 min.

The self-healing membrane was a laminated structure consisting of a self-healing elastic layer sandwiched between two reinforcement layers, shown schematically in figure 1. Specimens were prepared by cutting two 60 mm × 90 mm
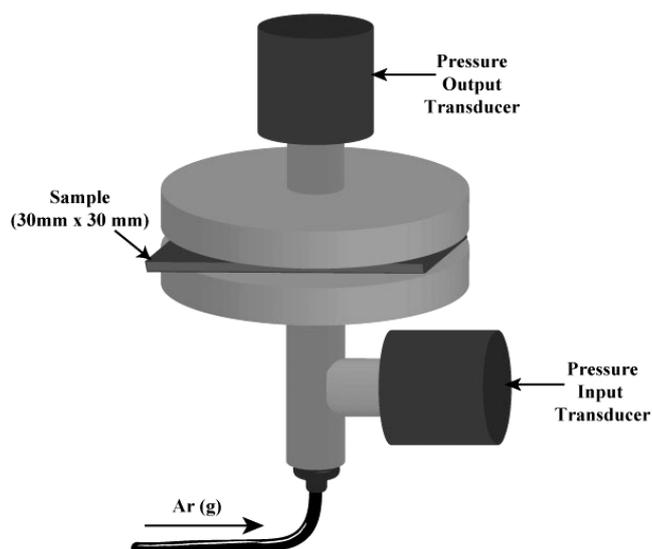
Figure 2. Schematic diagram of the pressure test cell showing gas flow into the chambers measured using pressure transducers.

Figure 3. Pressure change within the test cell for three punctured laminates.

sections of polyurethane coated nylon barrier material (ILC Dover Inc.). A commercial primer, Dow-Corning Primer-C, was applied to the surface of the barrier layer to promote adhesion between the poly(urethane) coating and PDMS. The microcapsule-embedded PDMS was poured over one of the barrier layers with a second ply positioned on top and a weight of approximately 1 kg was applied to flatten the laminate. The samples were cured for 24 h, yielding a three-layer laminated structure with a solid self-healing PDMS layer in the middle. Specimens 30 mm × 30 mm were cut from the 60 mm × 90 mm bulk material. The thickness of the PDMS layer was controlled by using silica microspheres as spacers. Laminates with thickness of 0.32, 0.50, and 1.0 mm were fabricated.

2.3. Testing protocol

Two methods were used to mechanically damage the laminates. Insertion of hypodermic needles with diameters of 0.49, 0.90, 1.27, 1.67 and 2.40 mm created a puncture hole in the laminate. Tear damage was simulated using a razor blade to make a 7 mm cut in the laminated bladder material. After the specimen was damaged, the laminates were allowed a 24 h, room temperature healing period under no load.

Healing performance was defined as the ability to seal puncture or cut damage and prevent leakage of test gas through the membrane. Samples were evaluated using a pressure test cell shown schematically in figure 2. A sample was held in the test cell sealed between o-rings. Argon gas was flowed into the test cell on one side of the laminate at 3.45 kPa s^{-1} via an electronically controlled regulator (IP411 Omega Inc.) until the target pressure of 103 kPa (~1 atm) was reached. Pressures on both sides of the specimen were continuously measured using strain gauge based pressure transducers (PX02-MV Omega Inc.). Data was recorded using LabView software and associated data acquisition hardware on a PC.
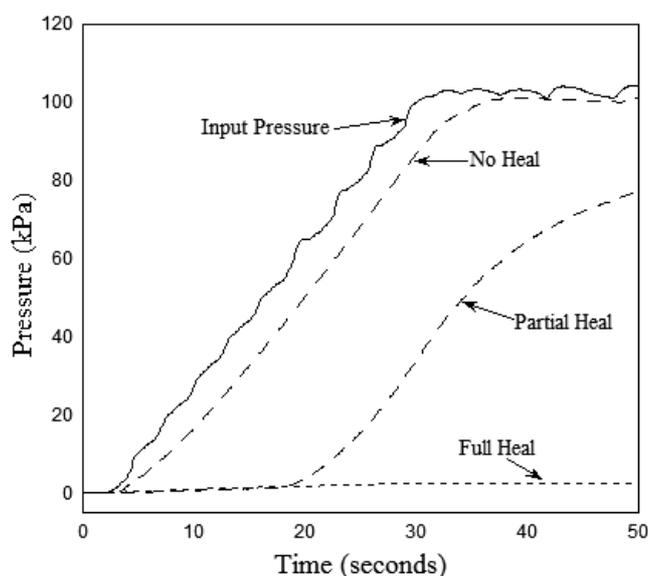
## 3. Results and discussion

