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Healing-on-demand composites based on polymer artificial muscle

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In this study, a new polymer artificial muscle based healing-on-demand composite was prepared and characterized. The composite consists of polymer artificial muscle made of commercial fishing line, thermoset host, and thermoplastic particle. Three-point bending damage to the beam sample can be healed even at a constrained boundary condition upon local heating, undergoing a close-then-heal procedure. The fractured beams were heated locally by a heat gun for 10 min. The healing efficiency was investigated at both free boundary condition and fixed boundary condition. The fast contraction of artificial muscle brings the fractured surfaces in spatial proximity; simultaneously, the melting thermoplastic agent fills the crack via capillary action and bonds the two fracture surfaces. With 60% pre-strain of the reinforcing polymer artificial muscles (8% volume fraction), over 60% of healing efficiency was achieved at free boundary condition and 54% at fixed boundary condition after repeated damage-healing events. Due to its low cost, high healing efficiency, good compatibility, and excellent flexibility, we envision that the polymer artificial muscle will be a new device in designing next generation healing-on-demand polymer composite.

1. Introduction

Engineering polymers are designed for a specific service life. With incidental damage or degradation over time, the lifespan tends to be shortened. Inspired by biological systems on prolonging service life, the development of polymeric materials that can heal by themselves has existed for decades [1–4]. Healing-on-demand polymers include ionomer [5], organometallic/metallo-supramolecular polymer [6,7], mendomer [8–12], rubber [13–15], polymer gel [16–19], organogel [20,21], metallo-gel [22], hydrogel [23–29], etc. The approaches for triggering healing-on-demand include extrinsic stimuli such as mechanical damage, chemical stimuli, thermal treatment, pH, water, photo, sonication, and electrical treatment, as well as intrinsic stimuli like labile bonds, fusion, reversible dissociation-association, covalent bonds, host–guest interaction, and metallo/ligand complexation. In some cases, both extrinsic and intrinsic stimuli are involved.

Healing-on-demand polymer composites can also be achieved by adding external healing agent. These extrinsic self-healing systems are capsule based [30], hollow fiber based [31], vascular based [32], shape memory based [33], and others. For the capsule based, healing agents are encapsulated into capsules and are released to cracks upon mechanical damage. While in the case of hollow fiber based, healing agents are stored in hollow fibers like hollow glass fibers or hollow polymer fibers and are released to cracks after damage. Likewise, in the case of vascular based, healing agents are stored in vascules and are released to crack sites after crack is created. In the case of shape memory based, polymer composites are programmed to have shape memory ability before use and cracks are closed by constrained shape recovery upon thermal treatment. Unlike these four extrinsic methods, the fifth includes those which have not been studied systematically by scientists and engineers for healing-on-demand polymer composites. One common theme to these schemes is that, once the damage is created, the healing-on-demand behavior through embedded healing agents is activated by external stimulus, such as photo, pH, water, thermal treatment, etc.

A common challenge facing all self-healing schemes is how to heal cracks with a wide-opening. As proposed by Li and John [34], Li and Nettles [33], and Li and Uppu [35], macrocracks due to external loading can be healed by a close-then-heal (CTH) method, inspired by surgical aspect on skin cut. The crack was first closed due to the on-demand shape memory behavior of the matrix under thermal

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activation. Then, at the healing temperature, the dispersed thermoplastic healing agents were melted and filled in the narrowed crack, establishing physical entanglements among molecules by diffusion and randomization. The crack was healed after the composite was cooled down to room temperature. While healing of cracks in shape memory polymer (SMP) matrix has been successful, the challenge is how to heal cracks in conventional thermosetting polymers which do not have sufficient shape memory capability or do not have any shape memory capability. One way is to add shape memory fibers to the matrix, similar to embedded sutures when doctor stitches wound in human skin [36–40]. However, one challenge is the low recovery force of SMP fibers, which limits the ability to heal wider cracks, particularly when the structural components are constrained in the boundary (free shape recovery is not allowed). Parallel to this SMP fiber approach, Kirkby et al. have investigated the influence of shape memory alloy (SMA) wires on the self-healing properties by combining SMA wires with polymer matrix [41,42]. The challenge for SMA wire is the poor interfacial bonding between the metal wire and the host polymer as well as the comparatively low recovery strain of SMA wire, which limits its capability in crack close. Also, SMA wires face other challenges such as higher cost and poor processability.

In all animals and humans, muscle is a soft tissue that consists of a part of the musculoskeletal system; and it is the only component of the system that enables our body to move through contracting and even fast contracting at higher speed upon stimuli. Analogous to natural muscle, polymer artificial muscle from fishing line could contract fast and deliver large strokes from inexpensive high-strength polymers fibers, such as commercial fishing lines [43,44]. As compared with other polymer artificial muscle [45,46], fishing lines are low cost and easily available. Also, actuation of muscles made of fishing lines is quite repeatable. If fishing line muscle is embedded in a composite, just as natural muscle in animal or human body, it will be able to close cracks in the polymer matrix, similar to the SMP fiber or SMA wire, because shrinkage is the fundamental requirement for embedded fibers to close wide-opened cracks. When thermoplastic healing agent is incorporated in the polymer matrix, the system could heal any damage or degradation on-demand at molecular length scale. In this study, we propose a new strategy by using artificial muscle in polymer composites for healing-on-demand applications, as schematically shown in Fig. 1. Fig. 1a shows an illustration of natural muscle contraction. Physically, the contraction of muscle generates tension on both connections (i.e., tendon). As illustrated in Fig. 1b, a healing-on-demand polymer composite, schematically, has the abilities to close or narrow macro crack and to heal it on-demand.

