Review

Recent developments in shape memory polymer nanocomposites: Actuation methods and mechanisms

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ABSTRACT

Research on shape memory polymer is developing promptly over the past three decades, holding the promise to apply in micro actuators, medicine, basic science, biological science, deployable structure, anti-counterfeit technology, sensor and automobile. Actuation methods and mechanisms are parts of the important developments in shape memory polymer. Shape memory polymer nanocomposites are usually constructed by functional nanomaterials such as mesoporous materials, hierarchical porous materials, nanocomposite membranes, nanotubes and nanowires. Numerous studies of shape memory polymer nanocomposite have been performed to interpret experimental data and provide rational design. This review focuses on state-of-the-art actuation methods such as chemo-responsive, electrically resistive Joule heating activated, light-activated, microwave heating triggered, and magnetically sensitive shape memory polymer nanocomposites in most recent studies. Specifically, emphases are placed on the actuation mechanism, the advanced design concept, and the potential application of novel shape memory polymer nanocomposite probabilities to a wide variety of areas.

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1. Introduction

Intelligent materials are important parts of contemporary chemistry research. As emerging intelligent materials, shape memory polymers (SMP) have the unique ability to undergo chemo-responsive, electrically activated, light-activated, microwave heating triggered, magnetically sensitive, and thermally triggered shape changes [1–5]. The molecular chains have an apparent coil/stretch transition with sliding when energy is consumed through an applied load which can be best explained through SMP's entropic elasticity property [4,6]. There is more energy storage in thermoset polymers than thermoplastics through the crosslinking bonds restricting sliding which freeze more energy in the temporary shape. Upon reheating, the SMP molecular chains coil due to entropy spontaneously increasing and the energy stored is released, so the polymer shows more macroscopic shape change. In a typical shape memory process, cycles of deformation, shape fixation, and shape recovery occur where the permanent shape is kept and recovered repeatedly from the temporary shape. When the orientations of polymer chains are changed, the free volume and distance between the chains are decreased due to deformation which are enhanced by multiple mechanisms including H-bonding and polar–polar interactions [1]. Subsequently, the micro-Brownian movements of the polymer chains are frozen and transformed to a rigid state during cooling to resist the recoiling of the polymer chains with the shape fixity. The chemical or physical crosslinking points and crystalline domains or stiff chains of the SMP network are responsible for the permanent shape of the SMP chain network. The crystalline, amorphous phases, liquid crystal phases, supramolecular entities, hydrogen-bonded polymer networks, and light-reversible coupling groups act as switches to change the structure of the SMP chain network which ultimately provide the ability of primary recovery and energy absorption [7–10]. The glass/rubber transition and the crystalline/melting transition are often utilized as switching transitions of SMP. According to the shape memory effect (SME) mechanism, the SMP is deformed into a temporary shape under extra force with freezing Brownian motion and stress. The SMP can recover to its permanent shape through releasing the frozen stress when it is exposed to a heating source or other external stimulus [11]. Although previous efforts have elucidated several SMP actuation methods, new SMP nanocomposites have had few breakthroughs in their actuation mechanisms. Currently, it is fundamentally significant to provide a reference model that describes the interconnectivity of actuation methods and mechanisms toward developing novel SMP nanocomposite systems.

Although SMPs exhibit the facile capability to change their shape, they also exhibit limited mechanical properties like low elastic modulus, stiffness, strength, and lack of functions [2]. Functional fillers have become a popular strategy for overcoming their innate deficiencies. The special functionality of mesoporous, bioactive nanoparticles, nanotubes, nanocellulose, and nanocomposite membranes provide a means for simple infiltrate composite nanotechnology. The functional elements within SMP nanocomposites not only provide an opportunity to improve the strength and modulus of the material, but can also be utilized to impart the materials with stimuli-responsive characteristics.

The directly thermal-induced SMP is closely related to thermal transitions of the reversible phase in the SMP. The external heat sources are usually used to stimulate the SMP, which is difficult to control for slow heat transfer and response. This review is primarily interesting in shape memory properties, actuation methods, and mechanisms of indirectly induced SMP nanocomposites as outlined in Fig. 1. The basic elements of the SME have been briefly introduced since different SMP nanocomposites feature different actuation mechanisms which are directly correlated

to the rational design of novel SMP nanocomposite systems. Consequently, we review chemo-responsive, electrically resistive Joule heating activated, light-activated, microwave heating triggered and magnetically sensitive SMP nanocomposites, respectively. These sections describe the design principle, fabrication, shape memory properties, and corresponding actuation mechanisms of the SMP nanocomposites. Finally, rational designing and relevant potential application of SMP nanocomposites are summarized.

2. Chemo-responsive shape memory polymer nanocomposites

Chemo-responsive SME has the advantage of being structurally and chemically tunable with a variable recovery rate that is independent of external heating which gives way to a more environmentally friendly and green energy saving approach than the thermally activated SME method. The absorbed solvent molecules of the chemo-responsive SMP nanocomposites enable shape recovery at a significantly lower temperature with disrupting intermolecular hydrogen bonds, plasticizing, and reducing the glass transition (T_g) temperature.

2.1. Nanostructure/microstructure shape memory polymer composites

Wang et al. have advocated the unique design concept to construct a novel sodium dodecyl sulfate/thermosetting epoxy water-driven nano/microstructure SMP composite and provided further clarification of the water-induced SME mechanism [6]. As shown in Fig. 2, the composite was designed based on the chemical interaction of sodium dodecyl sulfate (SDS) with water upon dissolution which consequently created 3D microvoids. The composite took advantage of SDS' amphiphilic nature, stemming from the sulfate group at the end of the 12 carbon chain, to increase the inherent water solubility. Mechanical mixing of the SDS and epoxy-based shape memory polymer constructed the composite and then produced 3D microvoids which enhanced the composite's specific surface area with water solubility lowered the SDS concentration in the composite [6]. The increased specific surface area benefitted from the water diffusivity which subsequently caused a physical swelling effect (PSE) [12].

1 mm cast thin films of epoxy-based SMP and sodium dodecyl sulfate/epoxy shape memory composite (SDS-ER) were evaluated in the water-induced SME test, while each film was under standard temperature and pressure (STP) separately in water and in atmosphere for an equal amount of time. Interestingly, only the SDS-ER exhibited good shape memory recovery properties in water, but the others had no visible effect. The shape recovery ratio of SDS-ER was small during the first 30 min, where it started to gradually recover and eventually exhibit macroscopically noticeable recovery. In water, the composite imbibed water molecules which migrated into the interstitial space of the polymer chains and the bulk structure resulting in the specimen's dimensional change. Furthermore, there were different force conditions between the inside and outside surfaces of the "U"-like shape composite as shown in Fig. 2. For this reason, the PSE of the inside surface was a part of shape recovery outputting force. It gives inspiration to design the composites with nonlinear/non-uniform PSE of programmed regions as the functionally graded SMP nanocomposite.

In the first step, the shape recovery rate was controlled by the slow diffusion process. In the middle stage, its large specific surface area benefitted the diffusion of water molecules from the external surface into the bulk which subsequently improved the shape recovery rate. Once the diffusion equilibrium condition was met, the diffusion of water molecules from the bulk to the solution was