3.1. Healing response

The membrane system proved effective in healing to the target pressure differential of 101.3 kPa (1 atm) without any leakage in many cases. However, the autonomic repair exhibited a range of healing behaviors, including partial heals which began leaking below the target pressure as well as no healing at all. Representative pressure traces are shown in figure 3 corresponding to laminates with a 1.0 mm self-healing PDMS layer thickness and average PDMS resin microcapsule diameter of 500 μm subjected to puncture damage with a diameter of 0.49 mm. The top curve shows the pressure input increase on one side of the membrane while the three lines below represent pressure outputs on the opposite side for three separate samples. Noise in the input curve is a result of a stepwise input of gas from the pressure regulator. The smooth line directly below the input pressure is indicative of a sample in which no effective healing occurred, allowing gas flow through the damaged region to the output chamber. A full heal is depicted by the virtually flat curve at the bottom of the graph. Input pressure was raised to 103 kPa and the resealed membrane impeded the flow of gas, thus no change in the output pressure. This pressure differential across the membrane was held for 300 s, and maintained a seal in every fully healed case. An increase of approximately 2.4 kPa in the output chamber was observed due to the pressure difference across the flexible sample causing a slight protrusion in the laminate and effectively increasing the pressure in the output chamber.

A third healing behavior is shown in the partially healed curve. The output pressure of the partially healed sample in figure 3 is initially constant, followed by a rapid increase in pressure after 18 s, corresponding to an input pressure of 55 kPa at rupture. This change in pressure indicates sealing
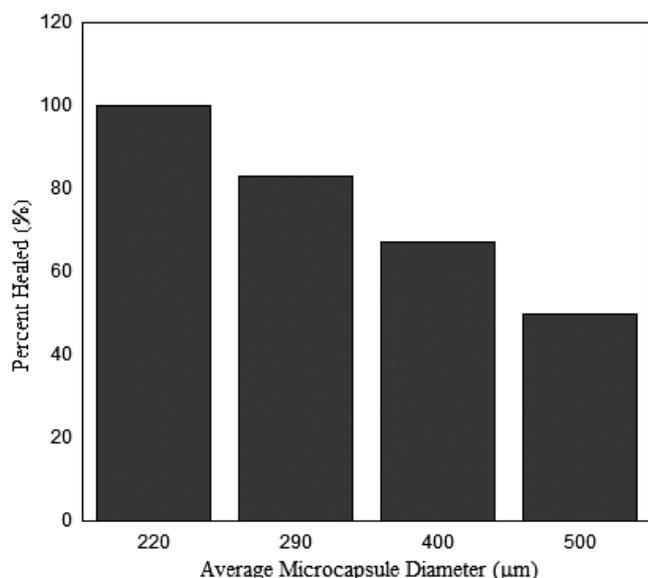
Figure 4. Effect of microcapsule diameter on healing probability for a self-healing matrix thickness of 1.0 mm and puncture diameter of 0.49 mm.
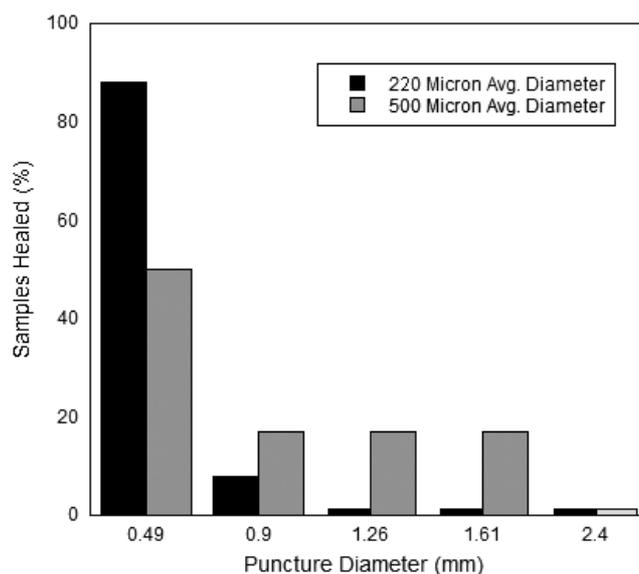
Figure 5. Comparison of healing at varied puncture diameters for two different resin capsules sizes. Self-healing layer thickness is 1.0 mm.

of the damaged membrane that ruptured before reaching the target pressure difference of 103 kPa across the membrane.

