



# Water-actuated shape-memory and mechanically-adaptive poly(ethylene vinyl acetate) achieved by adding hydrophilic poly (vinyl alcohol)



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## ABSTRACT

Water-actuated shape memory polymers (SMPs) have great potential applications in many fields. Although many strategies have been developed to endow polymers with water-active shape memory effect (SME), so far it is still challenging to prepare the water-actuated SMPs with a highly sensitive SME in a method as facile as possible. In this work, poly(vinyl alcohol) (PVA) was incorporated into poly(ethylene vinyl acetate) (EVA) through the simple solution compounding processing. The blends exhibited good interfacial interaction on one hand. On the other hand, PVA exhibited excellent reinforcement effect, leading to the great enhancement of modulus and strength. Further results showed that the samples had excellent water uptake and dehydration abilities, and the presence of water resulted in the dramatic decrease of modulus and large increase of tensile ductility, which endowed the materials with great potential to realize complicated deformation at gentle force. The water-active SME was evaluated through cycling measurements, i.e. wetting-stretching-drying processes. The results showed that the water-active SME of the blends was greatly dependent upon the blend compositions. After several cycling measurements, the water-active SME of samples became stable. Specifically, for the sample containing 35 wt% PVA, the shape fixity and shape recovery ratios were increased up to 98.7% and 99.5%, respectively. The mechanisms for the excellent water-active SME were then discussed.

## 1. Introduction

Shape memory polymers (SMPs) are usually considered as the smart materials because they have the ability of changing their shape from a temporary shape to the original shape or permanent shape under an appropriate stimulus and therefore, SMPs attract increasing concerns of researchers and have earned fast development in the past few years. To date, many kinds of SMPs have been developed. According to the mechanisms which activate the shape recovery, these SMPs can be classified into several types, such as temperature-actuated SMPs [1,2], pH value-actuated SMPs [3,4], light-actuated SMPs [5,6], solvent-actuated SMPs [7,8], and electric/magnetic-actuated SMPs [9–11], etc. SMPs have been thought as one of the most intriguing materials with great development prospect in the future because they have great potential applications in many fields ranging from biomedical materials, smart fabrics, temperature sensors, information carriers, actuators and aerospace application to self-healing material, etc [12,13].

Recently, water-actuated SMPs have attracted much attention of researchers due to the potential for biomedical applications, such as minimally invasive medical devices [14,15]. Different from the

common temperature-actuated SMPs, which are greatly restricted by the affordable temperature range of body, it is believed that water-actuated SMPs are more appropriate for body since the stimulus is body fluids (mainly water). So far, water-active shape memory effects (SMEs) have been demonstrated in many polymers [16–18].

To achieve the water-active SMEs, polymers must exhibit excellent hydrophilicity so that water could penetrate samples and enhance the flexibility of samples. To date, there are mainly two kinds of strategies to prepare the water-actuated SMPs. One design approach for such materials is relating to construct the hydrophilic segments in the thermo-responsive SMPs and in this condition, once the sample is immersed into water, water can penetrate into the hydrophilic segments of the polymer network and exhibits a plasticizing effect, which results in the reduction of the glass transition temperature ( $T_g$ ) of samples on one hand [19]. Once  $T_g$  of the hydrophilic segments drops to a temperature below the desired ambient temperature of the shape recovery and/or deformation, the shape recovery is then initiated due to the enhanced mobility of molecular chains [20,21]. On the other hand, water molecules also result in the change of the elastic modulus of water-actuated SMPs [12]. Based on the mechanism, to date, many water-actuated

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SMPs have been developed, such as polyurethane, [22] chemically cross-linked poly(vinyl alcohol) (PVA), etc [23,24].

The other kind of strategies are mainly relating to incorporating hydrophilic fillers into an elastomer matrix [25–29]. In these SMPs, one component that induces water-active SMEs in these materials is a resilient physically or chemically cross-linked network and the other component can achieve a reversible switching transition of modulus triggered by water absorption or desorption. Furthermore, the role of hydrophilic fillers in these materials is various. On one hand, the presence of hydrophilic fillers enhances the absorption ability of the SMPs toward water through enhancing the hydrophilicity of sample and providing more penetration channel for water along the weak interfaces between matrix and fillers [25,28]. On the other hand, the hydrophilic fillers at high content also form the network structure in the material, which may provide the driving force for the recovery of the deformed samples [25,28].

Recently, the designing and manufacturing of the SMPs based on polymer blends attracts increasing concerns of researchers [30–33]. Polymer blending is believed to be the most efficient method to develop the new materials through simple solution or melt compounding processing technologies, which is apparently different from the traditional synthesis method. The latter is usually complicated and inconvenient. Generally, most polymer blends are immiscible and they exhibit multiphase structure. Therefore, in the polymer blends, one component may be designed to play the role of cross-linking structure which provides the driving force for the shape recovery and the other component can be designed to play the role of switching unit which is responsible for controlling the shape fixity and recovery. So far, many polymer blends have been demonstrated to be the SMPs with excellent thermally active SMEs [30–40]. However, the water-actuated SMPs that are prepared based on polymer blends are seldom reported.

