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Research Paper

Water-assisted self-healing and property recovery in a natural dermal armor of pangolin scales

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ABSTRACT

Self-healing capacity, of which the inspiration comes from biological systems, is significant for restoring the mechanical properties of materials by autonomically repairing damages. Clarifying the naturally occurring self-healing behaviors and mechanisms may provide valuable inspiration for designing synthetic self-healing materials. In this study, water-assisted self-healing behavior was revealed in a natural dermal armor of pangolin scales. The indentation damages which imitate the injury caused by predatory attack can be continuously mitigated through hydration. The healing kinetics was characterized according to the variations of indentation crater dimension and quantitatively described in terms of the viscoelastic behavior of biopolymer. The mechanical properties of original, damaged, and recovered scales in both dry and wet states were systematically evaluated by three-point bending and compared through statistical analysis. The hydration effects and mechanisms were explored by examining the dynamic mechanical properties and thermal behaviors. The promoted self-healing process can be attributed to the improved flexibility of macromolecules in the biopolymer. This study may stimulate useful self-healing strategies in bio-inspired design and aid in developing high-performance synthetic self-healing materials.

1. Introduction

Living organisms have long been adept in synthesizing high-performance structural materials at mild conditions by using fairly simple building elements. The resulting materials generally display remarkable mechanical properties conferred by their intricate hierarchical structure with the combinations of strength and toughness far surpassing those of their components (Fratzl and Weinkamer, 2007; Ritchie, 2011; Weiner et al., 2000). Moreover, these materials always assist the organisms in accomplishing a variety of functions and making adaptations in response to environmental stimuli (Chen et al., 2012; Dawson et al., 1997; Fratzl and Barth, 2009). Such notable attributes have stimulated an extensive research on natural biological materials in pursuing useful inspiration for the development of high-performance synthetic materials. So far, a series of novel properties have been incorporated into synthetic materials by mimicking the strategies designed by

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nature (Chen et al., 2012; Liu and Jiang, 2011; Ma et al., 2013; White et al., 2001). Among them, the self-healing capability, of which the inspiration comes from the autonomic healing behavior of biological systems after being wounded, has attracted an increasing attention in recent years (Blaiszik et al., 2010; Toohey et al., 2007; Trask et al., 2007; van der Zwaag et al., 2009; White et al., 2001; Wool, 2008). In traditional engineering materials, the introduction of cracks or other types of damages generally results in the degradation of mechanical and functional properties and even leads to the failure of materials. In comparison, by repairing the damages without complex manual intervention, the self-healing capacity could contribute to higher reliability and longer lifetime of materials, thus bringing considerable benefits to their applications.

Although the concept is relatively new in engineering design, the self-healing capacity has been developed by nature in many biological materials over long periods of evolution. A prime example is the wound healing process in animals via the bleeding mechanism (Evens et al., 2013; Singer and Clark, 1999). Such function relies essentially on a healing network of blood vessels which delivers fluid to damaged tissues. Similar strategy has been introduced into self-healing polymer composites by embedding hollow fibers or capsules containing healing agents within matrices (Blaiszik et al., 2010; Toohey et al., 2007; Trask et al., 2007; van der Zwaag et al., 2009; White et al., 2001; Wool, 2008). The agents are released to the matrices containing catalysts upon crack intrusion and then polymerized to bond the crack faces. Despite an ingenious mimicry of the natural theme, such approach may encounter a series of problems concerning the stability of catalysts, the flowability of healing agents, the sensitivity of containers to damage, the ability to heal repeatedly, etc. Besides the above manner that has been mostly mimicked, there exist multiple other self-healing strategies in natural biological materials to restore their properties degraded by damages. For instance, the loss of mechanical properties caused by mechanical and chemical perturbations can be reversed in mussel byssal threads upon exposure to seawater by reforming intermolecular interactions (Holten-Andersen et al., 2011; Vaccaro and Waite, 2001). The biological materials can be regarded as natural paradigms for developing high-performance synthetic self-healing materials in respect of bio-inspired design. Definitely, it is essential to clarify the naturally occurring self-healing behaviors and corresponding mechanisms to gain possible inspiration.

As a natural flexible dermal armor, the scales of pangolins can provide the body with effective protection against predatory threats (Yang et al., 2013). Meanwhile, the scales possess outstanding properties of wear-resistance and anti-adhesion against soil and rocks which are critical for a series of living activities such as burrowing (Tong et al., 1995, 2000). In view of the pangolin's habitats, penetration and bending are two of the most common loading states sustained by the scales. The structure and mechanical properties of pangolin scales have been systematically investigated in our recent study (Liu et al., unpublished results). It has been revealed that the scales are composed of both α- and β-type keratins and contain no blood vessels within them (Liu et al., unpublished results; Spearman, 1967; Tong et al., 1995; Wang et al., 2016). Also, the scales cannot be molted during the lifetime of pangolins. As a result, it is reasonable to suppose that other self-healing strategies, rather than the bleeding one, may be activated in the scales once damaged so as to retain their mechanical functions. Here we reveal that the penetration-induced damages can be readily healed through hydration in pangolin scales, and as such, the bending mechanical properties, including the strength and reliability, can be recovered to a large extent. The healing kinetics is quantitatively analyzed in terms of the viscoelastic behavior of biopolymers. The mechanisms are explored by examining the thermal and dynamic mechanical properties.

2. Materials and methods

Pangolin scales in size of ~5 cm and thickness of ~2 mm were provided by the Pangolin Captivity Breeding Research Center, Guangzhou, China. The scales were collected from the back of a naturally dead adult pangolin (*Manis pentadactyla*) and dried in air for at least one month before testing. To quantify the moisture level, the scales were adequately dried at 80 °C for 50 h and then weighed. The moisture contents of the air-dried scales and those adequately hydrated by immersing in water for two days were determined to be ~6.3% and ~18.8% by weight, respectively. To imitate the actual damage caused by predatory penetration, indentation tests were performed on the exterior surfaces of both dry and wet scales along the thickness direction with a pyramidical indenter using a VH-5ACL hardness tester. The surfaces were carefully grinded and polished before testing. The indentation load and dwelling time were chosen as 10 kg and 60 s, respectively. To characterize the variation in sub-surface damage, an air-dried scale was firstly sectioned along its growth direction using a low speed diamond saw. The opposite faces of the two halves were then bonded together using a clip after being grinded and polished. The indenter was loaded on the top of bonding interface, and subsequently, the clip was removed to expose the internal morphology. The scales were then immersed in water after indentation. The damaged zones at the as-indented state and immersed for varying time were characterized for both originally dry and wet samples using an Olympus LEXT OLS 4000 3D-measuring microscope. The fine morphologies were also analyzed by scanning electron microscopy (SEM) at an accelerating voltage of 10 kV on an LEO Supra 35 instrument after drying and sputter-coating samples with gold film.

Rectangular samples in dimensions of $\sim 12 \times 1.6 \times 0.6\ \text{mm}^3$ were prepared using the low speed diamond saw with the sample length along the growth direction of scales. The surfaces were then carefully grinded. Penetration damages were introduced into some of the samples in both dry and wet states by indentation at the center of exterior surface using 10 kg load for 60 s with the diagonal of indenter perpendicular to lateral sides. About half of damaged specimens, also in both dry and wet states, were then immersed in water for 30 h; and subsequently, the originally dry samples were air-dried for at least two days. In this manner, all samples in both dry and wet states have been randomly categorized into three groups of original, damaged and