3.2. Effect of matrix thickness, puncture diameter, and microcapsule size

In situ laminate samples contained 25 wt% PDMS resin microcapsules and 6 wt% tin catalyst microcapsules in the PDMS matrix. Control samples containing no capsules were tested, and for both puncture (0.49 mm needle diameter) and cut damage no healing was observed. Samples containing only 6 wt% tin catalyst capsules (no resin microcapsules) also showed no healing. However, samples containing 25 wt% PDMS and no catalyst microcapsules demonstrated nearly identical successful healing probabilities when compared with fully *in situ* samples. The observed healing for resin-only samples is likely the result of polymerization of the released resin initiated by residual tin catalyst in the puncture site. Energy dispersive x-ray spectroscopy (EDS) confirmed the presence of tin on the damage surface. While the tin catalyst solution had a comparable viscosity to the encapsulated PDMS, healing was not seen in catalyst-only controls, indicating that the liquid alone does not stop air flow. Moreover, there was evidence of polymerized material in the damaged region for all healed samples and no evidence of residual liquid.

Healing was initially observed for *in situ* samples with a PDMS matrix thickness (solid PDMS layer embedded with two-part PDMS and tin catalyst microcapsule system) of approximately 1.0 mm and PDMS microcapsules with a mean diameter of approximately 500 μm. For a puncture 0.49 mm in diameter, 50% of the specimens healed. Healing of cut damage was less successful, with only 33% of specimens repaired. By decreasing the diameter of the liquid PDMS-filled microcapsules, the healing performance was significantly

improved for small puncture diameters, as shown in figure 4. Six or more samples were tested for each data point in this study. As the microcapsule diameter decreased, the healing performance improved until 100% of the specimens healed at an average microcapsule diameter of 220 μm (tin catalyst microcapsule diameter was kept constant at 180 μm).

In specimens subjected to cut damage, varying microcapsule size did not lead to the same trend in healing performance. Samples with average microcapsule diameters of 220 and 500 μm were subjected to a 7 mm long razor blade cut, and in both cases only 33% healed successfully.

A number of possible factors contribute to the variability in healing response seen in this self-healing system. Because of the random distribution of microcapsules within the matrix it is possible that samples showing no healing simply did not rupture microcapsules. Additionally, the shell material of the resin and catalyst microcapsules is slightly less dense than PDMS; thus, the capsules tended to float toward the top of the laminate, potentially leading to non-uniform healing through the thickness of the sample. Insufficient diffusion of the liquid healing material may have led to incomplete wetting and sealing of the entire damaged area. For cut damage, low healing percentages likely stem from small areas of unhealed material along the relatively large damage plane. These effects leading to no visible healing also account for the variability in bonding strength responsible for occasional partial healing.