Here, we would like to elucidate the meaning of “self-healing”. Based on Wool and O'Connor [47], crack healing experiences five stages, including (a) surface rearrangement; (b) surface approach; (c) wetting; (d) diffusion; and (e) randomization. Generally speaking, researchers are mainly concerned with surface rearrangement, wetting, diffusion, and randomization, i.e., reestablishment of chemical bonds or physical entanglements. Therefore, in the lab-scale experiment, the fractured specimens are usually manually brought into contact before healing starts. As indicated by Wool [48], and echoed by Binder [49] and Li [50], this simple operation represents the largest challenge in the real world applications. Obviously, we cannot bring a fractured structural panel together by hand in a Boeing aircraft; without creating new damage, we may not be able to manually bring a fractured specimen together if the boundary of the specimen is fixed. Therefore, external help is more or less required. It is noted that, for micro or sub-micro cracks, extrinsic healing by liquid healing agent is “autonomous healing” or true “self-healing” [30]. However, the healing efficiency is usually low and the healing time is usually very long. With some external help such as heating, the healing efficiency can be significantly increased and the healing time can be considerably shortened [51]. If the crack is wide-opened, some external help is needed to narrow the crack. Otherwise, there may not have sufficient healing agent to fill in the large crack volume, i.e., “self-healing” or “autonomous healing” will not occur. Although new efforts have been made to self-heal large crack volume, the vascular network may be damaged [52]. Therefore, it remains a challenge to self-heal or autonomously heal wide-opened cracks or cracks with large volume. This is also why we believe that CTH may be a way deserving exploration. To avoid confusion, we call the polymeric muscle based healing as healing-on-demand, instead of self-healing.

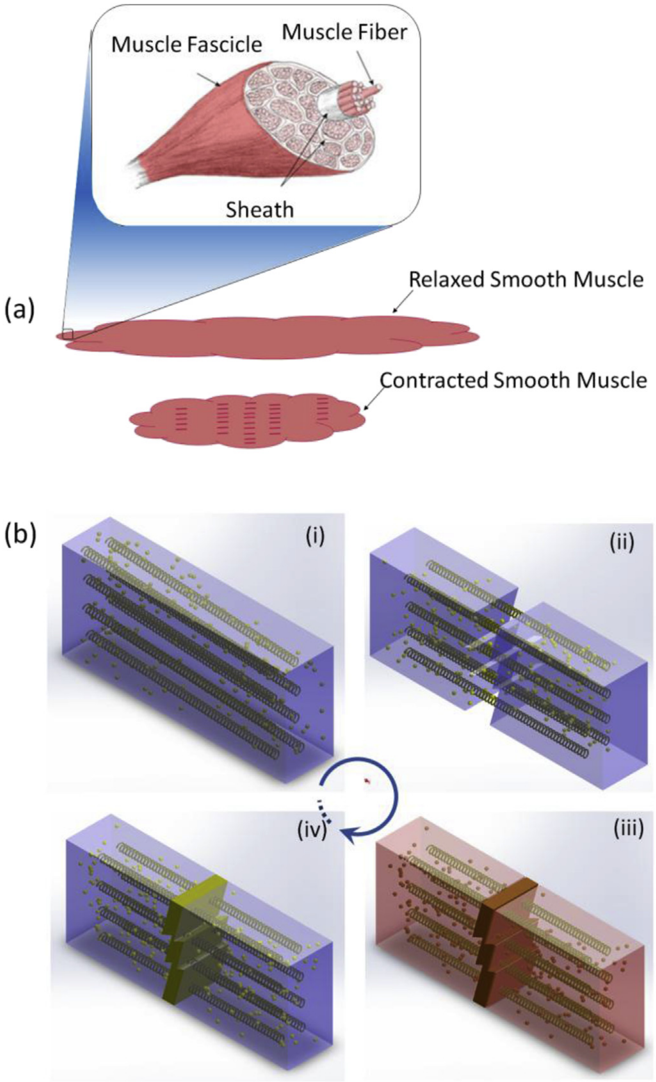

Fig. 1. (a) Structure of nature muscle. (b) Schematic of on-demand healing process: (i) a polymer composite sample reinforced by polymer artificial muscle (light golden coiled fiber) and thermoplastic particle (light golden spheres) in a matrix (blue); (ii) crack initiated by external load during service life; (iii) crack closed by thermally activated artificial muscle and healed by the healing agent; (iv) solid wedge formed after cooled down, establishing continuity between the healing agent and the matrix. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The objective of this study is to investigate (1) polymer artificial muscles from commercial fishing line; (2) the ability of polymer artificial muscles to repeatedly close wide-opened cracks at a constrained boundary condition; (3) the effect of spring index on