



Dual responsive shape memory polymer/clay nanocomposites



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ABSTRACT

In this study, a novel dual-responsive shape-memory polymer/clay nanocomposite is successfully prepared using in situ polymerization approach with the presence of exfoliated clay platelets. With the adjustable glass transition temperature, the nanocomposites have been used to construct triple shape memory devices via two-step polymerization methods. The physical crosslinking network formed by strong hydrogen interactions between polymer chains and clay platelets contribute to a significant enhancement in the mechanical properties of the resultant nanocomposites, which ensured that they can lift the load of 200 times its own weight upon exposure to infrared light (IR). Incorporation of clays into polymer matrix effectively improved the hydrophilic performance of materials, thus the water-induced shape recovery process of the nanocomposites can be finished within 6 s with excellent recovery ratio. Therefore, the preparation of dual responsive shape memory polymer/clay nanocomposites pave a new way to design and fabricate high mechanical shape memory materials with dual triggering mechanism.

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1. Introduction

Shape memory polymers (SMPs) are a class of smart materials capable of fixing one or many temporary shapes and recovering their permanent shape upon exposure to external stimulus [1,2]. The development of shape memory polymers have drawn much attentions due to their excellent structure versatility [3], low manufacturing cost [4], easy in processing [5], and high elastic deformation [6]. These unique properties of shape memory polymers let them to be used in various fields, including smart clothing manufacturing [7], deployable space structures [8], morphing aircraft [9], medical treatment [10], and many other applications [11]. However, the low tensile strength and stiffness of SMPs have extremely hindered their applications [12]. To address this problem, much research efforts have been directed towards improving the mechanical strength of shape memory polymers. The method of introducing nanoparticles as cross-linkers and reinforcing fillers has been proposed and used for preparation of shape memory polymer composites (SMPCs).

The field of SMPCs has witnessed a rapid growth in recent years. A large number of new materials with unprecedented properties

have been developed which greatly extended the application scopes of traditional shape memory polymers. Besides, the incorporation of nanoparticles have been proven useful for widening the range of alternate shape memory triggering mechanisms such as electric current [13] and magnetic fields [14]. For example, the incorporation of CNTs into SMPs provides a facile alternative to prepare the electrical sensitive SMPCs [15], and the application of magnetic particles in SMPs ensured that the materials can be actuated by an externally magnetic field [16]. Shape memory polymer composites with unique recovery characteristics have also appeared, such as two-way shape memory effect [17], triple or multiple shape memory effect [18], temperature-memory effect [19], magnetic memory effect [20], and stress memory effect [7]. Among them, triple shape memory shape memory polymer composites have been deeply investigated due to the numerous applications [21]. However, the time consuming synthesis process and the complicated molecular design of these materials significantly hindered their applications. In addition, water-induced shape memory polymer composites have attracted more attention due to the mild and friendly stimulus mechanism and wide potential biomedical applications [22]. For example, Wang and co-workers recently reported one novel water-induced sodium dodecyl sulfate/epoxy composite (SDS-ER) showing potential applications in wide ranges from humidity sensors to underwater deployable

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structure [23]. Fu et al. demonstrated a fast shape recovery process induced by water in the graphene oxide/polyvinyl alcohol nanocomposites (PVA/GO) [24]. However, some drawbacks arose from the nature of polymer matrix, such as slow recovery speed (SDS-ER) or inferior tensile strain (PVA/GO), might hamper their use in special fields. Hence, more attentions and efforts should be paid on the development of SMPCs possessing parameters involving large deformation, fast recovery speed, and dual or multiple response properties.

Clays and clay minerals as one kind of ideal reinforced fillers are abundant at or near the surface of Earth, and the polymer/clay nanocomposites have deserved an increasing interest because of their novel and unique physical properties including mechanical, thermal, barrier, electrical conductivity, biodegradability, and so on [25]. With the rapid development of material science, the molecular level incorporation of layered clays into polymer matrix had been achieved through the addition of modified clays, which can further improve the mechanical strength of composite materials [26]. Diverse of polymer/clay nanocomposites have been reported, and their available commercial and potential applications in packaging, coating and pigment, electrical materials, and in particular biomedical fields have been developed [27]. These developments extensively promote the emerging of clay enhanced shape memory polymer nanocomposites. For example, Lourdin et al. has fabricated starch/clay bionanocomposites by melting process, which demonstrate that the addition of clays lead to the improvement in elastic modulus and shape recovery ratio [28]. With similar concept, Jana and co-workers create nano-clay tethered shape memory polyurethane nanocomposites using bulk polymerization method, where the addition of clays increase the shape recovery force but negatively impact the room temperature tensile properties of materials [29]. Similar work reported by Fu [30] and Sadeghi [31] suggest that the incorporation of clay can effectively improve the mechanical strength and recovery force of the polyurethane nanocomposites. Although the successful preparation of clay-reinforced shape memory nanocomposites predict the promising future in the applications ranging from biomedical to engineering, the triple or multiple polymer/clay nanocomposites have been rarely reported. Besides, other triggering mechanism (such as water) of clay-based SMPCs may offer more possibilities in many applications, and the design and fabrication of these materials has still been a major challenge.