In order to observe healing for a range of damage scales, the puncture diameter was varied from 0.49 to 2.4 mm at a constant self-healing matrix thickness of 1.0 mm. An increase in puncture size was marked by a reduction in the probability of successful healing (figure 5). Smaller microcapsules improved healing performance for small (0.49 mm) punctures, but were significantly less effective when healing larger damage. Larger microcapsules did not perform as well as small capsules when healing small punctures, but were capable of healing larger
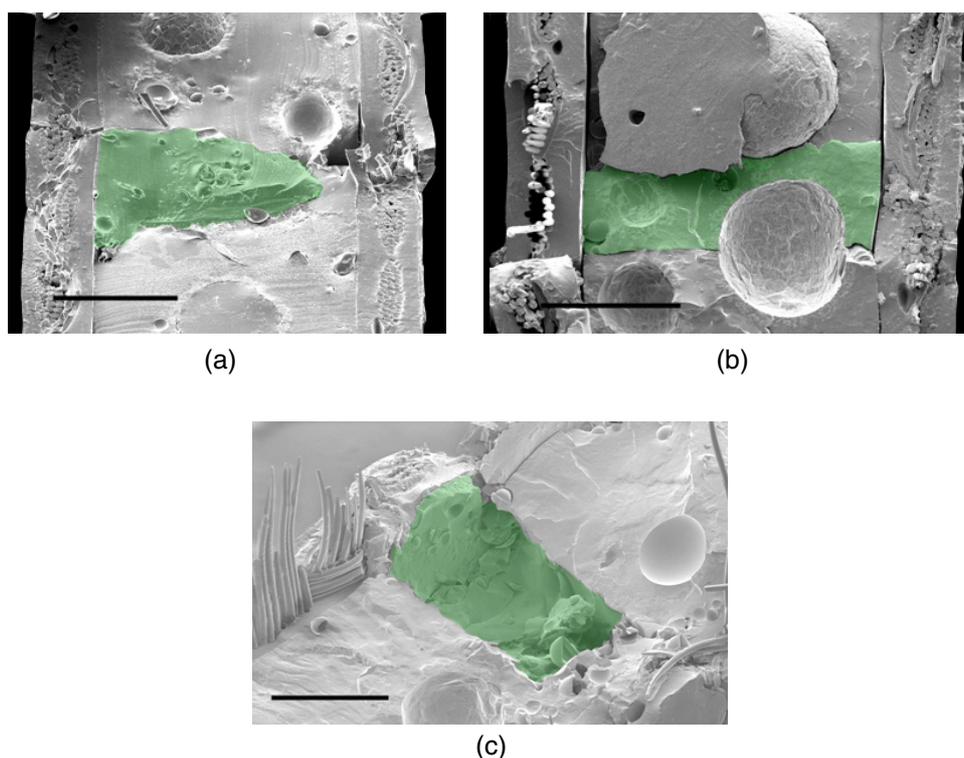
Figure 6. SEM imaging of sample cross-sections representing (a) a fully healed puncture, (b) a non-healed puncture, and (c) a partially healed puncture, all with damage areas highlighted. Scale bars are 500 μm.

punctures, up to 1.63 mm. The healing response for samples containing resin microcapsules 500 μm in diameter in figure 5 included two samples which were partially healed. One specimen healed with a 0.90 mm puncture ruptured at 55 kPa. The sample that healed after sustaining a 1.63 mm puncture ruptured at 101 kPa, sustaining 98% of the design pressure before failure.

For small puncture diameters, the smaller, and thus more numerous and well dispersed microcapsules are more likely to be ruptured by the hypodermic needle. However, for a larger puncture diameter, a larger microcapsule will deliver a greater volume of healing agent per capsule to wet the damage area, accounting for the trends seen in figure 5. A dispersion of large and small microcapsule sizes would likely improve healing efficiency in the current systems since both the volume of healing agent and the probability of capsule rupture would increase.

The thickness of the PDMS matrix layer was reduced to improve the flexibility of the structure. A series of samples with healing layer thicknesses of 0.32, 0.50 and 1.0 mm were tested for healing performance. In all samples, 280 μm resin capsules were used with a puncture diameter of 0.49 mm. Laminates with average PDMS matrix layers of 0.32 and 0.50 mm thick were fully healed in 50% of the samples, while a higher percentage (83%) of samples healed for a self-healing matrix thickness of 1.00 mm.

Tests carried out with a pressure gradient showed no effective healing, indicating that healing material was forced from the puncture before healing. Thus, the present system would be suited to structures which may remain under no

pressure for a period of 24 h before reuse. A faster cure catalyst would initiate more immediate healing, although this would deter full wetting of healing material in the puncture area. A more extensive study is required to determine the effects of the rate of the reaction on pressurized membrane healing.

