

**Self-Healing Systems**

**Self-Healing Systems Having a Design Stimulated by the Vertebrate Spine\*\***

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This work describes the design of two self-healing systems comprising mm-sized beads connected by elastomeric threads. Axial compressive stress exerted by the thread, and capillary interactions between drops of molten solder patterned on the beads, lead to their self-assembly into linear rods; cooling the solder makes the rods rigid. We demonstrate

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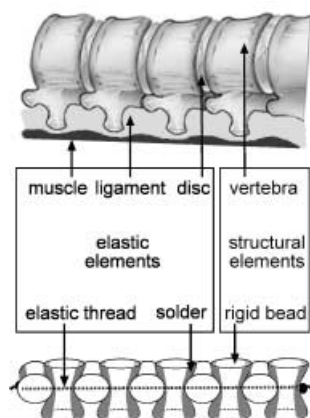
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the spontaneous realignment of the structures after breaking and dislocation.

We and others have used biomimetic approaches to design molecular and macroscale systems imitating the internal structure<sup>[1,2]</sup> and the principles of organization<sup>[3–7]</sup> of biological systems, or biological processes.<sup>[8–12]</sup> One distinguishing characteristic of living systems is their ability to heal themselves. Self-healing in living systems, however, involves complex cascades of out-of-equilibrium processes, and is therefore still difficult to reproduce in man-made systems.<sup>[13,14]</sup>

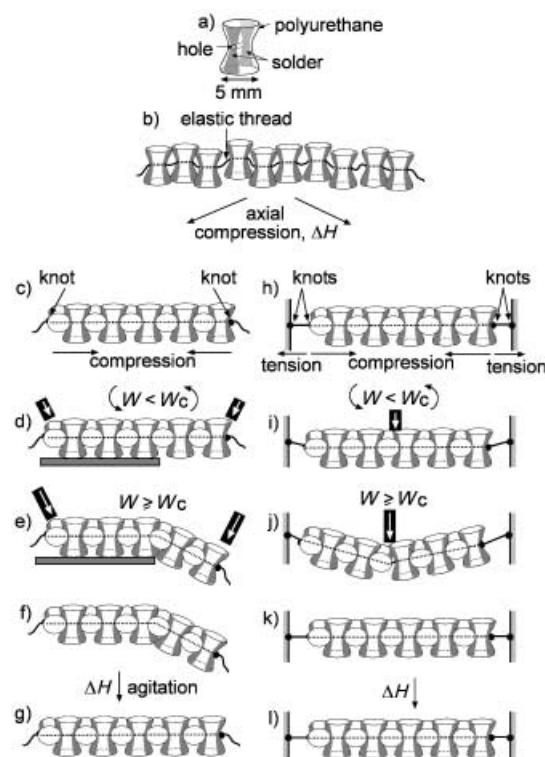
The design of self-healing structures is of considerable interest in engineering and microtechnology. One approach consists in developing so-called “smart” or self-healing materials, such as polymers,<sup>[15,16]</sup> ceramics,<sup>[17]</sup> and glasses.<sup>[18,19]</sup> Another approach can be based on self-assembly: after disruption, self-assembled systems return to their ordered state, provided that that state is a thermodynamic minimum.<sup>[20]</sup> Herein, we propose a strategy for designing self-healing, self-aligning structures, based on self-assembly of mm-sized components. The design of one system is inspired by (and loosely modeled on) the vertebrate spine; the design of the second one is modeled on the traction splints used for therapy of spinal fractures.

The spine consists of rigid, structural elements—vertebrae—separated by elastomeric discs and connected to one another by ligaments and muscles (Figure 1, top). The spine, like many other biological structures, serves several functions simultaneously: it provides both strength and flexibility to the body, dampens shock, and protects the spinal cord.<sup>[21]</sup>



**Figure 1.** Common features of the design of a vertebrate spine (top) and the self-assembling systems of mm-sized components (bottom). Both systems consist of rigid structural elements connected by elastomeric elements.

