Biomaterials 65 (2015) 13–21

Contents lists available at ScienceDirect

Biomaterials

journal homepage: www.elsevier.com/locate/biomaterials

Remarkable shape memory effect of a natural biopolymer in aqueous environment

Z.Q. Liu*, D. Jiao, Z.F. Zhang**

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:
Received 11 February 2015
Received in revised form
16 June 2015
Accepted 18 June 2015
Available online 20 June 2015

Keywords:
Shape memory
Viscoelasticity
Mechanical properties
Keratin
Biomimetic material

ABSTRACT

Remarkable water-stimulated shape memory effect was revealed in a natural biopolymer of peacock's tail covert feathers of which the innate shape can almost be fully recovered after severe deformation by a short hydration step. The shape memory effect manifests a good stability of high recovery rate and ratio during cycles of deformation and subsequent recovery. Both strength and energy absorption efficiency of medullary foam can be recovered despite the apparent decrease in the first deformation stroke caused by structural damage. A kinetic model developed from non-equilibrium thermodynamic fluctuation theory was adopted to describe the shape recovery process by considering the viscoelastic relaxation. The effects of hydration on mechanical properties, recovery kinetics, activation process and dynamic mechanical behaviors were also evaluated. Mechanisms were explored based on the lubrication, swelling effect and structural changes of macromolecular chains or segments in terms of their mobility. This study is expected to aid in understanding the responses of natural biological materials to environmental stimuli and to provide useful information for synthetic shape memory materials from the bio-inspiration perspective.

1. Introduction

The shape memory effect (SME) represents the attribute of materials to recover their original or permanent shape after deformation upon exposure to appropriate external stimuli [1]. Shape memory materials, having the ability of performing SME, belong to the class of smart materials and are encountering numerous applications, such as actuators, biomedical devices and self-healing components. Among them, shape memory alloys normally derive their SME from reversible transitions between martensite and austenite metallic phases [1]. In comparison, the SME in emerging shape memory polymers (SMPs) is closely associated with the changes in macromolecular structure, e.g., glass transition, crystallization, and melting [2–5]. This generally endows SMPs with a broad range of application temperatures that can be conveniently tailored. In addition, SMPs possess many other advantages compared with shape memory alloys, such as high recoverable strain, low density and cost, as well as superior processability, and accordingly have attracted considerable interest [2–8]. A number of SMPs have been synthesized in response to varying environmental stimuli, e.g., temperature, light, moisture, and magnetic field [2–6,9]. Much attention has been paid to their mechanical properties and stabilities which are of key importance for applications [4,7,10]. The biocompatibility, biofunctionality and biodegradability have also been concerned more in recent years, in particular from the biomedical and environmental friendly viewpoints [2–6,11]. Moreover, it is critical to quantitatively describe the SME and correlate it to the intrinsic structure and properties of materials. In this respect, a number of analytical models have been developed from different aspects [2,12–14].

Living organisms have long developed the ability to synthesize materials with notable properties through biologically-controlled self-assembly under ecological conditions [15,16]. In analogous manner to synthetic shape memory materials, many natural biological materials, in particular biopolymers, are also capable of undergoing intelligent adaptations and responses to environmental stimuli [17–20]. In turn, the responses of these materials provide organisms with multi-functions, such as mechanical protection and support, camouflage, metabolism, as well as mechanosensing and actuation. For instance, the collagen fibrils within Bouligand-type structured scales of *Arapaima gigas* can continuously self-reorient upon loading [17]. This helps to enhance the scale's ductility and

* Corresponding author.
** Corresponding author.
E-mail addresses: liuzq@imr.ac.cn (Z.Q. Liu), zhfzhang@imr.ac.cn (Z.F. Zhang).

http://dx.doi.org/10.1016/j.biomaterials.2015.06.032
0142-9612/

toughness to prevent fracture, thereby allowing the fish sufficient resistance to predation by piranhas inhabiting the same water body.

Through long-period evolution and selection, nature has become a great source of useful inspiration for the development of high-performance synthetic materials [15,16,21–25]. This can be exemplified by the design of various architectures to achieve superhydrophobic function by mimicking a series of organisms, such as lotus leaf, butterfly wing, and water strider leg [23]. Outstanding mechanical properties have also been obtained in several inorganic-organic composites that attempt to reproduce the brick-and-mortar structure of nacre [24,25]. Invariably, the bio-inspired design relies essentially on a deep understanding on the structure and properties of natural biological materials as well as their interactions with environment. Therefore, it is significant to clarify these issues for improving the properties of synthetic materials, including SMPs, from the bio-inspiration perspective.

In this study, water-stimulated remarkable SME was revealed in a natural biopolymer of bird feathers with associated mechanical properties evaluated. The shape recovery kinetics was quantitatively analyzed and correlated to intrinsic material structure and properties. The hydration effects and mechanisms were explored and discussed. This study is expected to provide useful inspiration for developing high-performance synthetic SMPs and aid in understanding the basic natural theorem about the significance of water in biological materials.