3.3. Puncture surface imaging

Samples which fully healed, partially healed, and did not heal were inspected using electron, fluorescence and optical microscopy to elucidate the mechanisms underlying each healing response. Scanning electron microscopy (SEM) was utilized to investigate cross-sections at the puncture site. All samples were sectioned by a razor blade and opposing sides of each sample were consistent with one another. The presence of healed material in the puncture area indicated that the sectioning process did not significantly damage the sample surface. A cross-section from a fully healed sample can be seen in figure 6(a). The punctured region is filled and sealed with healing material. Figure 6(b) is a cross-section of a non-healed sample. Interestingly, healing material is present in the damaged area, but sealing was inadequate and allowed gas flow. However, the partially healed puncture specimen seen in (c) shows a hollow depression (a corresponding hollow valley was seen in the opposite cross-section of the partially healed sample) where other samples appear to have filled in valleys. This fracture indicates a 'blow-out' occurred, in which pressure forced a plug of healed material to dislodge and allow gas flow (corresponding to the sharp increase in output pressure seen in figure 3).
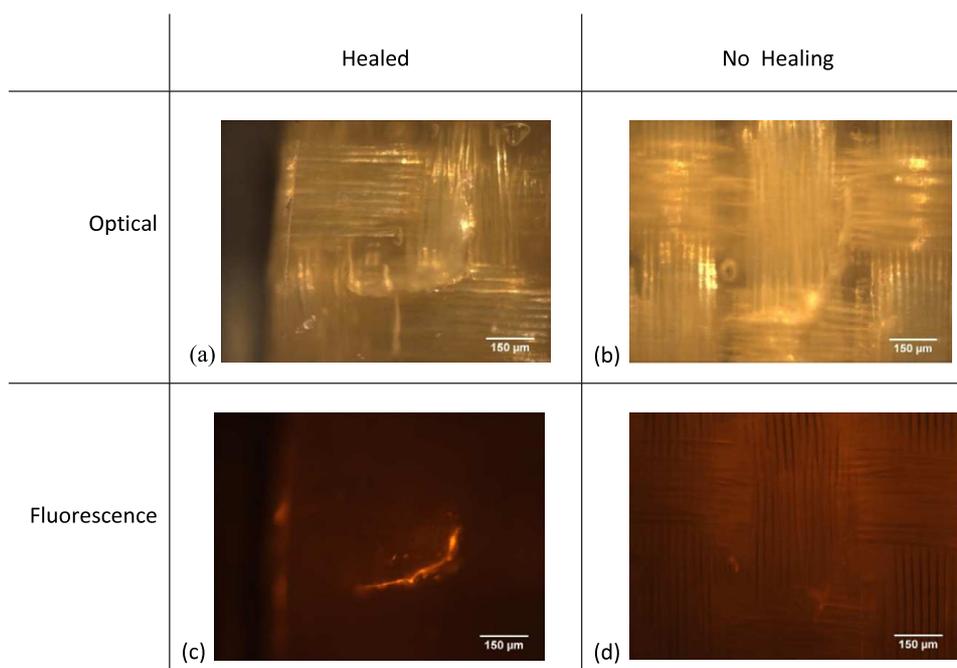
Figure 7. Top view optical imaging of (a) a healed sample and (b) a non-healed sample, with corresponding fluorescent images in (c) and (d), respectively.

A primary concern for self-healing materials is sufficient delivery of healing chemistry components to the damage surface. In this material system, delivery of healing components is determined by two mechanisms: rupture of microcapsules in the damage site and effective wetting of the liquid contents released from microcapsules. The effectiveness of these mechanisms was investigated by suspending fluorescent silica nanoparticles in the encapsulated PDMS resin. Healed and non-healed punctures incorporating these nanoparticles were examined using both optical (figures 7(a) and (b)) and fluorescence microscopy (figures 7(c) and (d)). All samples in figure 7 are fully *in situ*, i.e. 25 wt% resin, 6% catalyst. Puncture was initiated with 0.49 mm diameter hypodermic needles. Fluorescence is clearly evident in the punctured area of figure 7(c), indicating rupture and release of PDMS healing agent into the puncture. Virtually no fluorescence is seen in the damage site in figure 7(d), suggesting microcapsules did not rupture effectively and wet the damaged area.

4. Conclusions

A flexible, laminated bladder material was developed for autonomic healing of puncture damage. This laminate utilized an elastomeric self-healing system consisting of a PDMS matrix and microencapsulated liquid PDMS resin and curing catalyst. Samples which exhibited maximum healing had a PDMS layer thickness of 1.0 mm, PDMS resin microcapsules with an average diameter of 220 μm and a puncture diameter of 0.49 mm. Healing was observed for puncture damage up to 1.63 mm in diameter. In addition to puncture damage, healing was also observed for cut damage. Variability in healing efficiency was the result of several parameters, including

unruptured PDMS microcapsules and incomplete wetting of the puncture surface by the healing liquid.

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