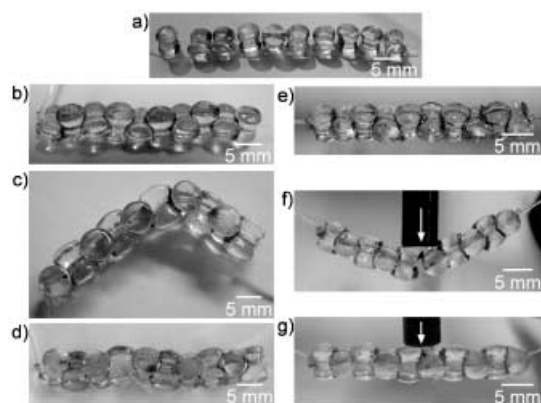
The structures we used share with the spine the design of a set of rigid structural units connected by elastomeric element(s) (Figure 1, bottom). In both systems, the structural components, which mimic the function (if not the structure) of vertebrae, were hourglass-shaped polyurethane beads that have a hole through the waist. The beads were patterned with rectangular patches of copper covered with solder (Figure 2a). We strung the beads together onto an elastic thread



**Figure 2.** Design of self-aligning systems mimicking the spine of vertebrates. a) One structural element (bead). b) A string of ten beads on an elastic thread. Two types of structures were generated from this string: c)–g) a rigid rod in which only compressive forces acted on the beads; h)–l) a rigid rod in which compressive and tensile forces acted on the beads. The direction of the forces acting in each of these systems is shown schematically as arrows. These structures could support weight  $W$  (schematically shown as white arrows) applied to both ends (d) or to a point in the middle (i), but broke into two parts (e, j) when the applied weight exceeded the critical weight of  $W_c \approx 250$  g. f, k) After removing the weight, the structure shown in e) remained dislocated, while the structure shown in j) spontaneously realigned. g, l) Both structures recovered their structure and mechanical strength after removing the weight, heating under water to a temperature above the melting point of the solder, and cooling to room temperature.

(Figure 2b, Figure 3a), and secured the ends of the thread by tying large knots; the thread mimicked the function of muscles and ligaments of the spine. In both designs, the elastic thread put the systems in compression, and the beads self-aligned with the long axes of adjacent beads perpendicular. In the first system (Figure 2c–2g), we cut the length of thread close to the knots; in this system, as in the human spine, compressive forces were the only type of force acting on the beads in the string (Figure 2c). In a second system (Figure 2h–2l), we cut the length of thread to extend approximately 1 cm beyond the knots, and tied the ends around a holder; we selected the width of this holder such that the length of the string between the beads and the holder was kept under tension. In this system, two types of forces were acting on the beads: compressive and counteracting tensile forces (Figure 2h). The regions of the thread that exerted tensile forces on the beads mimic the action of traction splints used to stabilize fractures and dislocations by counteracting the compression.

When heated to a temperature above the melting point of the solder, the droplets of solder on neighboring beads fused, and connected the beads into a compact linear rod (Figure 3b, 3e); the drops of metal thus mimic one function of the discs connecting the bone vertebrae in the spine. After cooling, the solidified solder rendered the structures sufficiently strong mechanically to support weight of up to approximately 250 g.<sup>[22]</sup> The weight was applied manually to the end of the rod, or to an arbitrary point in the middle, by using the piston of a syringe (Figure 2d, 2i).



**Figure 3.** Properties of the self-aligning systems that mimic a vertebrate spine. a) A loose string of ten beads on an elastic thread. b), e) Rigid linear structures generated from the string shown in a). c), f) The same structures when a weight of 250 g was applied to both ends (c), or at a point in the middle of the string of beads (f). d), g) The structures after removing the weight and heating under water to 55°C. A weight of 100 g was applied to the middle portion of the structure shown in g). The arrows in f), and g) indicate the direction of the applied weight.