2. Materials and methods

Bird feathers, which are among the most complex integumentary appendages found in vertebrates, are a unique biopolymer composed of β-keratin [26]. The peacock's tail coverts were used here because they are favorably thick and long. Naturally shed tail covert feathers of adult peacocks (*Pavo cristatus*) in length of ~1.05 m were provided by a local farm. The mean moisture content of air-dried feathers was measured to be ~7.9 wt.%. Structures of feather shaft and its components of cortex and medullary foam were characterized by field emission scanning electron microscopy (SEM) at an accelerating voltage of 10 kV using an LEO Supra 35 instrument. The samples were sputter-coated with gold film before observation. Cortex and foam specimens were excised from the calamus and rachis of feather shaft, respectively, using a low speed diamond saw. Their accurate dimensions were determined by optical observation using a Keyence VHX-1000 digital microscope.

Uniaxial compression tests were performed on both dry and wet foams at a constant strain rate of 1×10^{-3} s^{-1} at room temperature and relative humidity of ~30% using a Shimadzu MMT 101N micromechanical tester with an accuracy of 0.005 N. The specimens were rectangular in shape with dimensions of ~$2.3 \times 2.3 \times 5.1$ mm^3. After compression to over 90% strain, the samples were unloaded at a strain rate of 10^{-1} s^{-1}. The shape recovery processes upon unloading were recorded using a Keyence VW9000 high speed microscope. Before subsequent compression testing, the samples were hydrated by water to recover their original shape. For the dry samples, the recovered specimens were then re-dried at constant temperature of 40 °C in an oven for about 1 h. Each test was repeated for at least three times to ensure a good reproducibility. Morphologies of deformed samples after recovery were examined by SEM.

Variations in dynamic mechanical properties and size of feather rachis as a function of time during the drying process were monitored by dynamic mechanical analysis (DMA) in flowing argon gas at room temperature of 293 K using a Netzsch DMA 242E apparatus. This was performed under compression mode by applying a sinusoidal cyclic stress ranging from 0.18 MPa to 0.76 MPa at a frequency of 1 Hz. The sample, which has a near cylindrical shape with height of 5.75 mm and cross-sectional area of 13.72 mm^2, was cut from feather rachis using the low speed diamond saw. To examine the corresponding stress-strain responses, cyclic compression tests were performed on similar sized rachis at both dry and wet states with the same experimental parameters as those of DMA using the Shimadzu MMT 101N micromechanical tester. Phase constituents of both dry and wet cortices were examined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation on a D/MAX-2500PC diffractometer. Thermal behaviors were characterized by differential scanning calorimetry (DSC) at a heating rate of 5 K/min in flowing argon gas using a Perkin–Elmer DSC7 calorimeter. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy was conducted using a Nicolet 560 spectrophotometer.

3. Results

3.1. Water-stimulated shape memory effect

Fig. 1(a) shows the appearances of part of one tail covert feather in its original state, after severe manual deformation, and after recovery by immersing in water for 1 min and subsequent drying. The imposed deformation was maintained to a large extent in the air-dried feather. In contrast, the feather, along with its shaft and vane, almost fully recovered its original shape, i.e. the innate shape constructed by living organism, in a short time upon contacting water. The vane and its barbs even appeared naturally smoother through recovery. Moreover, the water-stimulated shape recovery was also verified in the components of feather rachis. As illustrated in Fig. 1(b), the rachis is featured as a near cylinder composed of cortex shell filled with medullary foam. The detailed structure and mechanical properties of feather rachis and its components have been systematically presented in our recent work [27]. The cortex is constituted by well-aligned β-keratin fibers which are organized in a series of periodically arranged lamellae (Fig. 1(d)). In comparison, the foam is constructed by almost equiaxed closed cells with an average size of ~35 μm and sealed by thin membranes (Fig. 1(c)). A continuous skeleton exists within the foam formed by interconnected struts in thickness of less than ~5 μm. The porosity was estimated to be ~95% by comparing the densities of foam and dense cortex. Analogously, rapid full recovery to original shape can also be stimulated by water in both foam and cortex, as shown in Fig. 1(e) and (f). This still holds even when the samples have been severely damaged. As displayed in Fig. 2, open cracks can be fully closed through water-assisted shape recovery as long as a critical integrity is still maintained. Such process is necessary for the self-healing of biological materials by metabolism to rejuvenate their multifunctions in organisms [28].

It is noted that only the innate shape can be memorized by feather and its components, yet the temporary deformed shape cannot be recovered again after drying. Thus the recovery strictly signifies a dual or one-way shape memory effect (SME) in response to the stimulus of water [1,2,4]. Indeed, slight shape recovery does also occur in air-dried biopolymer after deformation [27]. Nonetheless, both the recovery rate and extent that can be recovered differ significantly under dry and wet conditions. Representative shape recovery processes of medullary foam with and without contacting water can be seen by referring to Supplementary Materials S1 and S2, respectively. In contrast to the slow partial recovery in dry sample, the original shape can be recovered by more than 90% within 1 min in aqueous environment, markedly highlighting the key role of water. The shape recovery kinetics and hydration effects will be quantitatively analyzed and discussed in the following section.

Supplementary video related to this article can be found at