Poly(ethylene vinyl acetate) (EVA) is a kind of thermoplastic elastomer in which molecular chains are composed of crystalline polyethylene (PE) segments and amorphous poly(vinyl acetate) segments (VA) and therefore, EVA exhibits excellent flexibility. Adjusting the content of VA in the material, EVA exhibits different microstructural and performance characteristics [41]. For example, it varies from thermoplastic elastomer with crystalline structure to elastomer without any crystallites with increasing content of VA. Specifically, for the semicrystalline EVA, the melting point ( $T_m$ ) also varies with VA content [42]. EVA exhibits wide applications in many fields ranging from pipe, building material, packing container and film to biomedical apparatus and instruments, etc. Actually, the unique microstructures endow EVA with great potential applications as SMPs. First, the crystalline structure can simultaneously show the roles of network and reversible switching transition. In the former condition, the reversible switch unit can be the glass transition of the material and sample may exhibit low-temperature SME [43]. In the latter condition, once the chemical-crosslinking structure is introduced, the sample may exhibit high-temperature SME [44,45]. Specifically, with the presence of crosslinking structure, EVA exhibits broad melting transitions and consequently, the sample is endowed with a triple shape memory effects (triple-SME) [46]. To date, many researches have been carried out to prepare the EVA-based SMPs [43–47]. In our previous work, EVA-based blends or blend composites with various stimulus-active SME have been systematically investigated. For example, through adjusting the morphologies of the blends and crystalline structures of components, the morphology-controlled SME and crystallization-controlled SME are successfully achieved in the EVA/poly(L-lactide) (PLLA) blends [36,37]. Through incorporating cross-linking structure, the trip-SME can be achieved for the EVA/poly( $\epsilon$ -caprolactone) (PCL) blends [38]. Specifically, through incorporating carbon nanotubes (CNTs) into the EVA/PCL blends and simultaneously controlling the selective location of CNTs in the blends, the electrically actuated SME with relatively low motivate voltage and high shape recovery rate is achieved [39]. However, it is worth noting that the previous researches are mainly focused on prepare the thermal-

active SMPs.

In this work, we attempt to prepare the water-actuated SMPs based on EVA and poly(vinyl alcohol) (PVA). To achieve the EVA-based SMPs with water-active SME, different contents of PVA are introduced into EVA to prepare the EVA/PVA blends. PVA has been of great interest and widely used in pharmaceutical and biomedical applications for decades, because of its biocompatible, nontoxic, noncarcinogenic, swelling properties, and bioadhesive characteristics, such as contact lenses, artificial pancreases, hemodialysis, and synthetic vitreous [48,49]. Furthermore, PVA has already been demonstrated an ideal candidate for preparing the water-actuated SMPs [50]. It is expected that in the blends, EVA provides the driving force for the shape recovery while PVA acts as the switch unit which realizes a reversible switching transition of modulus triggered by water absorption or desorption, relating to the plasticizing effect of water molecules. The microstructure, mechanical properties as well as the water-active SME of the blends are comparatively investigated.

## 2. Experimental part

### 2.1. Materials

In this work, both EVA and PVA are commercially available. EVA (trade name of Levapren®, with a VA content of  $50 \pm 1.5$  wt%, and the density of  $1.00 \text{ g/cm}^3$ ) was purchased from LANXESS Chemical Co., Ltd, China. PVA was 99% hydrolyzed with an average polymerization degree of 1700 (SINOPEC Sichuan Vinylon Works) and it was used as received.

### 2.2. Sample preparation

EVA/PVA blends were prepared through solution blending. To begin with, EVA solution and PVA solution were prepared respectively. And then, these two kinds of solutions were mixed together. Taking the EVA/PVA (90/10, wt/wt) blend (named as E90P10) as an example, the detailed procedures were described as follows. Firstly, EVA (9 g) was dissolved in 100 ml mixed DMF/THF (50/50, vol/vol) solvents at  $60^\circ\text{C}$  for 2 h with the aid of magnetic stirring. PVA (1 g) was dissolved in 100 ml DMF solvent at  $150^\circ\text{C}$  for about 2 h under the stirring condition. Subsequently, the EVA solution was gradually dropped into the PVA solution, and the mixture was further stirred for 1.5 h. Finally, the EVA/PVA mixture was poured into a glass dish and kept in an oven set at  $80^\circ\text{C}$  for enough time to remove the residual solvent. Similarly, the other EVA/PVA blends (E80P20 and E65P35, representing 80/20 and 65/35, respectively) were also prepared. For further characterization, the blends were compression-molded at a melt temperature of  $130^\circ\text{C}$  and a pressure of 5 MPa to obtain the sheets with a thickness of about 0.25 mm.

### 2.3. Fourier transform infrared (FTIR)

The interaction between EVA and PVA was characterized by A Fourier transform infrared (FTIR) AVATAR360 (Thermo Nicolet, USA). The wavenumber range was  $400\text{--}4000 \text{ cm}^{-1}$ , and the measurements were performed at a resolution of  $4 \text{ cm}^{-1}$  under an attenuated total reflection (ATR) mode.

### 2.4. Scanning electron microscopy (SEM)

Phase morphologies of the EVA/PVA blends were characterized using a scanning electron microscope (SEM) Fei Inspect (FEI, the Netherlands). The characterization was operated at an accelerating voltage of 5.0 kV. Before SEM characterization, the cryo-fractured surface, which was obtained through breaking the sample in liquid nitrogen, was coated with a thin layer of gold.

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