Upon exceeding this load, the structures broke into two parts, still connected by the thread (Figure 2e, 2j; Figure 3c, 3f). The fracture occurred either in the middle of a solder drop, or at the interface between solder and copper. When the applied weight was removed, the structure of the string of beads differed in the two systems. In the system in which only compressive forces were acting, the two parts remained dislocated (Figure 2f); in the system in which both compressive and tensile forces were acting, the structure spontaneously realigned to its initial, linear configuration because of the tension applied by the taut thread (Figure 2k). The strings of beads were transferred to water heated to 55°C. The droplets of molten metal at the point of fracture melted and fused, or molten solder rewetted the copper. Manual agitation of the vessel containing the dislocated structure for about 2 min led to spontaneous realignment of the two parts (Figure 2g). The resulting structures, when cooled to room temperature, were indistinguishable from the structures before the fracture (Figure 2g, 2l, Figure 3d, 3g). They could again support weight applied to the point that had been fractured and healed. We repeated the breaking–heating–cooling cycles three times, and observed indistinguishable behavior in each case.

We have designed two self-healing structures that are loosely analogous to a vertebrate spine and a spine under splint traction, using a system of millimeter-sized, solid beads that self-align under axial compressive or tensile stress. The combination of the shapes of the units and the forces exerted by the elastomeric connectors tends to return the system to a linear configuration; analogous forces act on the spine. The compressive element in the system—the elastic thread—plays a role both in maintaining the relative positions of the beads after breaking, and in keeping the system under compression.

Our self-healing systems differ from their biological counterpart in most details: the structures are not flexible; the entire array of complex biological processes involved in tissue repair is replaced by the coalescence and solidification of drops of solder; the self-healing of the systems is initiated externally, by increasing the temperature of the surrounding aqueous solution.

The effectiveness of the two systems differed considerably. The system in which only compressive forces acted on the beads required external agitation to realign, while realignment of the dislocated parts occurred spontaneously in the system in which both compressive and tensile forces acted on the beads. While the first system is structurally a more accurate mimic of the vertebrate spine, the second one is functionally more efficient.

Synthetic self-healing composites open one promising route to the fabrication of structures that can heal without external mediation.<sup>[15]</sup> Our results suggest an alternative approach to the design of self-healing structures: instead of fabricating a monolithic structure made entirely of a *self-healing material*, it is possible to design a *composite, self-healing structure* comprising rigid and elastic elements, and self-healing joints. This design offers several advantages: 1) the rigid elements can be made of any material, that is, the choice is not limited only to self-healing composites; 2) the structure aligns spontaneously to its initial configuration; 3) the structure can be fractured and healed multiple times at the same joint; in contrast, self-healing in composite materials depends on the availability of healing agent at the point of fracture, and can therefore occur only once at a given point.

This work demonstrates that by using biomimetic (and medical-mimetic) design in a self-assembling system, one can build structures that are mechanically strong, self-aligning, and self-repairing. Such structures can find application as weight-bearing elements in devices where external repair is not possible because of inaccessibility, or is difficult because of the small size of the structures.

## Experimental Section

The beads were prepared by replica molding in UV-curable mercapto-ester (NOA-81, Norland Optical Products) by using poly-(dimethylsiloxane) (PDMS) molds (Sylgard 184, Dow Corning) and porcelain masters (Beadworks, Cambridge, MA). We placed the beads in PDMS molds that covered their entire surface, except for two rectangular patches around the holes. A 10 nm thick adhesive layer of titanium and a 400 nm thick layer of copper were evaporated thermally onto the exposed rectangular surfaces of the beads. After removing the molds, we dipped the beads into molten solder ( $T_m = 47^\circ\text{C}$ , Small Parts, Inc., <http://www.smallparts.com>); the solder was

kept under water brought to pH 1 with HCl to dissolve oxides formed on its surface. The solder wetted only the patterns of copper. We strung the beads together manually onto stretched elastic threads (Stretch Magic, Pepperell Braiding Company), and secured the threads by tying large knots next to the beads at the end of the sequence. In one string, we cut the thread close to the knots. We mounted the other string of beads on a holder by tying the ends of the string on the holder; we selected the width of this holder such that the portions of the string extending between the sequence of beads and the holder were kept under tension. The strings of beads were then immersed in hot water ( $T=55^{\circ}\text{C}$ ) for 2 min. The drops of solder melted; to minimize the high interfacial energy of the molten metal/water interface<sup>[23]</sup> ( $\approx 400\text{ ergs cm}^{-2}$ ), droplets of molten metal patterned on neighboring beads fused. On cooling the strings of beads, a compact, rigid structure was generated.

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