Here, we successfully prepared a novel thermal-responsive and water-responsive polymer/clay nanocomposites based on the previous reported copolymer elastomers [32]. We propose that the polymer chains bridge with the clay nano-platelets across reversible hydrogen bond to form a three-dimensional network, in which the clay act as the cross-linking net-points to prevent the deformed molecular chains from sliding during the deformation. The fabrication of the polymer/clay nanocomposites provides a new avenue to prepare novel mechanical-enhanced SMPs. Using the two-step polymerization methods, triple shape memory materials with well-separated switching transition temperatures could be readily designed and fabricated. Besides, the plasticizing effect of water molecules increase the flexibility of polymer chains resulting in the rapid drop in glass transition temperature and leading to the shape recovery process occurred at ambient temperature. Thus, with the improvement of hydrophilic performance resulting from the incorporation of clay platelets, water-triggered shape memory effect of the polymer/clay nanocomposites can be also achieved.

2. Experimental

2.1. Materials

2-Methoxyethyl acrylate (MEA) was purchased from Alfa Aesar, and used without further purification. *N,N'*-dimethylacrylamide (DMAA) was purchased from TCI Shanghai Co., and purified by filtering through activated alumina. Other reagents, potassium peroxydisulfate (KPS) and *N,N,N',N'*-tetramethylethyl enediamine (TEMED) were used as initiator and catalyst, respectively. The water used for all experiments was ultrapure water. Oxygen dissolved in pure water was removed by bubbling N_2 gas for more than 3 h prior to use, and oxygen was excluded from the system throughout the synthesis process. The inorganic clay, synthetic hectorite "Laponite XLG" (Rockwood Ltd., U.K.; $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$; layer size = 30 nm in diameter \times 1 nm in thickness; cation exchange capacity = 104 mequiv/100 g), was used after vacuum drying in 120 °C for 4 h.

2.2. Synthesis of polymer composites

The polymer/clay composites were synthesized similarly to previously described procedures [32]. The appropriate amount of MEA, DMAA, and clay (Laponite XLG) were added in ultrapure water with N_2 gas bubbling to remove soluble O_2 . After vigorous stirring for another 15 min, the solution was cooled to 0 °C before catalyst (TEMED, 8 μ L) and initiator (KPS, 0.01 g in 0.5 ml water) were added. Finally, the final mixture was transferred to a tailored glass tube or a customized Teflon mould (inside dimension: 5 cm \times 5 cm \times 2 mm), and polymerized at 60 °C for 12 h to obtain the desired gels. The resulting gels were washed thoroughly with distilled water to remove the unreacted monomer and other impurities, and the water on the surface of hydrogels was then swept by filter paper. The resulting gels were subsequently dried at room temperature for 24 h followed by drying for 24 h at 80 °C under vacuum. Thus, the cylinder or plate samples were obtained. The sample codes for resultant elastomers were defined as MD x -NC n by the molar fraction of DMAA and the clay concentration, where $x = 100 \times ([DMAA])/([DMAA] + [MEA])$ and $C_{clay} = n \text{ mol/L } H_2O$.

The triple shape memory polymer/clay nanocomposites were synthesized through two-step polymerization methods. Briefly, the feed solution of MD50-NC2 was first transferred to a glass tube and partially polymerized for 20 min, then the mixture of MD80-NC2 was added on the top of the first region and fully polymerized. After washed thoroughly with distilled water and dried, the triple shape memory polymer/clay nanocomposite was obtained.

2.3. Measurements

FT-IR spectra were performed with a Nicolet 6700 instrument (Thermal Scientific, USA) by the KBr method in the range 500–4000 cm^{-1} . The mechanical properties of polymers were measured on an ASG-J electronic universal testing machine (Shimadzu Co., Japan) at room temperature. Clubbed samples with size of 3 mm \times 40 mm (diameter \times length) were used for tensile tests with a crosshead speed of 20 mm/min. Plate samples with size of 40 mm \times 4 mm \times 0.5 mm (length \times width \times thickness) was used for dynamic mechanical analysis with a TA Q800 Dynamic Mechanical Analysis (DMA) instrument (TA Instrument Inc.) in the tensile mode. The dynamic storage and loss moduli were determined at a frequency of 10 Hz and a heating rate of 3 °C/min. Thermogravimetric analysis (TGA) was carried out using a TA instrument (TG-DTA 6200), and a 5 mg sample was heated in an alumina crucible with a heating rate of 10 °C/min from room temperature to 900 °C under N_2 atmosphere. Scanning electron

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